Ain Shams University
Faculty of Women
for Arts, Science, and
Education
Department of Chemistry

# "Synthesis of polyaniline and nano polyaniline with some new quaternary salts, study of their electrical conductivity and antifouling effect."

**A Thesis Submitted for the Degree of M. Sc**

***In***

Organic Chemistry
**Presented**

***By***

*Nada Zakaria El-sayed Soliman*
Chemistry Department
Faculty of Women for Arts, Science and Education
Ain Shams University

**Supervised**

***By***

***Prof. Dr. Samia A. El-Abbady***
Prof. of Organic Chemistry

***Prof. Dr.Manal Gamal Mohamed***
Polymer lap. Petrochemical Dep.
Egyptian Petroleum research Institute

***Ass. Prof. Dr. Samia M. Agamy***
Ass.Prof. of Organic Chemistry

**(2019)**

Ain Shams University
Faculty of Women
for Arts, Science, and
Education
Department of Chemistry

# "Synthesis of polyaniline and nano polyaniline with some new quaternary salts, study of their electrical conductivity and antifouling effect."

**Thesis Advisors**

***Prof. Dr. Samia A. El-Abbady***
Prof. of Organic Chemistry

***Prof. Dr.Manal Gamal Mohamed***
Polymer lap. Petrochemical Dep.
Egyptian Petroleum research Institute

***Ass. Prof. Dr. Samia M. Agamy***
Ass.Prof. of Organic Chemistry

**Thesis Approved**

***Head of Chemistry Department***
**Prof. Dr. Mansoura Ismail**

**……**

**Approval of Chemistry Department Council** **/ /2019**

**Approval of Faculty Council** **/ /2019**

**Approval of University Council** **/ /2019**

## *Acknowledgement*

*In the name of Allah*

*The candidate is cordially acknowledge to* ***Prof. Dr. Samia A. El-Abbady,*** *Professor of Organic Chemistry, Chemistry Department, Faculty of Women for Arts, Science and Education, Ain Shams University, not only for suggesting the subject investigated, but also for her continuous advice and valuable criticism throughout the work.*

***Prof. Dr. Manal Gamal,*** *Prof. of Petro Chemical Petroleum Institute for her continuous advice and great help through the work, also during the preparation of the thesis.*

*The candidate is also appreciated* ***Dr. Samia M. Agamy,*** *Assistant Professor of Organic Chemistry, Chemistry Department, Faculty of Women for Arts, Science and Education, Ain Shams University, for her continuous assistance, encouragement and great help through the work, also during the preparation of the thesis.*

*&*

*The candidate is grateful to* ***Dr. Nesreen A. Fatthallah*** *Assoc. professor of environmental biotechnology, Egyptian Petroleum research Institute.*

*All the team of this work is indebted to* ***Dr. Asmaa Abo El-Naga*** *Faculty of Women for Arts, Science and Education, Ain Shams University.*

*Finally; I would like to express many thanks to all members of Chemistry Department especially* ***Prof. Dr. Mansoura M. Ismail*** *head of the department Faculty of Women for Arts, Science and Education, Ain Shams University, for their cooperation, sincere support and for all facilities provided during my research study.*

---

## DEDICATION

*To my distinguished family:*

*I do appreciate Allah for giving me*

*such wonderful family for their continuous support,*

*encouragement, and enlighten my life.*

# QUALIFICATION

**Name:** Nada Zakaria El-Sayed

**Scientific Degree:** B. Sc.

**Department:** Chemistry

**Faculty:** Faculty of Women for Arts, Science, and Education

**University:** Ain Shams University

**B. Sc. Graduation Year:** 2011

**M. Sc. Graduation Year:** 2019

# Contents

# Summary

The present work aimed to synthesize novel heterocyclic compounds containing sulphure, phosphorous, and silicon by ultrasound induced 1,3-dipolar cycloaddition as an alternative clean energy. PANI is favored because of its characteristics as a conductive electro active polymer to be used in different purposes such as electrical conductive, batteries, chemical and biological sensors, coating and corrosion protection.

The synthesized PANI, Nano PANI cycloadducts were evaluated via different criteria:

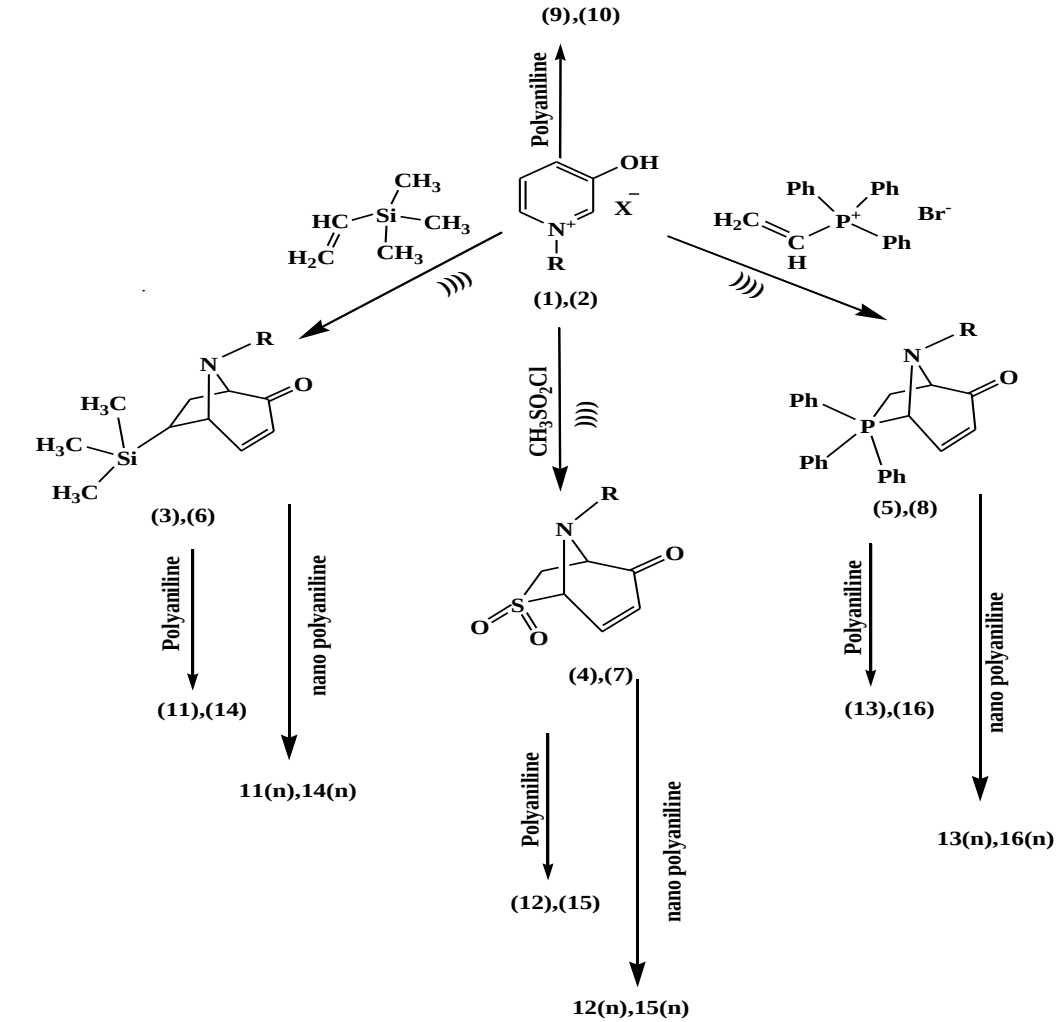
1- Electrical conductivity.

2- Antimicrobial and macro biofouling.

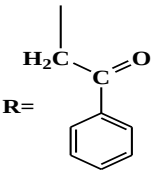
The prepared nano polyaniline cycloadducts with phosphorus showed the highest activity followed by those with silicon then by those with sulphure.

3- Environmental safety (toxicity test)

The prepared nano cycloadducts showed almost low or no activity against representative of non-target sea organisms.

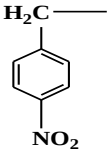



(1),((3),(4),(5),(9)
(11),(12),(13)
11(n),12(n),13(n) R=




(1,9) X⁻= Br⁻

(2),(6),(7),(8),(10)
(14),(15),(16)
14(n),(15(n),16(n) R=




(2,10) X= Cl⁻

**General scheme**

# 1. Introduction to Green chemistry and Sonochemistry.

## 1.1. Definition of green chemistry.

Green or Sustainable Chemistry is a term that refers to the creation of chemical products and processes that reduce or eliminate the use and production of harmful substances. They are used exclusively chemicals and chemical processes that do not have negative consequences for the environment. It is based on twelve principles that can be used to initially create or recreate molecules, materials, reactions and processes that are safer for human health and the environment. The processes of the Green Chemistry that have been developed to date include almost all areas of chemistry, including organic, inorganic, biochemistry, polymer, toxicology, environmental, physical, technological, etc. Through the several prevailing trends of the green program such as catalysis, bio catalysis and the use of alternative: renewable feedstock (biomass), reaction media (water, ionic liquids and supercritical fluids), reaction conditions (microwave irradiation) and new synthetic pathways (photocatalytic reaction), the dual goals – environmental protection and economic benefit can be achieved.**(Ivanković, Dronjić et al. 2017)**

## 1.2. Sonochemistry.

A renaissance in Sono chemistry took place in the 1980's, soon after the advent of inexpensive and reliable generators of high-intensity ultrasound (sound pitched above human hearing at frequencies greater than 16 kilohertz).**(Doktycz and Suslick 1990)**When a liquid is exposed to ultrasonic waves, bubble growth is created which is known as cavitation. Sound waves stress these bubbles, causing them to grow, contract and eventually to implode. With implosion, immense heat and pressure are produced that enhances the speed reactions. Every imploding bubble is a micro reactor in itself. This is due to the extreme heat released upon implosion that creates a local hot spot. Temperatures can reach 5000 °C with pressures of several hundred atmospheres. These benefits make ultrasound a useful tool for the synthesis of chemicals, pharmaceuticals and the production of new materials with unusual properties. Such uses of ultrasound have been grouped under the general name sonochemistry. **(Bang and Suslick 2010)**

## 1.3. What is Sonochemistry?

Sonochemistry is a term used to describe the effect of ultrasound on chemical reactions. The name is derived from the prefix "sono" indicating sound paralleling the longer established techniques which use light (photochemistry), pressure (piezochemistry), heat (thermo chemistry) and electricity (electrochemistry) to achieve chemical activation. Sonochemistry is a branch of chemistry dealing with the chemical effects and applications of ultrasonic waves i.e. sound with frequencies above 20 kHz (20,000 cycles per second) that lie beyond the upper limit of human hearing.**(Mason 1988)** Although the range of ultrasonic frequencies can be extended up to 100 MHz, it is customary to divide ultrasound into two distinct regions: conventional power ultrasound, up to 100 kHz, that especially affects chemical reactivity in liquids (although higher frequencies can also do so), and diagnostic ultrasound (above 2 MHz and up to 10 MHz) with applications in both medicine and materials processing. Over the last two decades there has been an ever-increasing interest in specific uses of power ultrasound to affect organic, inorganic and organometallic reactions.**(Alivisatos, Johnsson et al. 1996)**In addition, the best uses of power ultrasound are to Target detection using **So**und **N**avigation and **R**anging **(SONAR)** and in the medical applications field; Medical sonography (ultrasonography), acoustic targeted drug delivery and cleaning teeth in dental hygiene. and in the Industrial Applications ;ultrasonic testing (non-destructive) and ultrasonic cleaning.**(Suslick and Price 1999)**

## 1.4. Sonochemistry and green chemistry.

Many applications of ultrasound represent innovative and attractive advances, as a green chemistry point of view. Indeed, green chemistry is based on five basic concepts: (i) prevention, (ii) better use of the raw material, (iii) better waste management, (iv) energy savings, and (v) use of solvent compatible with the environment.**(Anastas and Warner 2000, Anastas and Eghbali 2010)** When the experimental conditions are optimized, the use of ultrasound is, in the majority of cases, in favor of the twelve principles of green chemistry. With better yields and selectivities, reduced reaction times, new reactivity, use of water as solvent, increasing or optimization of the reactivity in the presence of catalysts, the sonochemical reactions are often greener than those performed under silent conditions.**(Sillanpää, Pham et al. 2011)**Green chemistry and sonochemistry are both multidisciplinary, and the eco-friendly processes based on ultrasound have been reported in many areas such as sono catalysis, organic chemistry, preparation of

materials, polymer chemistry, biomass conversion, extraction, electrochemistry, enzymatic catalysis, environmental remediation, etc. **(Chatel 2018).**

## 1.5. Origin of Sonochemical effects.

Sound (ultrasound) is transmitted *via* waves, which alternately compress and stretch the molecular structure of the medium through which it passes. Liquids irradiated with ultrasound can produce bubbles. These bubbles oscillate, growing a little more during the expansion phase of the sound wave than they shrink during the compression phase. Under the proper conditions these bubbles can undergo a violent collapse, which generates very high pressures and temperatures. This process is called cavitation.**(Bidin 1995)**Thus the average distance between molecules in a liquid varies as the molecules oscillate about their mean position. If sufficiently large negative pressure *(i.e.* sufficiently below ambient) is applied on the liquid (here it is the acoustic pressure on rarefaction) the liquid breaks down and voids are created, *i.e.* cavitation bubbles form. In practice, cavitation occurs at considerably lower applied acoustic pressure owing to the presence of weak spots in the liquid, which lower its tensile strength.**(Brennen 2013)**Weak spots include the presence of gas nuclei in the form of dissolved gas, minute suspended gas bubbles or tiny suspended particles. The cavitation bubbles which are initiated during the rarefaction cycle grow over a few cycles taking in some vapour or gas from the medium, to an equilibrium size which matches the frequency of bubble resonance to that of the sound frequency applied.**(Shah, Pandit et al. 2012)** The acoustic field experienced by an individual bubble is not stable because of the interference of other bubbles forming and resonating. As a result, some bubbles suffer sudden expansion to an unstable size and collapse violently. These cavities generate the energy for chemical and mechanical effects when they collapse.**(Doktycz and Suslick 1990)** The parameters which affect in cavitation are frequency, solvent viscosity, solvent surface tension, temperature, solvent vapor pressure, bubbled gas and attenuation of sound.

## 1.6. Applications in Organic synthesis.

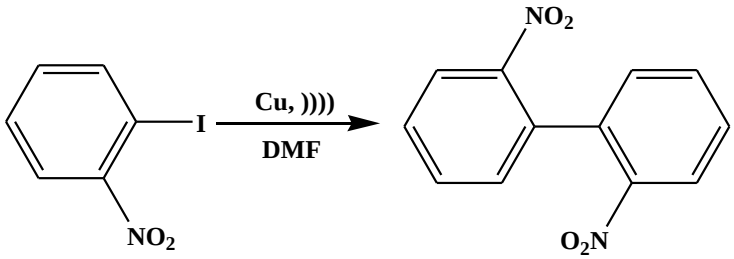
### 1.6.1. Organometallic reactions.

The important area of organometallic sonochemistry was pioneered in 1950 by Renaud, who reported that certain organometallics could be prepared in undried solvents, with inactivated metals, in shorter reaction times, using a simple cleaning bath. At the time ultrasonic transducers were not commonly available and therefore this work, which was also hold on non-

aqueous sonochemistry, remained unknown. Thirty years later, Luche and Damiano described the facile sonochemical preparation of organolithium and Grignard reagents and their Barbier-type coupling with carbonyls.**(Luche and Damiano 1980)**This, together with the reductive dehalogenation of dibromoketones with ultrasonically dispersed mercury was the jumping-off point of modern sonochemistry**.(Fry and Bujanauskas 1978)**

## 1.6.2. .Ullman coupling reaction.

The Ullman coupling of 2-iodonitrobenzene to dinitrobiphenyl in dimethylformamide **(Suslick, Casadonte et al. 1989)** at 60 °C shows a 64-fold rate increase under sonication using substantially less metal than in conventional methodology. This is mainly explained by reduction in particle size and continuous surface activation of copper used.**(Repič and Vogt 1982)**(cf. scheme 1)

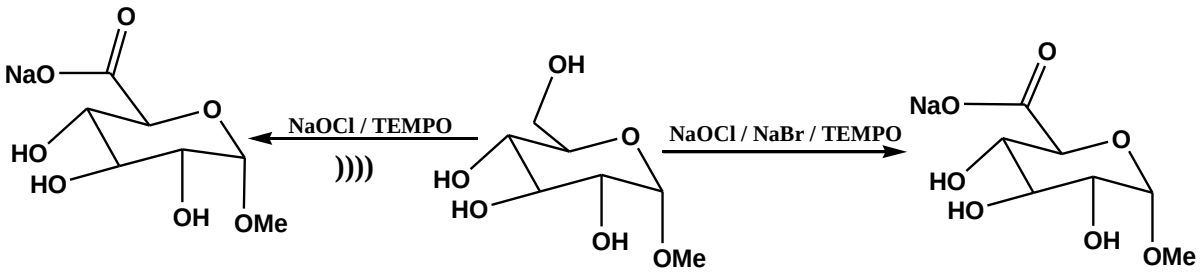



**Scheme (1)**

## 1.6.3. Oxidation reactions.

## Oxidation of methyl α-D-glucopyranoside.

Brochette *et al* reported the **TEMPO** (2,2,6,6-Tetramethylpiperidine-l-oxyl) mediated oxidation of methyl α-D-glucopyranoside or sucrose in the presence of stoichiometric amounts of sodium hypochlorite in basic aqueous medium under sonic condition. The reaction can occur without the usually necessary sodium bromide, showing that ultrasound acts at the level of the formation of the nitrosonium ion, the active oxidizing species in the catalytic cycle.**(Brochette-Lemoine, Joannard et al. 1999)**(cf. scheme 2)



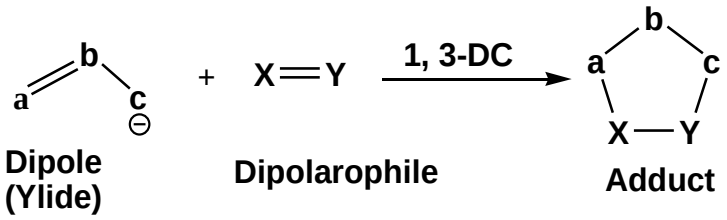

**Scheme (2)**

## 2. Introduction to 1,3-dipolar cycloaddition reactions.

The chemistry of heterocyclic compounds is one of the most important branches of organic chemistry, of equal interest for its theoretical implications, for the diversity of its synthetic procedures and for the biological and industrial applications. Over the decades, the cycloaddition chemistry has continued to maintain a significant place in synthetic organic chemistry, for the construction of mono- and polycyclic systems, as a consequence of being able to deliver high selectivity and molecular complexity from relatively simple and accessible compounds. 1,3-Dipolar cycloaddition reaction (herein after referred to as 1,3-DC reaction) has taken a prominent place for the preparation of biologically active nitrogen containing five membered heterocycles.**(Pelletier 1999)** The 1,3-DC reactions has offered numerous diversity for the organic chemists to accomplish the synthesis of complex heterocyclic systems with high selectivity.**(Coldham and Hufton 2005, Lashgari and Ziarani 2012)**

### 2.1. Origin of 1,3-DC reactions.

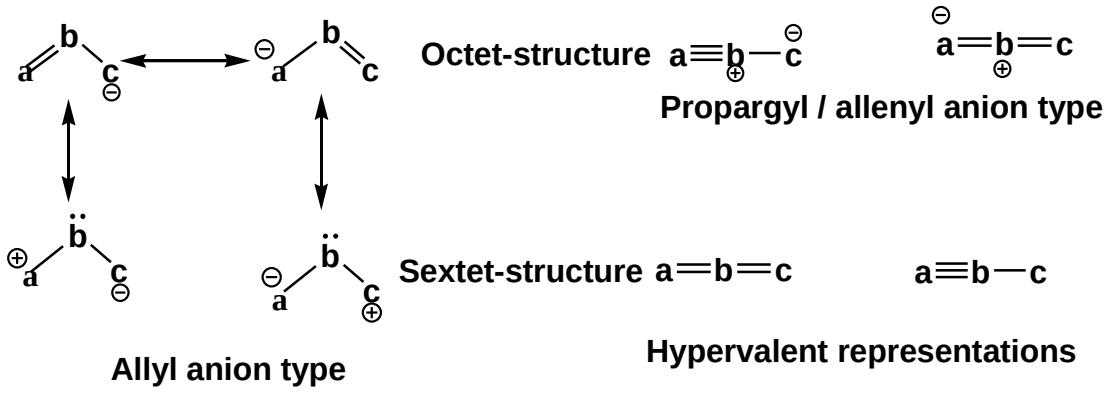
The 1,3-dipolar cycloadditions are pericyclic reactions like Diels-Alder reaction and proceed through a 6π-electron 'aromatic' transition state. The phenomenal difference is, in a Diels-Alder reaction, the πs 4 component having four atoms undergo cycloaddition with a πs component resulting in a six-membered cyclic framework, whereas in 1,3-dipolar cycloaddition reaction the zwitterionic πs 4 component having triad of atoms undergo cycloaddition with a πs 2 component resulting in five-membered heterocycles. Although Huisgen**(Huisgen 1963)** classified the 1,3-dipoles and introduced the concept of 1,3- dipolar cycloaddition in 1963, it was not popular until the first intramolecular 1,3-DC reaction of azomethineylide was reported by Padwa in 1976.**(Padwa and Pearson 2003)** Since then remarkable developments have taken place in 1,3-DC reaction, with the establishment of various useful methods for the formation of a variety of heterocycles. (cf. scheme 3)




**Scheme (3)**

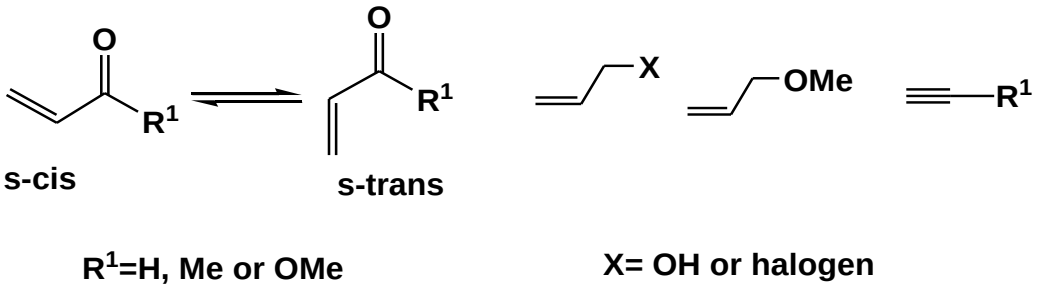
## 2.2. The dipole/ylide.

The "1,3-dipole" can be represented as a zwitterionic resonance structures of **a-b-c** unit having four electrons in three parallel atomic π orbitals perpendicular to the plane of the dipole, which undergoes 1,3-cycloaddition to a multiple bond system, the "dipolarophile" to give a five-membered ring system. In general, 1,3-dipoles can be classified into two different types: **(i)** The allyl anion type **(ii)** The propargyl/allenyl anion type The allyl anion type is characterized by four electrons in three parallel pz orbitals perpendicular to the plane of the dipole in which the dipole has bent structure. Two resonance structures in which the three centers have an electron octet and two structures in which **'a'** or **'c'** has an electron sextet, can be drawn. The central **'b'** can be nitrogen, oxygen, or sulfur. The propargyl/allenyl anion type has an extra π electron located in the plane orthogonal to the allenyl anion type molecular orbital (MO), and the former orbital is, therefore, not directly involved in the resonance structures and reactions of the dipole. The propargyl/allenyl anion type is linear, and the central atom 'b' is limited to nitrogen. The 1,3-dipoles are occasionally represented as hypervalent structures.**(Pandey, Banerjee et al. 2006)**(cf. scheme 4)




**Scheme (4)**

The 1,3-dipoles containing various combinations of carbon and hetero atoms are theoretically possible and Huisgen classified eighteen possibilities of 1,3-dipoles into allyl and propargyl type.**(Huisgen and Weinberger 1985)**Of all the 1,3-dipoles, cycloaddition reaction of azomethineylides has been more intensely studied than most of other dipoles due to their remarkable synthetic possibilities.**(Nájera and Sansano 2008)** According to Huisgen, "azomethineylides are planar molecules composed of one nitrogen atom and two terminal $sp^2$ carbons and belong to a class of azomethinebetaines that do not possess a double bond in the sextet structure but have internal octet stabilization".**(GAVASKAR 2010)**Generally cycloaddition of azomethineylides to olefinic and acetylinic dipolarophiles leads to the formation of pyrrolidines and $\Delta^3$-pyrrolines, respectively. Dipolarophile like a dienophile in Diels Alder reaction is a reactive alkene or alkyne containing $2\pi$ electrons. Therefore, α,β-unsaturated aldehydes, ketones, esters, allylic alcohols, allylic halides, vinylic ethers, and alkynes readily act as good dipolarophiles. The alkene moiety may contain mono-, di-, tri- or even tetra-substituents (only monosubstituted ones are shown here), but due to steric factors, tri- and tetra-substituted alkenes often display very low reactivity in reactions with dipoles. (cf. scheme 5)




**Scheme (5)**

The chemical reaction between a 1,3-dipole and a dipolarophile to form a five-membered ring. The earliest 1,3-dipolar cycloadditions were described in the late 19th century to the early 20th century, following the discovery of 1,3-dipoles. Mechanistic investigation and synthetic application were established in the 1960s, primarily through the work of Rolf Huisgen.**(Huisgen 1963)** Hence, the reaction is sometimes referred to as the **Huisgen cycloaddition** (this term is often used to specifically describe the 1,3-dipolar cycloaddition between an organic azide and an alkyne to generate 1,2,3-triazole). 1,3-dipolar cycloaddition is an important route to the regio- and stereoselective synthesis of five-membered heterocycles and their ring-opened acyclic derivatives. (cf. scheme 6)