جامعة
بنغازي الحديثة

مجلة جامعة بنغازي الحديثة للعلوم والدراسات الإنسانية

مجلة علمية الكترونية محكمة

Journal of Benghazi Modern University of Sciences and Humanities

العـــدد الرابع

لسنة 2019

شروط كتابة البحث العلمي في مجلة جامعة بنغازي الحديثة للعلوم والدراسات الإنسانية

1- الملخص باللغة العربية وباللغة الانجليزية (150 كلمة).
2- المقدمة، وتشمل التالي:
- ❖ نبذة عن موضوع الدراسة (مدخل).
- ❖ مشكلة الدراسة.
- ❖ أهمية الدراسة.
- ❖ أهداف الدراسة.
- ❖ المنهج العلمي المتبع في الدراسة.

3- الخاتمة. (أهم نتائج البحث - التوصيات).
4- قائمة المصادر والمراجع.
5- عدد صفحات البحث لا تزيد عن (25) صفحة متضمنة الملاحق وقائمة المصادر والمراجع.

القواعد العامة لقبول النشر

1. تقبل المجلة نشر البحوث باللغتين العربية والانجليزية؛ والتي تتوافر فيها الشروط الآتية:

- أن يكون البحث أصيلاً، وتتوافر فيه شروط البحث العلمي المعتمد على الأصول العلمية والمنهجية المتعارف عليها من حيث الإحاطة والاستقصاء والإضافة المعرفية (النتائج) والمنهجية والتوثيق وسلامة اللغة ودقة التعبير.
- ألا يكون البحث قد سبق نشرة أو قُدم للنشر في أي جهة أخرى أو مستل من رسالة أو اطروحة علمية.
- أن يكون البحث مراعياً لقواعد الضبط ودقة الرسوم والأشكال - إن وجدت - ومطبوعاً على ملف وورد، حجم الخط (14) وبخط (Arial 'Body') للغة العربية. وحجم الخط (12) بخط (Times New Roman) للغة الإنجليزية.
- أن تكون الجداول والأشكال مدرجة في أماكنها الصحيحة، وأن تشمل العناوين والبيانات الإيضاحية.
- أن يكون البحث ملتزما بدقة التوثيق حسب دليل جمعية علم النفس الأمريكية (APA) وتثبيت هوامش البحث في نفس الصفحة والمصادر والمراجع في نهاية البحث على النحو الآتي:
- أن تُثبت المراجع بذكر اسم المؤلف، ثم يوضع تاريخ نشرة بين حاصرتين، ويلي ذلك عنوان المصدر، متبوعاً باسم المحقق أو المترجم، ودار النشر، ومكان النشر، ورقم الجزء، ورقم الصفحة.
- عند استخدام الدوريات (المجلات، المؤتمرات العلمية، الندوات) بوصفها مراجع للبحث: يُذكر اسم صاحب المقالة كاملاً، ثم تاريخ النشر بين حاصرتين، ثم عنوان المقالة، ثم ذكر اسم المجلة، ثم رقم المجلد، ثم رقم العدد، ودار النشر، ومكان النشر، ورقم الصفحة.

2. يقدم الباحث ملخص باللغتين العربية والانجليزية في حدود (150 كلمة) بحيث يتضمن مشكلة الدراسة، والهدف الرئيسي للدراسة، ومنهجية الدراسة، ونتائج الدراسة. ووضع الكلمات الرئيسية في نهاية الملخص (خمس كلمات).

3. تحتفظ مجلة جامعة بنغازي الحديثة بحقها في أسلوب إخراج البحث النهائي عند النشر.

إجراءات النشر

ترسل جميع المواد عبر البريد الالكتروني الخاص بالمجلة جامعة بنغازي الحديثة وهو كالتالي:

- ✓ يرسل البحث الكترونياً (Word + Pdf) إلى عنوان المجلة info.jmbush@bmu.edu.ly او نسخة على CD بحيث يظهر في البحث اسم الباحث ولقبة العلمي، ومكان عملة، ومجاله.
- ✓ يرفق مع البحث نموذج تقديم ورقة بحثية للنشر (موجود على موقع المجلة) وكذلك ارفاق موجز للسيرة الذاتية للباحث إلكترونياً.
- ✓ لا يقبل استلام الورقة العلمية الا بشروط وفورمات مجلة جامعة بنغازي الحديثة.
- ✓ في حالة قبول البحث مبدئياً يتم عرضة على مُحكِّمين من ذوي الاختصاص في مجال البحث، ويتم اختيارهم بسرية تامة، ولا يُعرض عليهم اسم الباحث أو بياناته، وذلك لإبداء آرائهم حول مدى أصالة البحث، وقيمته العلمية، ومدى التزام الباحث بالمنهجية المتعارف عليها، ويطلب من المحكم تحديد مدى صلاحية البحث للنشر في المجلة من عدمها.
- ✓ يُخطر الباحث بقرار صلاحية بحثه للنشر من عدمها خلال شهرين من تاريخ الاستلام للبحث، وبموعد النشر، ورقم العدد الذي سينشر فيه البحث.
- ✓ في حالة ورود ملاحظات من المحكِّمين، تُرسل تلك الملاحظات إلى الباحث لإجراء التعديلات اللازمة بموجبها، على أن تعاد للمجلة خلال مدة أقصاها عشرة أيام.
- ✓ الأبحاث التي لم تتم الموافقة على نشرها لا تعاد إلى الباحثين.
- ✓ الأفكار الواردة فيما ينشر من دراسات وبحوث وعروض تعبر عن أراء أصحابها.
- ✓ لا يجوز نشر إي من المواد المنشورة في المجلة مرة أخرى.
- ✓ يدفع الراغب في نشر بحثه مبلغ قدره (400 د.ل) دينار ليبي إذا كان الباحث من داخل ليبيا، و (200 $) دولار أمريكي إذا كان الباحث من خارج ليبيا. علماً بأن حسابنا القابل للتحويل هو: **(بنغازي – ليبيا - مصرف التجارة والتنمية، الفرع الرئيسي - بنغازي، رقم 001-225540-0011. الاسم (صلاح الأمين عبدالله محمد)**.
- ✓ جميع المواد المنشورة في المجلة تخضع لقانون حقوق الملكية الفكرية للمجلة.

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MALONONITRIL REACTION

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(Chemistry department. Benghazi, university Benghazi, faculty of arts and science, Elmarj. Libya)

Abstract.

The role of malononitrile title in the development of the Knoevenagel condensation and the addition reaction of the nucleus Organic synthesis and new discoveries are explored in this review. The active methylene group of malononitriles is a very important part of the attack in heterogeneous transformations and has a significant force towards some microbial and biological systems.

Keywords: Malononitrile, Active methylene group.

تفاعلات الملونونيتريل

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(عضو هيئة التدريس بقسم الكيمياء - كلية الآداب والعلوم المرج - جامعة بنغازي – ليبيا)

الملخص:

نبذة مختصرة: يتم استكشاف دور malononitrile في تطوير تكاثف Knoevenagel ورد الفعل الإضافي للتخليق العضوي للنواة واكتشافات جديدة في هذا الاستعراض. تعد مجموعة الميثيلين النشطة من الملونونيتريل جزءا مهمًا للغاية من الهجوم على التحولات غير المتجانسة ولديها أيضًا قوة مهمة تجاه بعض الأنظمة الميكروبية والبيولوجية.

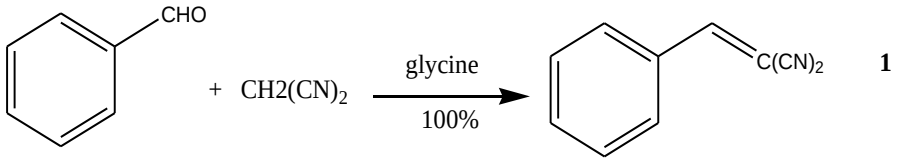
الكلمات الأساسية: Malononitrile ، مجموعة الميثيلين النشطة

1. Introduction.

Active methylene carbon reaction with carbonyl compounds is a classical synthetic route to make carbon–carbon bond. Knoevenagel[1] condensation is one of the most important methods for the synthesis of substituted alkenes and have many applications in an elegant Synthesis of fine chemicals that are valuable precursors for a wide range of target molecules in pharmaceutical industry. May be transported either in a homogenous or heterogeneous phase. Ammonium[2] salts (primary, secondary, and tertiary) generally catalyzed these reactions. These reactions are generally catalysed using bases or Lewis acids in the liquid phase system[3]. Recently, use of inorganic solid supports as catalysts, resulting in higher selectivity, milder conditions and Simplest work-up, has rapidly increased and has been reported as a useful condition for Knoevenagel reaction[4]

Condensation Reactions with Aldehydes and Ketones.

Malononitrile pass by it the Knoevenagel condensation with aldehydes and ketones. Effective catalysts to condensation include glycine and β-alanine.[5,6] Benzaldehyde condenses with malononitrile in the presence of a catalytic amount of glycine to give benzalmalononitrile, which is valuable in heterocyclic synthesis, in quantitative yield (eq 1)[7] The condensation of 1,4-cyclohexanedione with malononitrile proceeds approximate quantitatively to 1,4-bis(dicyanomethylene)cyclohexane by catalysis by β-alanine (eq 2).[8] 1,4-Bis(dicyanomethylene)cyclohexane is user to prepare the quinomethane electron acceptor 7,7,8,8-tetracyanoquinonedimethane (TCNQ)[9] generally, the Knoevenagel condensation of malononitrile with ketones or esters is efficiently catalyzed by weak bases (β-alanine, ammonium acetate) while more powerful bases (KF, KOAc, NaOAc) encourages telomerization of malononitrile.[10] Dimethylformamide (DMF) is a useful solvent for a wide variety of Knoevenagel reactions.[11] Dialkylidenemalononitriles existence cyclic and terpenoid groups are possible cytostatic and pesticides agents that may be useful in regulating insect ev



1

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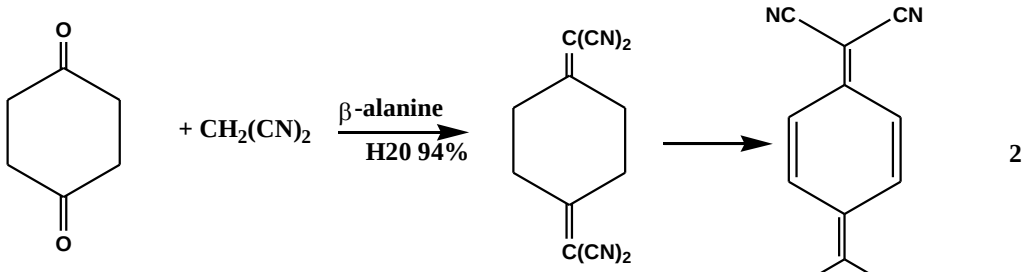
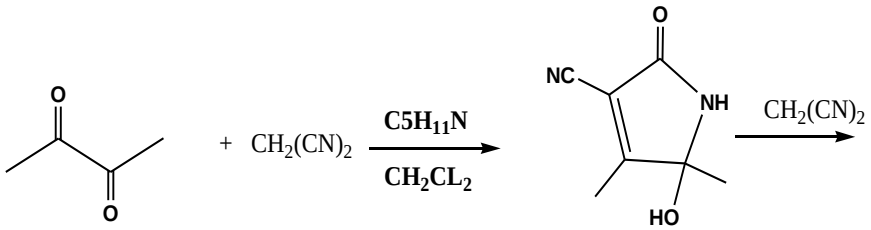


2

2

2,3- Butanedione reacts with malononitrile to produce 4,5-dimethyl-5-hydroxy-2-oxo-3-pyrroline-3-carbonitrile, 1,5-dimethyl-3,7-dioxo-2,6-diaza-cis-bicyclo[3.3.0]octane-βazatetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecane-4,8-dicarbonitrile (eq 3), and the isomeric bislactam1,5-dimethyl-3,7-dioxo-2,8-diaza-cis-bicyclo[3.3.0]octane-4,6-dicarbonitrile

(eq 4).[13,14] Benzil reacts with malononitrile to give the Knoevenagel product or the γ-lactam (4-cyano-2,3-diphenyl-5-oxo-3-pyrrolin-2-ylmalononitrile) (eq 5).[15-17]



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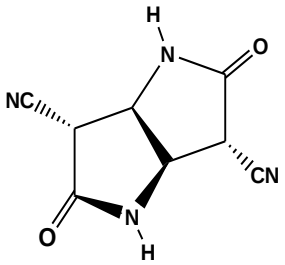

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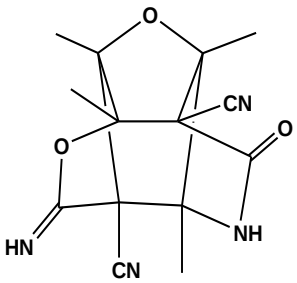

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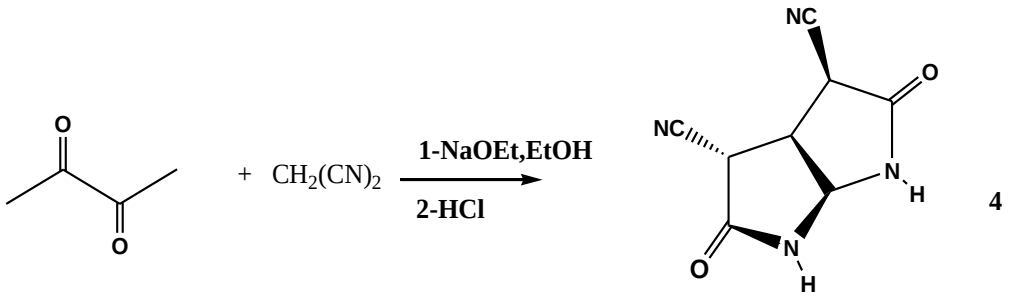

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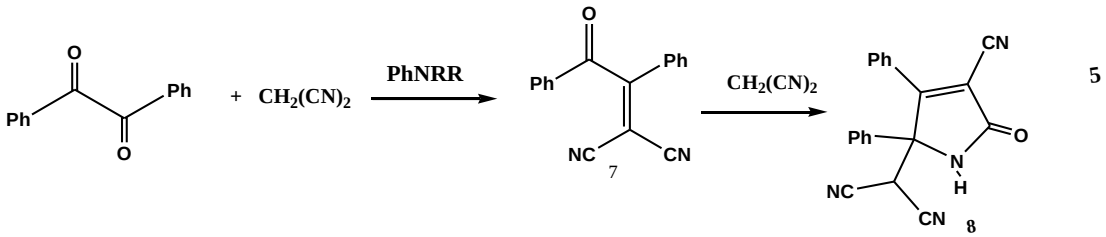
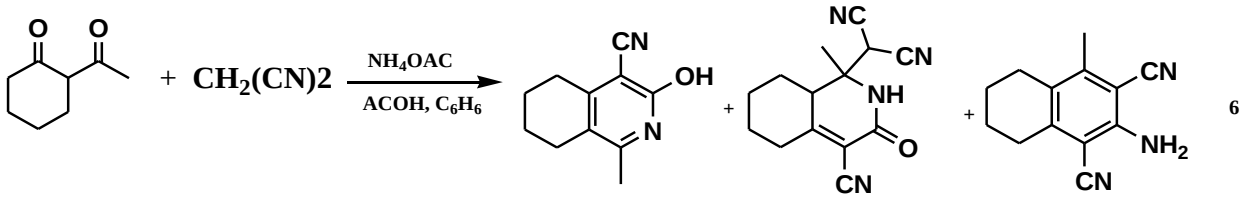


5

2- Acetylcyclohexanones react with malononitrile to give a mixture of products including polyhydrobenzo[c]pyridines (isoquinolines) and tetrahydronaphthalenes (eq 6).[18-20] The reaction with 2-acetylcyclopentanone proceeds similarly. Enolizable aliphatic and aromatic 1,4-diketones (e.g. 2,5-hexanedione) react with malononitrile in benzene in the presence of ammonium acetate or piperidinium acetate to give an array of products including double Knoevenagel adducts, cyclopentadiene derivatives, and 1-pyrindine derivatives (eq 7).[21-23]



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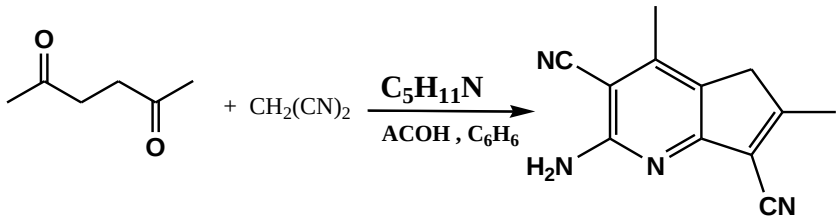
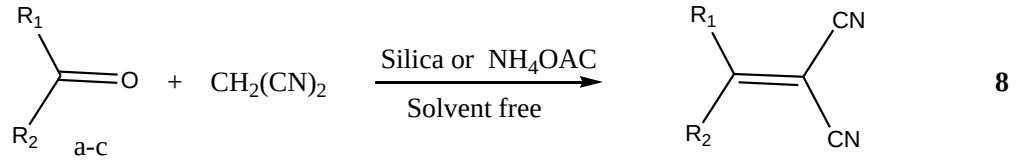


7

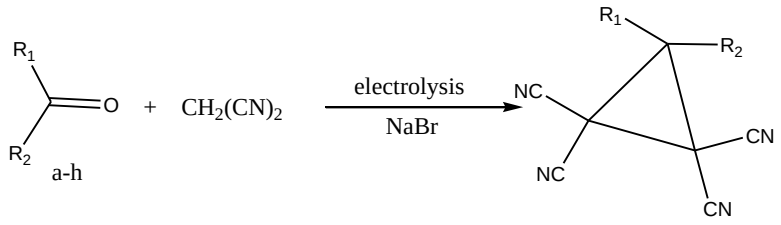
Synthesized the arylidene **(a-c)** malononitrile analogs by uniform mixture of substituted ketones **(a-c)** and dicyanomethane catalyzed by ammonium acetate or silica gel under the microwave assisted solvent free synthesis. [24]



8

a-R_1,R_2 =fluorenyl
b-R_1=Ph,R_2 =CH_3
c-R_1,R_2 =Ph

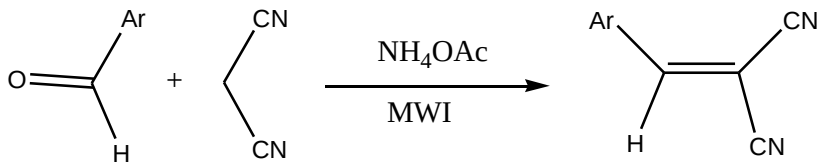
Synthesized the different substituted tetracyanopropanes by the elctrolysis of malononitrile and carbonyl groups (ketones / aldehydes) in presence of sodium bromide undivided electrolytic cell reaction.



9

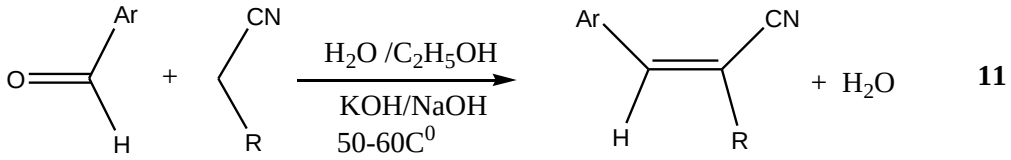
a-$R_{1\,=\,Me}$,R_2 =Et
b-R_1=Me , R_2 =Pr
c-$R_{1\,=\,Me}$,R_2 =Bu
d-$R_{1=Me(CH2)5}$
e- R_1 =Pr ,R_2 =Pr
f -R_1,R_2 = $(CH2)_4$
g-R_1,R_2 = $(CH2)_6$
h-$R_{1\,=Me}$,R_2 =Ph

Synthesized arylidene malononitrile derivatives by parable mixture of substituted aromatic aldehydes and malononitrile by catalytic amount of ammonium acetate under microwave irradiation. [26]



10

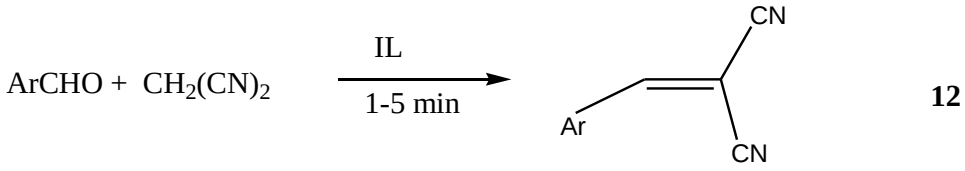
In case of reaction, counterpart mixture of the substituted aldehydes and nitrile groups she was carried out under ethanol-aqueous media in presence of KOH or NaOH catalyst at 50-60ºC temperature enabled the productive derivatives.[27]



11

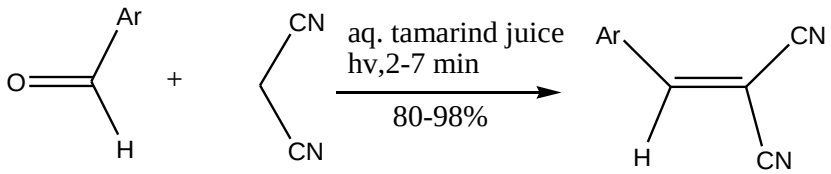
R =CN , COOEt

Has been reported as simple effective and rapid Knoevenagel condensation synthesis by using ionic liquid media. The mixture of aromatic aldehyde and dicyanomethane. They were equally carried out in pyridinium salicylate ionic liquid refluxed on 40ºC for few minutes occupied the malononitrile derivatives. [28]



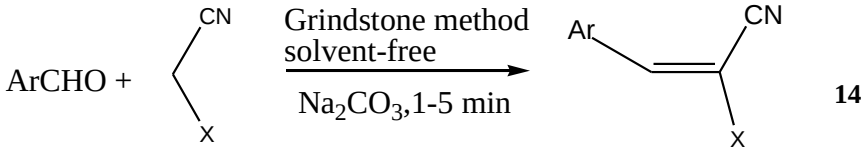
12

Reaction by using fruit juice accelerators. The Parallel mixture of different substituted aldehydes and malonic nitrile by tamarind juice catalyst in an aqueous media in presence visible light for few minutes enabled the malononitrile similar.[29]



13

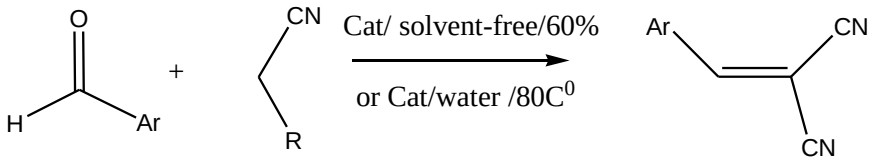
In case of reaction, the substituted aldehyde and nitriles uniformly mixed with Na_2CO3 catalyst under grindstone method enable aryl-methylidene. [30]



14

X= COOEt,CN

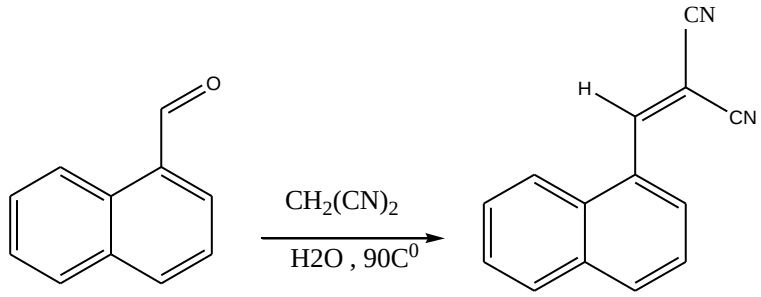
Synthesized the malononitrile derivatives in presence of modified form of polyacrylamide catalyst heated under water by using equimolar mixture of aromatic aldehyde and nitrile analogs. [31]



15

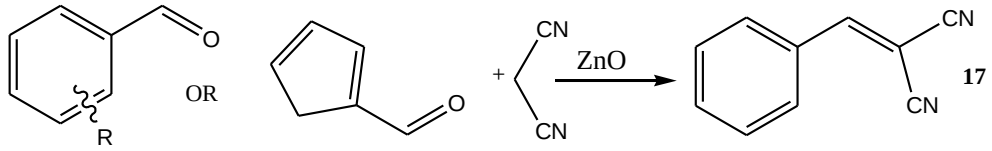
R= CN, $CONH_2$and CO2Et

Condensation between napthaldehyde with mlononitrile heated at 90°C from 2 hrs inaqueous media by green synthesis.[32]



16

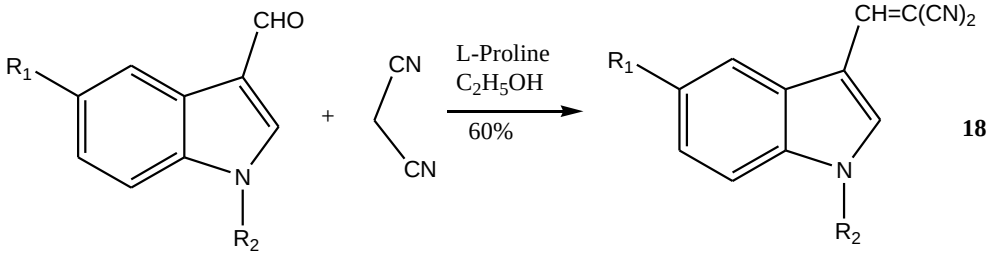
Substituted aryl aldehydes reacts with malononitrile in presence of ZnO catalyst in an aqueous case at ambient temperature that gives finished products [33]



17

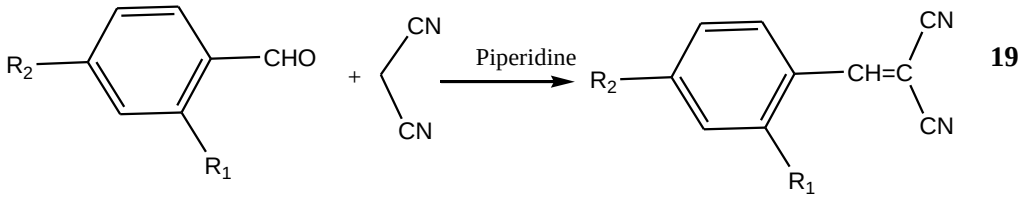
R= Cl,OCH_3,NO_2

Has created a new indole derivatives promoted by L-proline catalyst. Indole aldehydes mixed evenly with active methylene nitrile groups under Knoevenagel condensation reaction catalyzed by L-proline refluxed on 60ºC in ethanol. [34]



18

Benzylidene malononitrile groups. It is manufactured by mixture of substituted aromatic aldehydes and malononitrile in presence of highly alkaline catalyst like piperidine refluxed in cyclohexane solvent. They are bio-significant riot-control agents. [35]

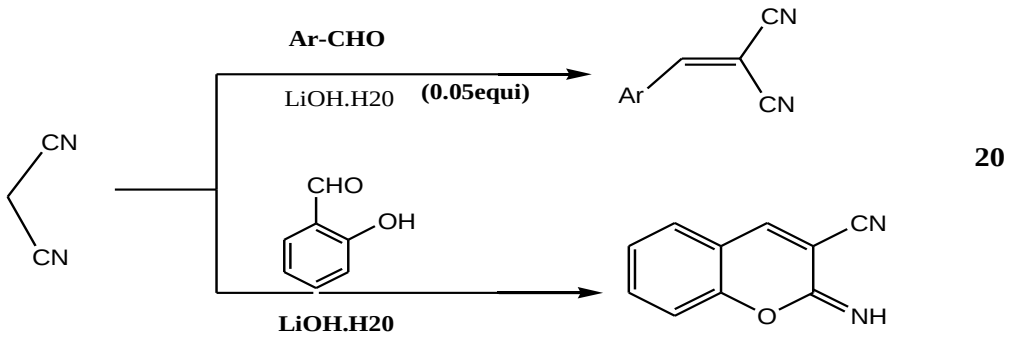


19

R1= H, Cl, Br ,NO2,CH3,OCH_3,COOH

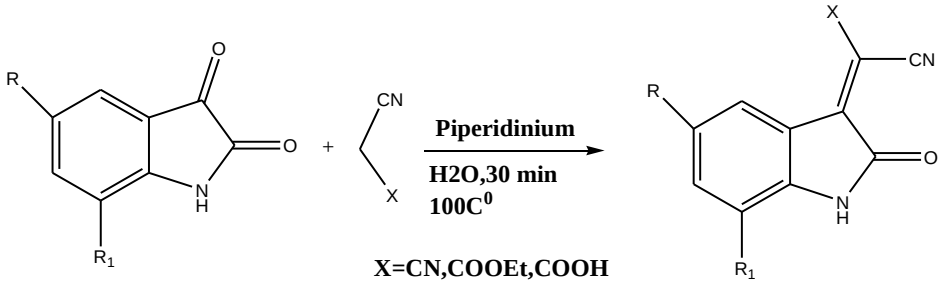
R_2=H,F,Cl,Br,NO_2,CH_3,OCH_3,OH,$N(CH3)_2$

Synthesis of malononitrile derivatives in an aqueous media. In the Knoevenagel condensation synthesis of aromatic aldehydes and malononitrile They were mixed equally using lithium hydroxide monohydrate catalyst which acts as dual-activator nature. **[36]**



20

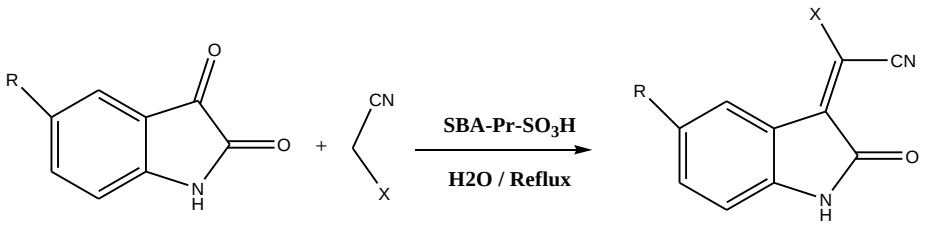
Have configured the differernt substituted isatins. were enabled by suitable quantity of substituted indole-1,3-diketone reacts with malononitrile in presence of piperidinium acetate catalyst heated at 100ºC for 30 min in aqueous media. [37]



21

R=H,CL,Br,FI
R1=H,F

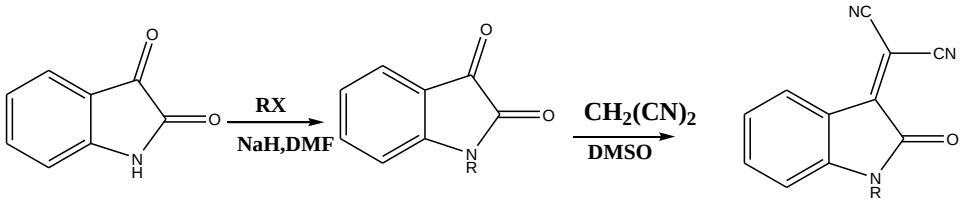
Synthesized isatins by the parallel mixture of indoles and nitriles refluxed in presence of silica based sulphonic acid (SBA-Pr-SO3H) catalyst under water. [38]



22

R=H,CL,Br,NO_2

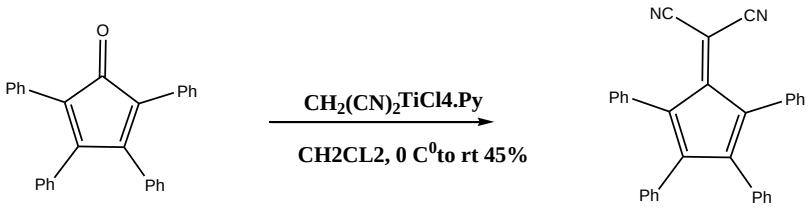
The isatin refluxed with alkyl halides and DMF which gave N-alkylisatins , in addition to refluxed with malononitrile under DMSO easily turn into corresponding 1-alkyl-3cyanomethylideneindol-2-ones [39]



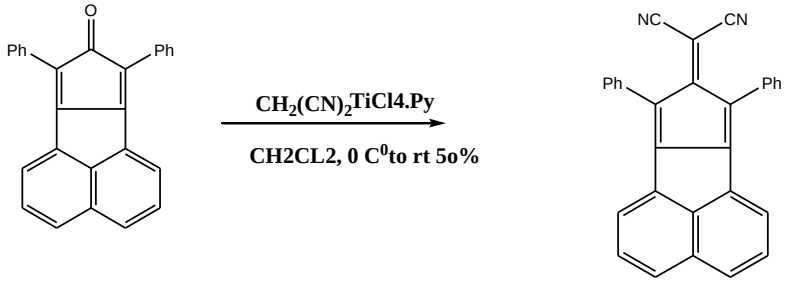
23

R=H, CH3, n-Pr,n-hexyl ,$PhCH_2$, $PhCHCH_3$, 1-(benzotriazole)CH_2

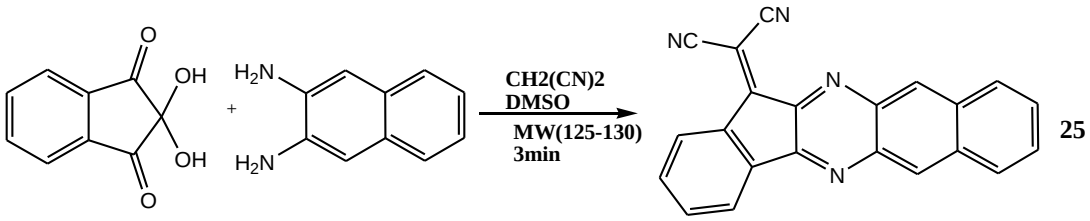
Synthesized 6,6-dicyanofulvenes derived from monomeric and dimeric forms of cyclopentadienones with malononitrile by using TiCl4 and pyridine catalyst stirred from 0ºC to room temperature in the methylene dichloride solvent. [40]



24

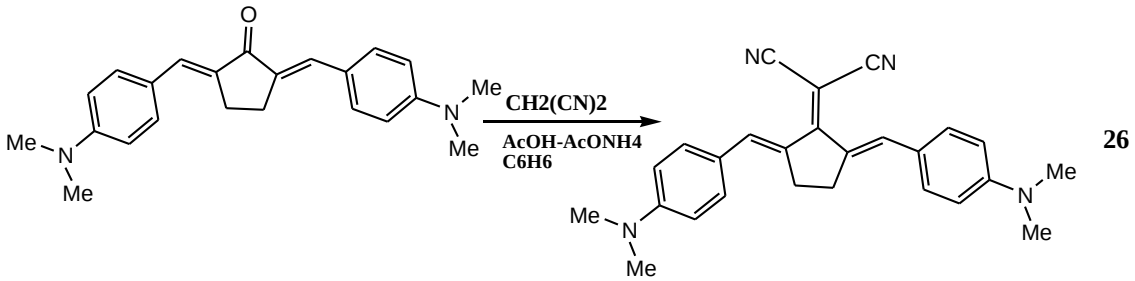


The quinoxalines derivatives it was synthesized by the mixture of ninhydrin and napthalen-2,3-diamine counterparts of malononitrile with litle drops of DMSO in solvent free microwave conditions. [41]



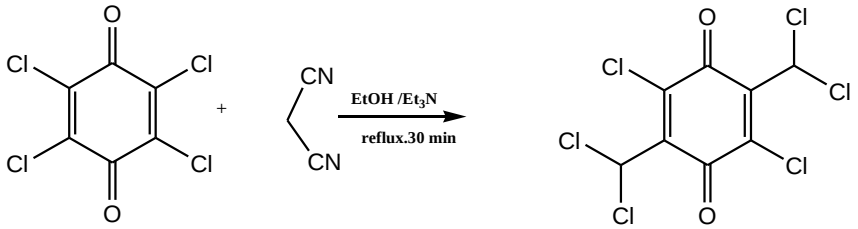
25

Synthesized the bis-methine dyes from chalcones and malononitrile. A solution of enabeld chalcones were refluxed with malononitrile catalyzed by ammonium acetate and acetic acid under benzne, the 2,5-bis-arylidene-1-dicyanomethylene-cyclopentane are produced. The enable compounds find committed antifungal activities. [42]



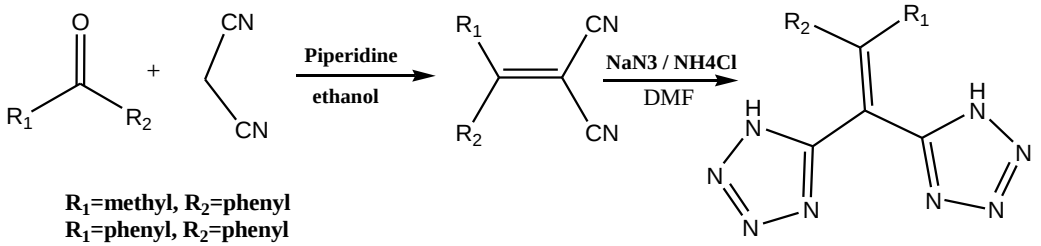
26

Pyrrolo[2,3-f]indole-3,7-dicarbonitrile derivatives. These are obtained by the reaction mixture chloranils and malononitrile (1:2) ration in presence of triethylamine catalyst refluxed in ethanolic conditions. The choose compunds possesess the significant antimicrobial activities. 43]



27

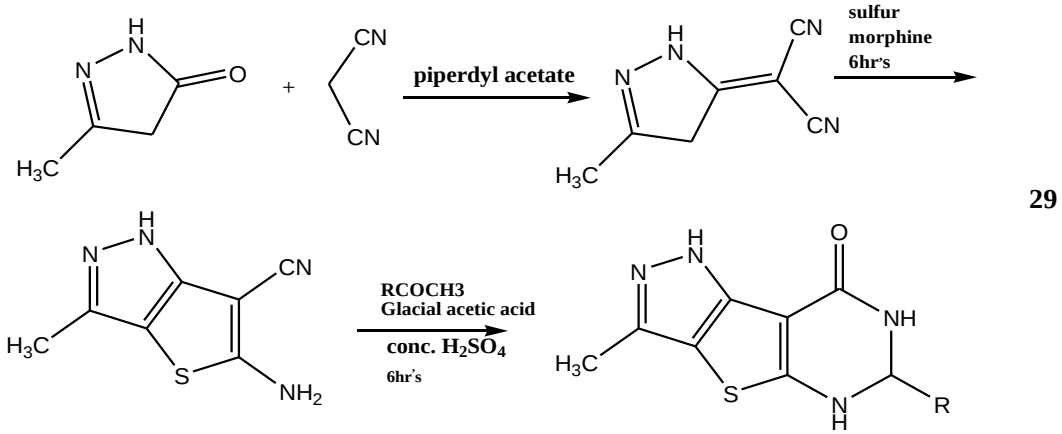
The 5,5'-(arylalkene-1,1-diyl) bis(1Htetrazoles) derived fro (arylalkene)malononitrile intermediates. The (arylalkene) malononitriles were prepared by substituted ketones and propane-di-nitrile with piperidine refluxed in the presence of ethanolic condition. Then beyond cyclization by using sodiumazide with ammonium chloride catalyst heated in DMF solvent acquired the final products are reveals the significant antibacterial activities. [44]



28

R_1=methyl, R_2=phenyl
R_1=phenyl, R_2=phenyl

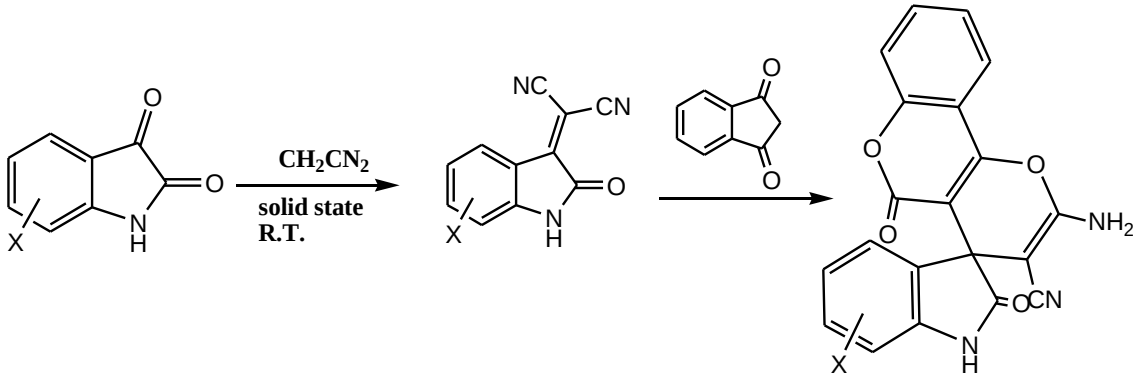
Synthesized some novel pyrazolo[3',4':4,5]thieno[2,3-d] pyrimidine-8- ones by malononitrile intermediates by three-step Gewald reaction. (5-methyl-2,4-dihydro-3H-pyrazol-3-ylide-ne) malononitrile were enabled from and with help of piperidyl acetate catalyst, then complated with sulphur morphine at 60ºC for 6 min **.** By closing the last step, glacial acetic acid was catalyzed by the mixture of substituted aldehydes and furnishes the novel pyrazolo-pyrimidine synthons are positive antimicrobial agents. [45]



29

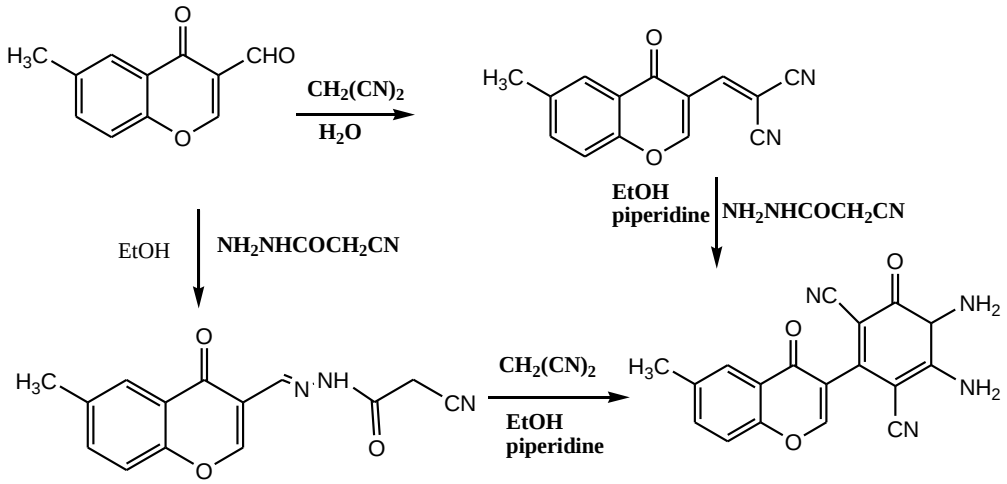
R= phenyl,2-hydroxy phenyl,4-fluoropenyl,4-chlorophenyl,4-bromo phenyl , 4-nitro phenyl
4-methyl phenyl, 4-methoxy phenyl

The new reformer 2-amino-3-carbonitrile-spiro[(indeno-1,2,b)pyran-4(5H),3'-(3,H)indole]2',5(1'H)-diones done by 3dicyano/carboethoxycyanomethylene-2H-indol-2-ones intermediates from malononitrile derivatives and substituted indoles. **[46]**



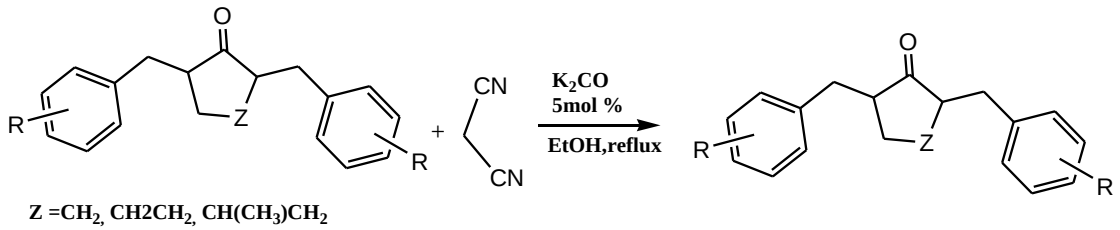
30

The diaminopyridone of nitrogen substituted fused heterocyclic compounds derived from malononitrile and [(6-methyl-4-oxo-4H-chromene-3-yl)methylene] starting components. intermediates in presence of piperidine catalyst refluxed in ethanol. The synthesized products emphasized the substantial antimicrobial activities. [47]



31

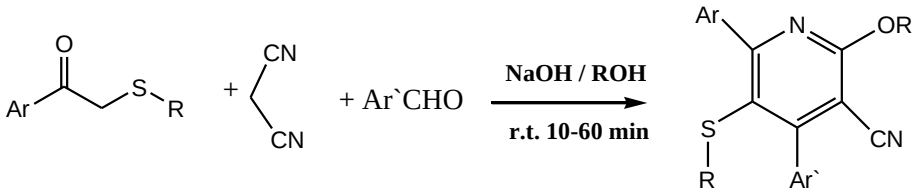
Synthesis of 2-amino-4H-pyran-3-carbonitrile series reaction of α,α‘-bis (arylidene) cycloalkanones and malononitrile were refluxed underethanol condition by using K2CO3 catalyst. [48]



Z =CH_2, $CH2CH_2$, $CH(CH_3)CH_2$

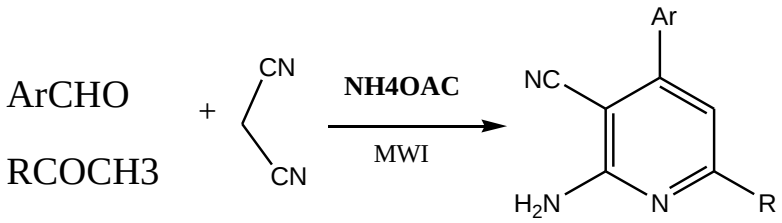
32

Synthesis of polysubstituted pyridines by using the equivalent combination of substituted ketones, malononitrile and aromatic aldehydes in presence of alcoholic sodium hydroxide stirred for 10-60 min. Then the configured compounds were check up their anti-tubercular activities on mycobactrium tuberculosis. These compounds were found more potent activities than the standards. [49]



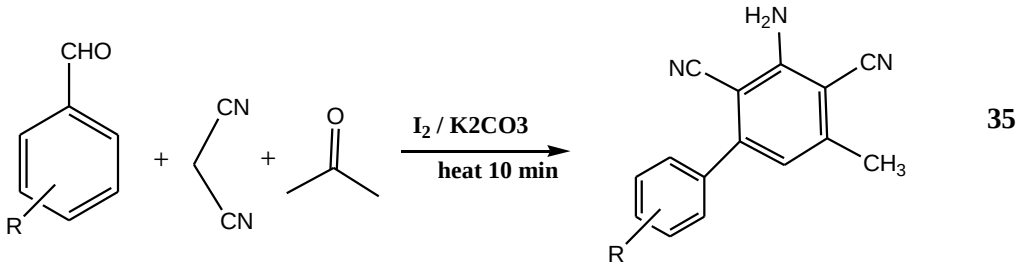
33

Synthesis of 2-amino-cyanopyridines by method with help of microwave assisted. The substituted aromatic aldehydes, ketones and malononitrile are uniformly mixed with the addition of ammonium acetate catalyst was irradiated in one component system intended the final products. [50]



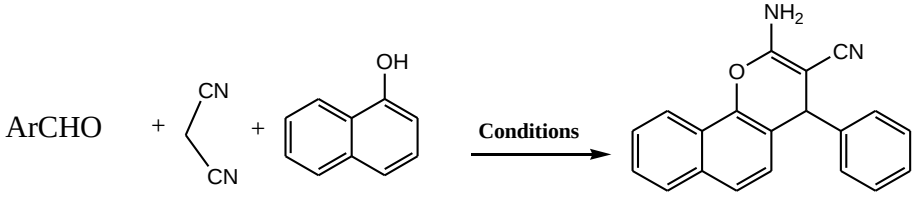
34

Synthesis the polysubstituted dicyanoaniline under thermal condition. Reaction of the malononitrile, substituted ketones and aromatic aldehydes were heated with iodized K2CO3 catalyst, done in a very short time.[51]



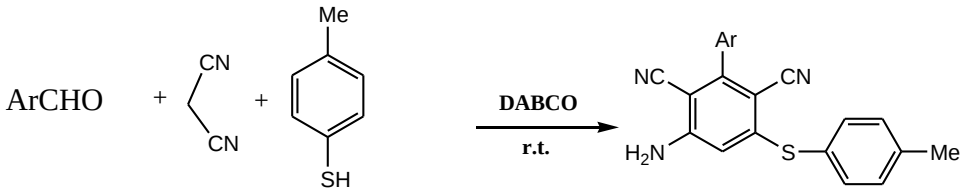
35

The combination mixture of methylenedinitrile, aromatic aldehydesand 1-napthol were catalysed by p-dimethylaminopyridine which produces 2-amino-2-chromenes derivatives. [52]



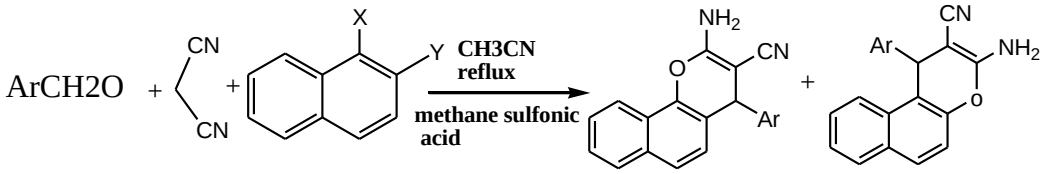
36

The novel was presented DABCO catalyst in one pot multicomponent synthesis of pyridine dicarbonitrile by the reaction mixture of paramethyl thiophenol, malonicnitrile and substituted aromatic aldehydes. [53]



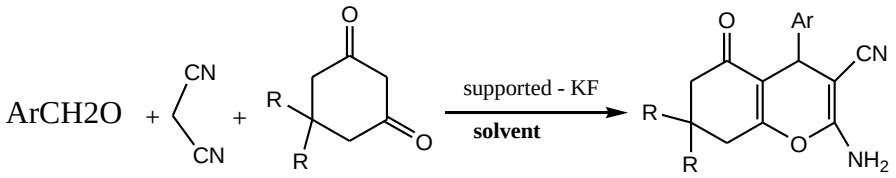
37

Synthesized 2-amino-4-H-chromene derivatives and in presence methane sulfonic acid catalyst refluxing with the mixture of aryl aldehydes ,malononitrile and α,β-disubstituted napthols in one a step. [54]



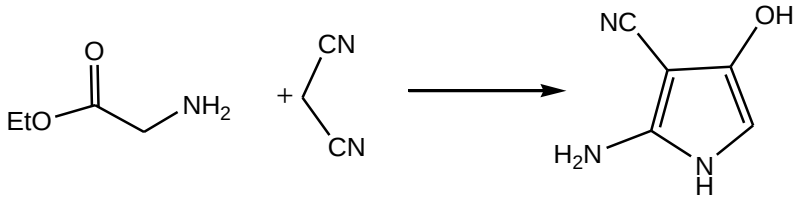
38

Alumina supported recyclable potassium fluoride catalyst they were created and used to synthesis of benzopyran by using the uniform mixture malononitrile ,substituted cyclohexane-1,3-dione and aromatic aldehydes were refluxed under ethanolic condition. [55]



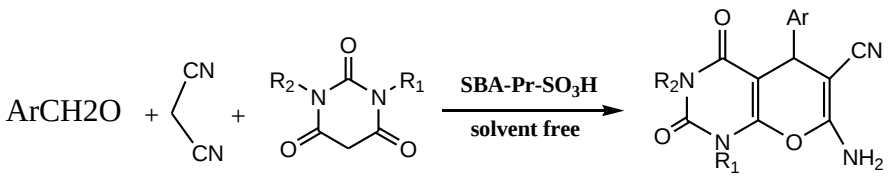
39

Synthesized 2-amino-4-hydroxy-1H pyrrole-3-carbonitrile **108** by mixture of glycine and malononitrile accelerated by piperidine under the microwave efficient conditions. **(Scheme – 37)**[56]



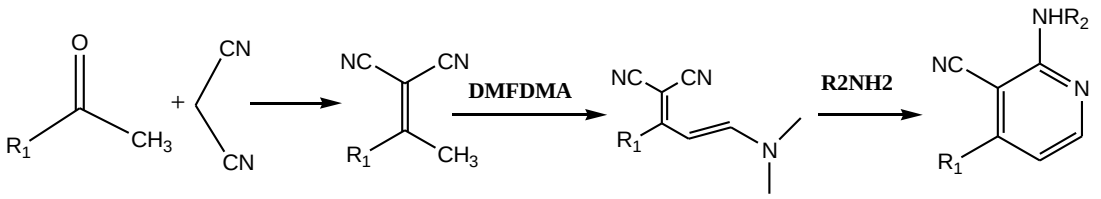
40

Synthesized pyrano[2,3-d]-pyrimidine by reaction the barbituric acid, malononitrile and substituted aldehydes carried out with SBA-Pr-SO3H nanocatalyst under the solvent free conditions. The end compounds great urea inhibition activities were held. [57]



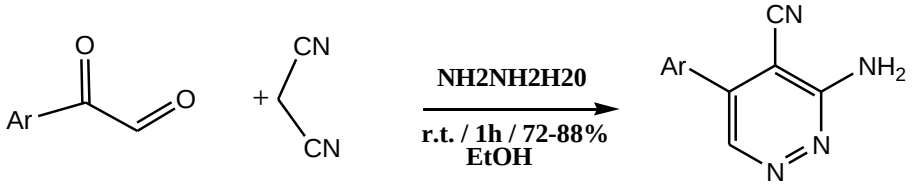
41

Reaction of the substituted ketones and malononitrile produced enaminonitriles intermediate by the solvent free microwave method with help. The final compounds Synthesized 2-amino-3-cyanopyridines [58]



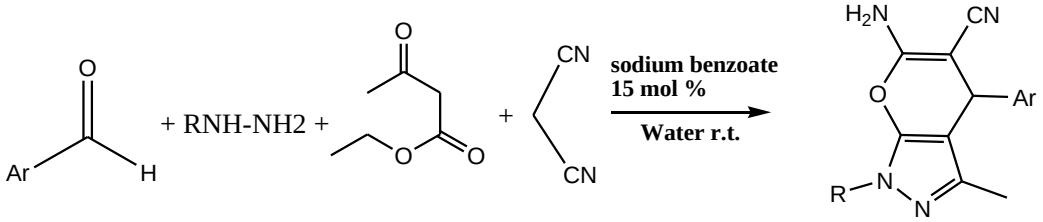
42

Synthesized 3-amino-5-arylpyridazine-4-carbonitril by reaction arylglyoxal and malononitrile in presence of hydrazine hydrate stirred for 30 min at room temperature under ethanol and water (1:1) ratio. [59]



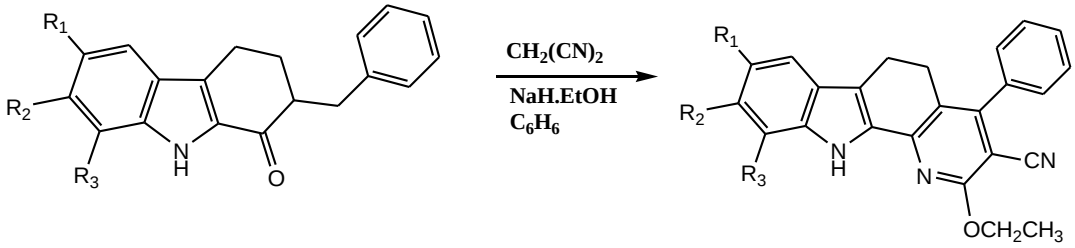
43

Pyranopyrazoles were synthesis by mixture of aromatic aldehydes, hydrazines, ehtyl acetoacetate and malononitrile by using sodium acetoacetate catalyst stirred under water at room temperature. [60]



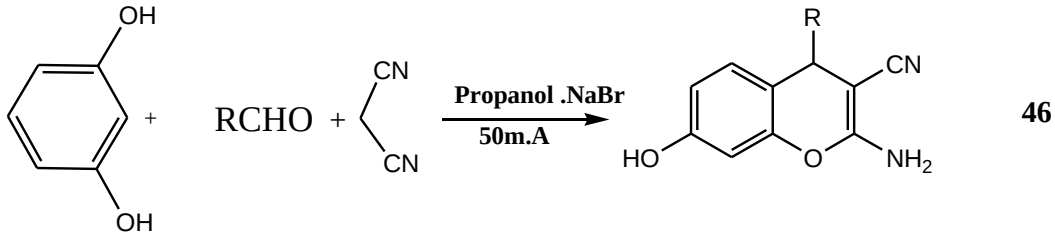
44

Synthesiszed 3-cyano-5,6-dihydro-2-ethoxy-4-phenylpyrido[2,3-a] carbazoles from the reaction mixture of 2-benzylidene-8-methyl-1-oxo-1,2,3,4-tetrahydracarbazoles and malononitrile with anhydrous ethanol in presence of sodium hydride catalyst refluxed under dryer benzene. [61]



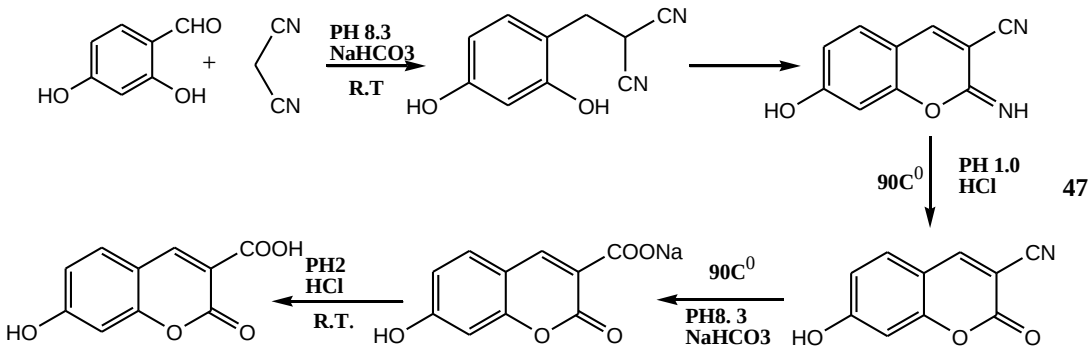
45

Synthesized 2-amino-4H-chromenes from the reaction mixture of resorcinol, substituted aldehydes and malononitrile were evenly condensed in propanol by using NaBr electrolytes [62]



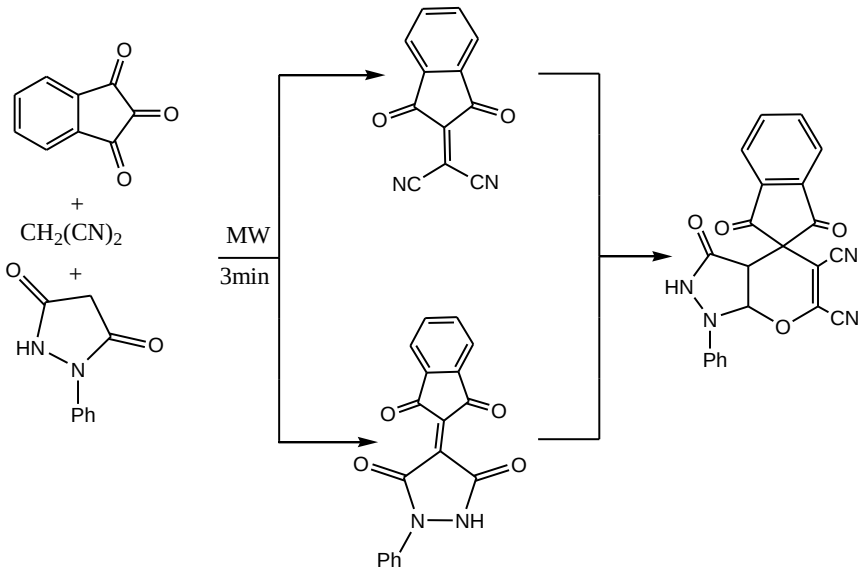
46

Synthesiszed 7-hydroxy-3-carboxy coumarins in one pot reaction in aqueous media by equimolar equal mixture of 2, 4, dihydroxy benzaldehyde and propane-dinitrile were carried out under water in heterogeneous conditions. There are four types of fundamental reaction are stepwise carried out such as Knoevenagel, aldol condensation, Pinner reaction, acid catalyst, base catalyst and acid-base equilibrium synthesis simultaneously monitoring pH scales from starting medium to the final coumarins. [63]



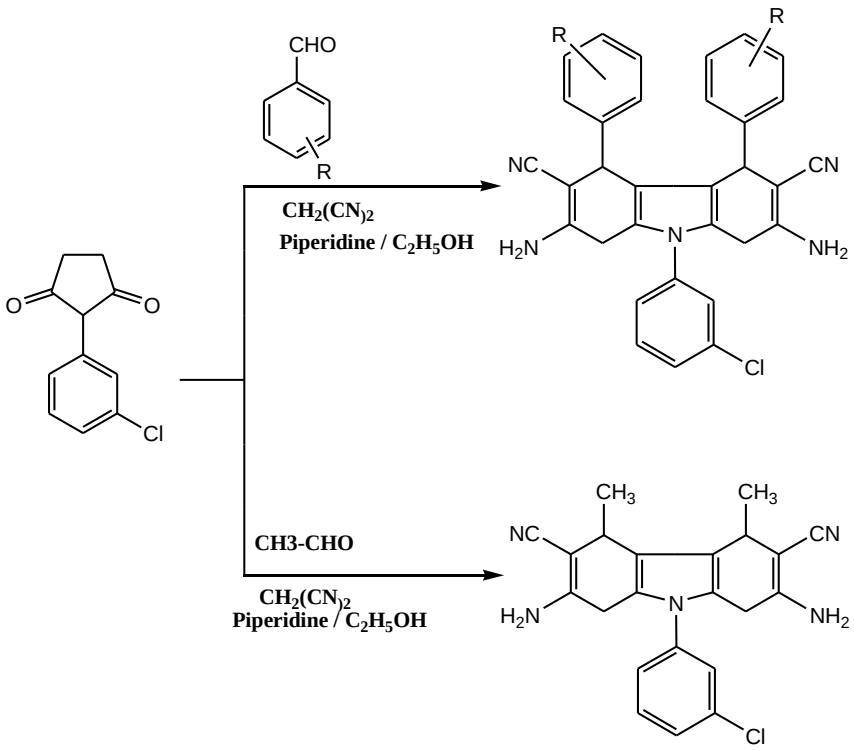
47

Put the novel Spiro-fused pyran derivatives by solvent less microwave assisted synthesis. These pyran derivatives were made by the cyclization mixture of ninhydrin**,** malononitrile and phenyl pyrazoline-3, 5-dione irradiated in presence of the neutral Al_2O_3 catalyst. **[64]**



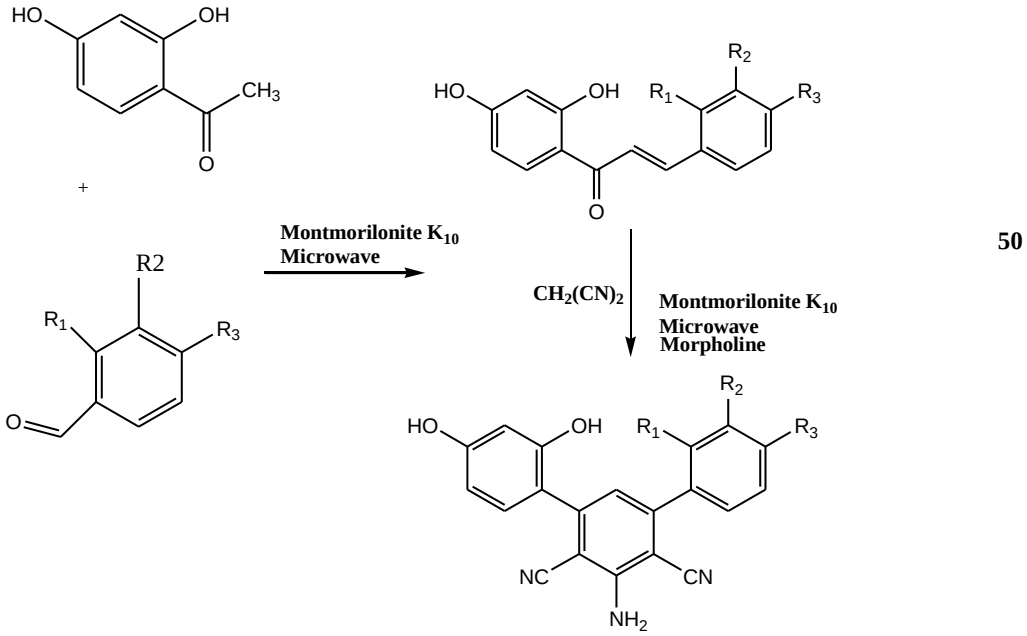
48

The malononitrile derivatives azoflurorenes, furnished by the mixture of 4-chlorophenyl-succinimides, substituted aromatic aldehydes and acetaldehyde with malononitrile by using piperidine catalyst refluxed under ethanolic conditions. **[65]**



49

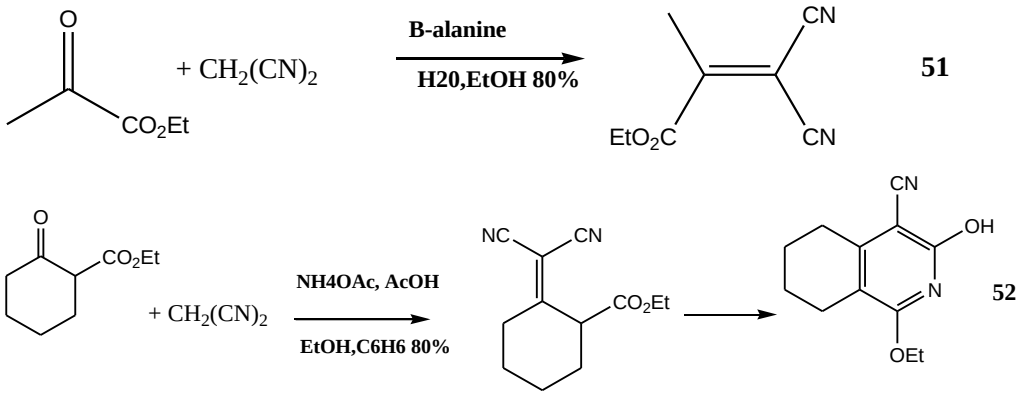
Synthesized malononitrile analogous by the mixture of substituted aromatic aldehydes and 2,4-dihydroxy-acetophenone under microwave in presence of montmorilonite K10 the catalyst forms chalk. More treatment with malononitrile by used of catalytic amount of morpholine Submit the required product.[66]



50

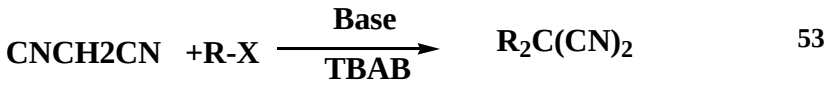
Condensation Reactions with Esters.

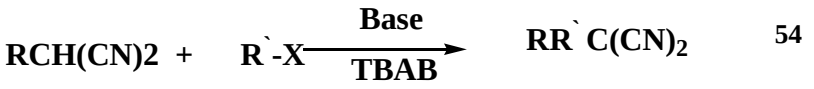
Ethyl pyruvate condenses with malononitrile to give ethyl 2-dicyanomethylenepropanoate, a useful dienophile in the Diels-Alder reaction and in natural products synthesis.[9,67]Ethoxycarbonyl-1-cyclohexanone reacts with malononitrile to give the Knoevenagel condensation product, which rearranges to the tetrahydroisoquinoline.[18-20-,68 ,69]



Reactions with alkyl halides.

The mono-alkyl-malononitrile and di-alkyl-malononitriles by using tetra-butyl ammonium bromide catalyst in solvent free basic medium. [70]



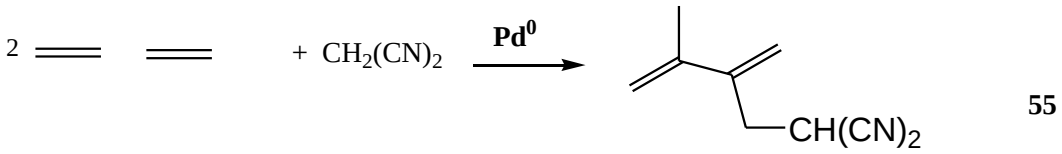


Reactions with α,β-Unsaturated Carbonyl Compounds.

The Knoevenagel reaction of aliphatic methyl ketones with malononitrile produces 6-alkyl-2,4-diamino-3,5-dicyanopyridines in moderate yield.[71] The Michael reaction between aliphatic α,β-unsaturated ketones and malononitrile gives 2-amino-3-cyano-4,6-dialkylpyridines.[71]Conjugated aromatic ketones react with malononitrile by used of ammonium acetate to give 2-amino-4,6-diarylnicotinonitriles[72]The Michael addition of malononitrile to α-acetylcinnamamides and chiral α-acylacrylates to form 2-amino-4H-pyrans and polyfunctionalized carbocycles,[73,74] and the first asymmetric synthesis of polyfunctionalized 4H-pyrans via Michael addition of malononitrile to 2-acyl acrylates. [75] Polyfunctionalized 4H-pyrans are a common structural unit in a number of natural products.

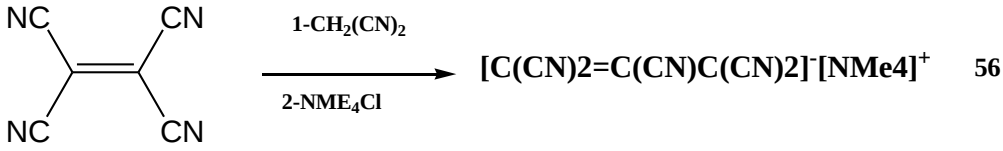
Reaction with Allene.

Malononitrile reacts with allene in the presence of catalytic Pd^0 complexes, such as (Maleicanhydride)bis(triphenylphosphine)palladium, to bear a 2-(1,1-dicyanoethyl)-3-methyl-1,3-butadiene.[76]



Reaction with Tetracyanoethylene.

Tetramethylammonium 1,1,2,3,3-pentacyanopropenide, It is useful for preparing pentacyanopropenide salts of other metals and quaternary ammonium Positive ions by the situation changed, is prepared from malononitrile and tetracyanoethylene.[77]

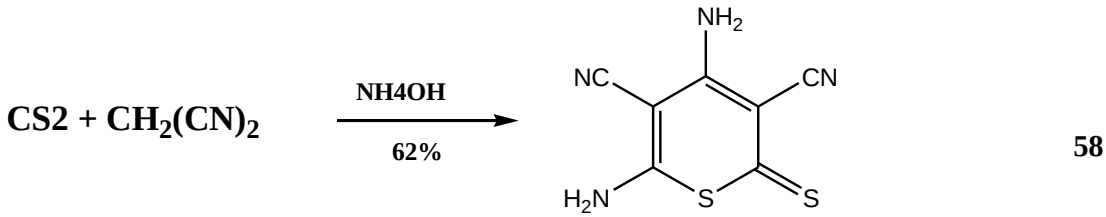


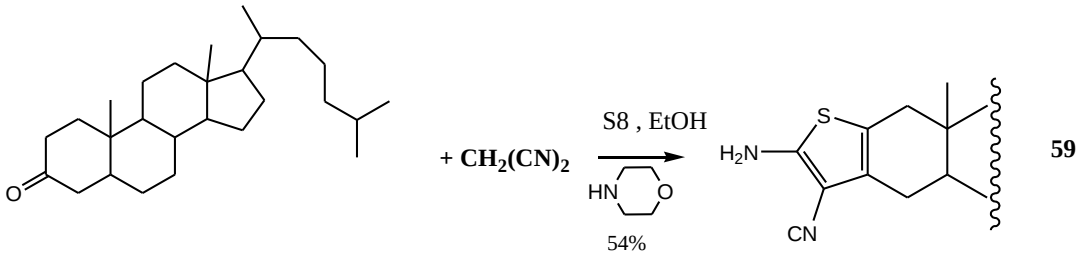
Reactions with Alkyl- and Cycloalkylureas.

Malononitrile condenses with heptylurea and ethyl triorthoformate to form the 3-heptylureidomethylenemalononitrile, It is an introduction to3-heptyl-5-cyanocytosine (eq 12).[78] The reaction is effective for preparing 3-alkyl- and 3-cycloalkyl-5-cyanocytosines, but not for 3- and 5-cyanocytosines from arylureas.

Reactions with Carbon Disulfide andor Sulfur.

Malononitrile reacts with carbon disulfide in aqueous ammonia to give 4,6-diamino-3,5-dicyano-2H-1-thiapyran-2-thione.[79]Malononitrile reacts with carbon disulfide and sulfur in the presence of secondary or tertiary amines to produced 4-cyano-5-amino-1,2-dithiole-3-thione.[80] 2-Amino-3-cyano-4,5-dialkylthiophenes are obtained from malononitrile, ketones, and sulfur.[81] Cholestan-3-one reacts with malononitrile and sulfur in ethanol containing morpholine to produce cholestanothiophene (2-aminocholest-2-eno[3,2-b]thiophene-4-carbonitrile).[82]

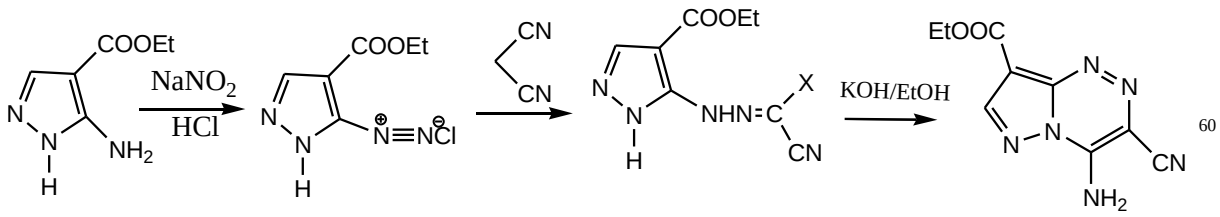




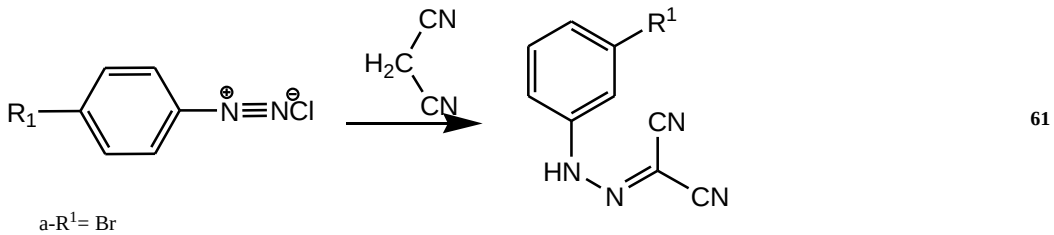
Nucleophilic addition reaction with diazonium salt.

Treatment of the produced diazonium salt with some activated methylene compounds, malononitrile and yielded the corresponding azo

Derivatives[83]

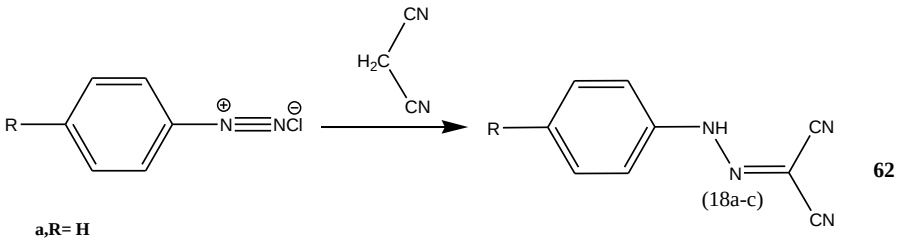


The reaction starts by diazotization of substituted anilines and reaction of the corresponding diazonium salts with malononitrile to give arylazomalononitrile (a-c)[84,85]



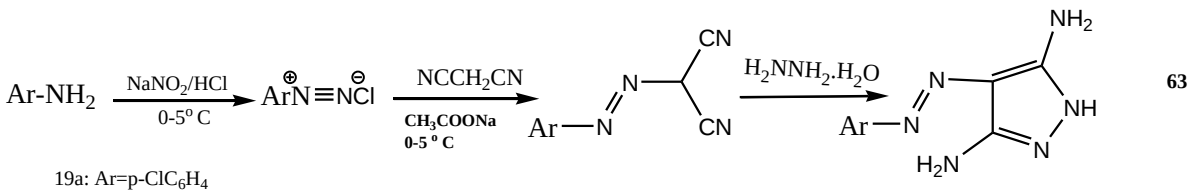
a-R^1= Br
b-R^1 = COMe
c-R^1= NO_2

Aniline , p-nitroaniline and p-anisidine were diazotized to afford the diazonium salts (a-c) which when allow to coupling with malononitril in sodium acetate buffered solution afforded the 2- arylhydrazonomalononitriles (a-c)[86]



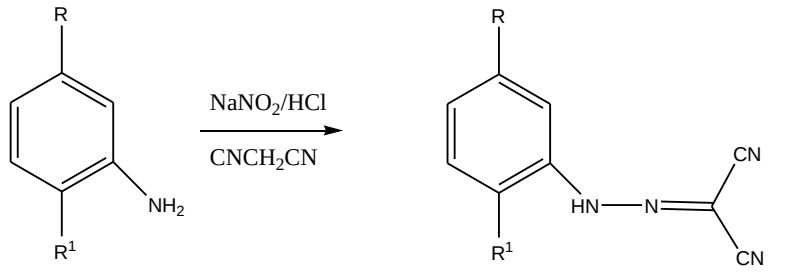
a,R= H
b,R = NO_2
C,R=O CH3

preparation of symmetrical and asymmetrical heterocyclic diazo dyes when aniline derivatives (a-b) were diazotized using sodium nitrite in hydrochloric acid ,the temperature was maintained below 5 ^{o}C in an ice bath .The diazotized products were then coupled with malononitrile to give the desired products (a-b) followed by reflux with hydrazine hydrate in ethanol , the cyclized compound (a-b) was obtained under reflux[87,88]



19a: Ar=p-ClC_6H_4
19b: Ar = p-NO2C_6H_4

The reaction starts by diazotization of aminobenzoic acid and reaction of the corresponding diazonium salts with malononitrile to give arylazomalononitriles.[89]



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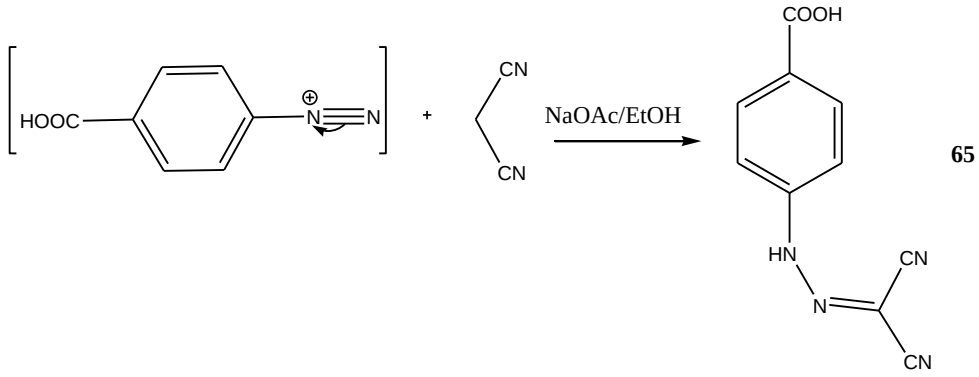
R= CO_2H
a: R^1= H b R^1=Me
c: R^1=CL d R^1=OMe

R^1=H
R= Br , b: R=CN
c: R= OMe

R= CO_2H
a: R^1= H b R^1=Me
c: R^1=CL d R^1=OMe

R^1=H
a: R= Br , b:R=CN
c: R= OMe

When p-amino benzoic acid was reacted with sodium nitrite and hydrochloric acid at 0 ^{0}C diazonium salts was obtaind which reacted in situ with malononitrile to afford. The explanation of this reaction is a nuclophilic attack of the active methylene of malononitrile on the diazonium salt to give 4-[(N\ - Dicyano methylene) hydrazino] benzoic acid (I)[90]



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CONCLUSION

This review attempted to summarize the synthetic methods and reactions of malononitrile groups. Many biologically inactive cyclic compounds were manufactured from that group. These reactions greatly extended artifical capabilities in organic chemistry.

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