

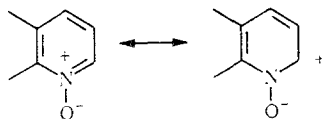
AROMATIC N-OXIDES AS 1,3-DIPOLES AND π -DONORS IN REACTIONS WITH UNSATURATED COMPOUNDS.

REVIEW

A. V. Ryzhakov and L. L. Rodina

A summary is given for the data on 1,3-dipolar cycloaddition reactions of aromatic N-oxides, which are convenient one-step methods for the synthesis of several heterocyclic compounds. Special attention was given to N-oxides as possible ambident donors in the formation of molecular complexes with dipolarophiles.

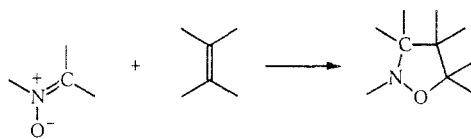
The higher activity of aromatic N-oxides in comparison with the corresponding bases both relative to electrophilic and nucleophilic reagents has made these compounds very important synthones in the preparation of pyridine derivatives [1, 2]. However, the synthetic value of N-oxides in ring substitution has not been exhausted. These compounds may also be seen as nitrene analogs characterized by 1,3-dipolarophilic cycloaddition reactions.



The present review covers the reactions of aromatic N-oxides with dipolarophiles proceeding through various mechanisms though all involve initial formation of [3+2]-cycloadducts I and II (Schemes 1 and 2).

1. GENERAL CHARACTERISTICS OF DIPOLAR CYCLOADDITION TO AROMATIC N-OXIDES

Most of the reactions of nitrones with dipolarophiles lead to rather stable five-membered isoxazolidine cycloadducts [3]:



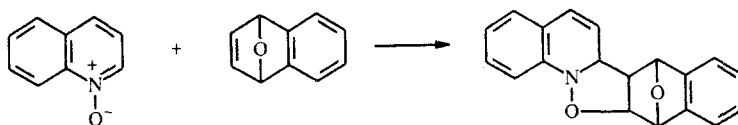
In contrast to nitrones, the N-oxide 1,3-dipole is often included within an aromatic system, which breaks down upon the formation of new bonds. Thus, on one hand, N-oxides are less reactive than nitrones relative to dipolarophiles and, on the other, when the cycloaddition reaction nevertheless occurs, it is usually accompanied by further rearrangements. The driving force for most of these secondary reactions is the restoration of the aromaticity of the heterocyclic ring lost in the primary cycloadducts. The major directions for such reactions are given in Schemes 1 and 2.

Although primary cycloadducts I and II have been only rarely isolated, their prior formation is assumed in all the reactions described below.

The major condition for cycloaddition is the complementary nature of the reagents. However, in most reported reactions, the electron density in the N-oxide is greater than in dipolarophiles. Thus, there is matching of the reagents: The

O. V. Kuusinen Petrozavodsk State University, Petrozavodsk. Saint Petersburg State University, Saint Petersburg. Translated from *Khimiya Geterotsiklicheskih Soedinenii*, No. 5, pp. 579-591, May, 1992. Original article submitted June 25, 1991.

most reactive dipolarophiles have the greatest number of electron-withdrawing substituents, while the most reactive N-oxides have the greatest number of electron-donor substituents. Furthermore, the activity of N-oxides increases in going from monocyclic to polycyclic compounds. The question of the possibility of carrying out reactions with inversed electronic nature of the reagents still remains open. In this regard, considerable interest is found in the work of Wittig and Steinhoff [4], who described the reaction of quinoline N-oxide or pyridine N-oxides containing electron-withdrawing substituents with 1,4-epoxy-1,4-dihydronaphthalene:



In this case, the reaction occurs between the HOMO of the dipolarophile and LUMO of the N-oxide. We should note that a stable [3+2]-cycloadduct is isolated as the reaction product.

We should also note that some of the most active dipolarophiles are also strong π -acceptors capable of forming charge transfer complexes with potential electron donors, including aromatic N-oxides.

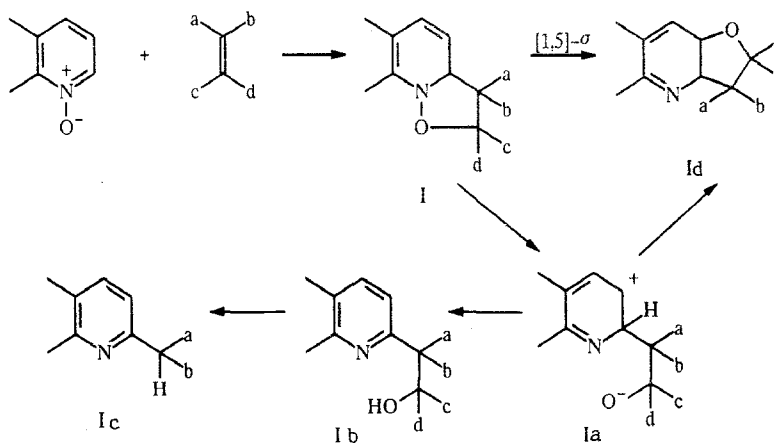
In analyzing the literature data, the major pathways for the reactions of N-oxides with unsaturated compounds may be discerned.

2. FORMATION OF A STABLE CYCLOADDUCT

The formation of a stable cycloadduct has been observed in only a few cases upon the reaction of N-oxides with strained ethylenic dipolarophiles. The driving force for such reactions is apparently a reduction in the strain in these molecules [4, 5].

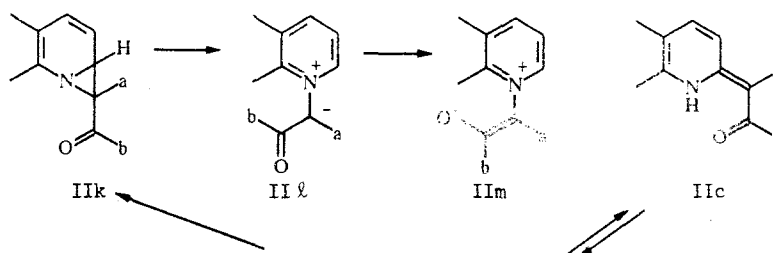
Scheme 1

Mechanism for the Reaction of N-Oxides with Alkenes and Heterocumulenes

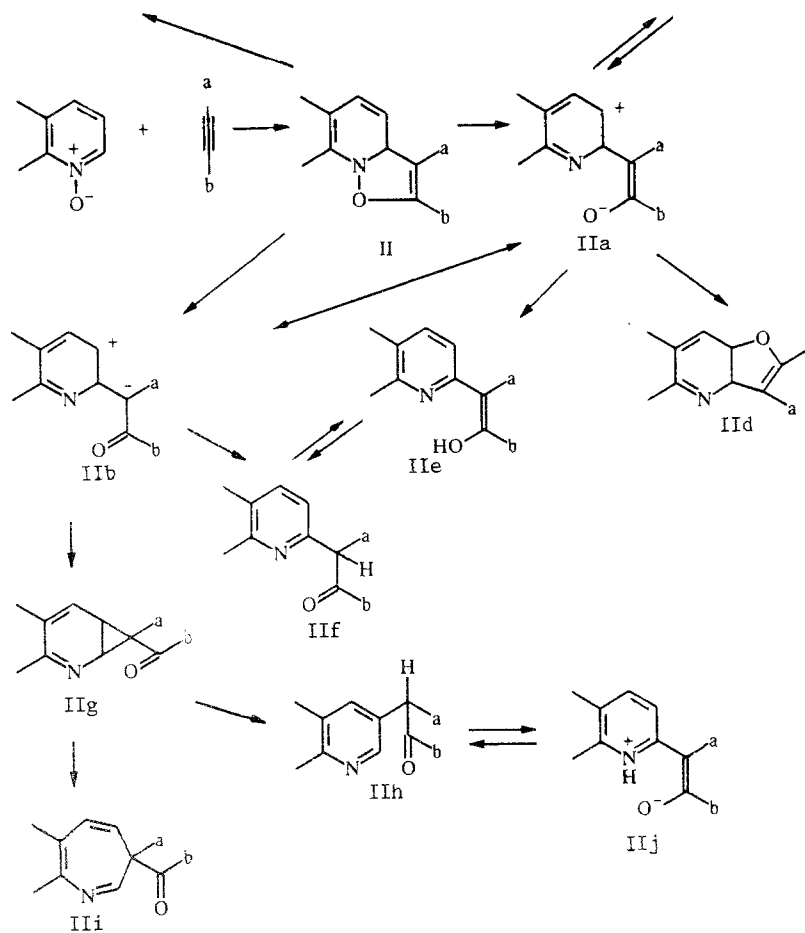


Scheme 2

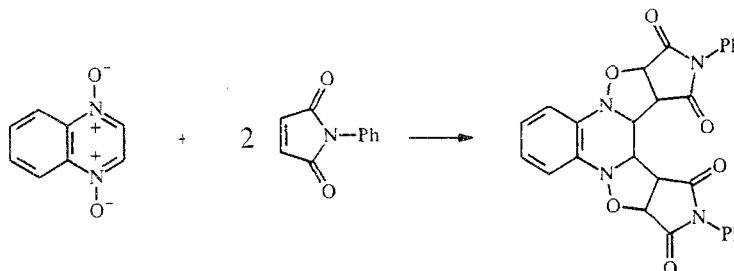
Mechanism for the Reaction of N-Oxides with Alkynes



(continued on next page)

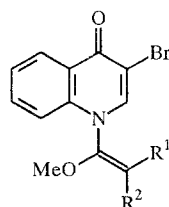


Quinoxaline N,N'-dioxide has a greater tendency than other N-oxides to give stable cycloadducts. An example may be found in the reaction of this dioxide with N-phenylmaleimide, which proceeds at 80°C in DMF for 12 h at both the N-oxide groups [6]:



The reaction of quinoxaline N-monoxide with dimethyl maleate proceeds analogously.

Yoshida et al. [7] have isolated stable cycloadducts in the reaction of 3-bromo-4-methoxyquinoline N-oxide with methyl propiolate and dimethyl acetylenedicarboxylate [7]. However, a more detailed study carried out also by Yoshida et al. [8] showed that these compounds have the following structure:



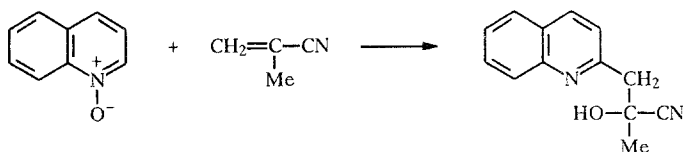
There have been no other reports of stable primary cycloadducts although the formation of such intermediates has been proposed in all the cases described below.

3. FORMATION OF 2-SUBSTITUTED DERIVATIVES

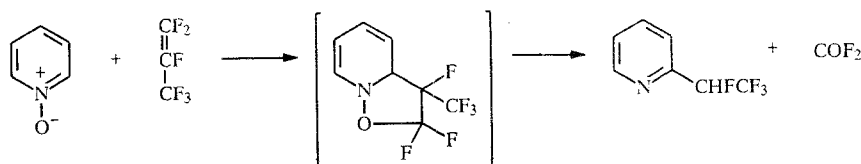
As a rule, the reaction of N-oxides with activated alkenes leads to 2-substituted derivatives. The same reaction course is found in the reactions of these compounds with some alkynes.

Zwitterions Ia and IIa are presumably formed upon cleavage of the N—O bond in primary cycloadducts I and II. In the latter case, resonance stabilization is possible with negative charge transfer to a carbon atom (structure IIb) [9, 10]. 2-Substituted derivatives Ib, IIe, and IIf are formed due to intramolecular hydrogen atom migration in ions Ia, IIa, and IIb.

Quinoline N-oxide and methacrylonitrile react in accord with this mechanism [11]:

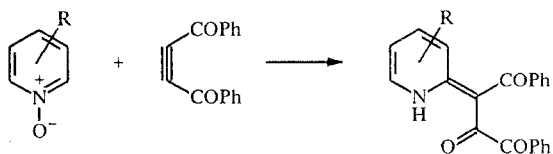


The reaction with acrylonitrile proceeds analogously [12]. Under similar conditions, isoquinoline N-oxide forms only 1-substituted derivatives [11]. This behavior is in accord with the greater stability of the isoquinolinium cation in position 1 than in position 3 [13]. When groups capable of leaving are present, compounds such as Ib may decompose to give simpler derivatives Ic. An example may be found in the reaction of pyridine N-oxide with perfluoropropylene [14]:



In order to prevent the polymerization of ethylenic dipolarophiles by the action of N-oxides, small amounts of hydroquinone should be added to the reaction mixture [12, 15].

Among acetylenic dipolarophiles, dibenzoylacetylene gives 2-substituted derivatives [16, 17]. In this case, the compounds isolated correspond to structure IIc:



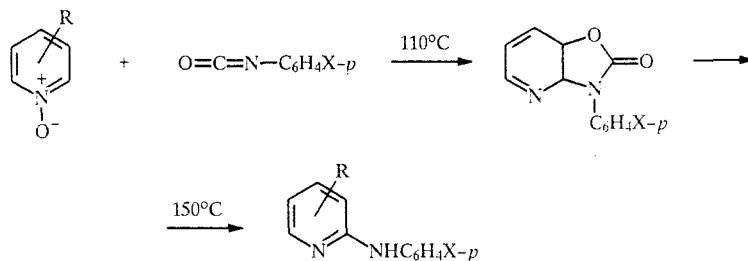
2-Substituted derivatives are also formed in small amounts in the reactions of 4-methoxyquinoline N-oxide with the dimethyl ester of acylenedicarboxylic acid [18] and or pyridine N-oxide with phenylcyanoacetylene [19].

These reactions have synthetic importance in the preparation of 2-substituted pyridines and quinolines [20].

4. FORMATION OF CONDENSED SYSTEMS

Another possibility for the stabilization of zwitterions Ia and IIa lies in ring closure at C₍₃₎ of the pyridine ring. The formation of structures Id and IId may be seen as a concerted [1,5]-sigmatropic shift in primary cycloadducts I and II. This pathway is predominant when heterocumulenes such as aryl and tosyl isocyanates are used as the dipolarophiles [21-27].

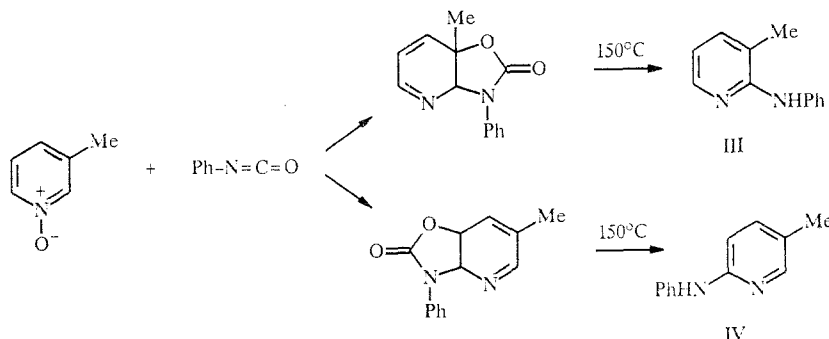
The reaction of pyridine N-oxides with aryl isocyanates has been studied extensively. The effect of the substituents in the N-oxide and isocyanate on the reaction rate was predicted on the basis of a MINDO calculation and experimentally confirmed [24]:



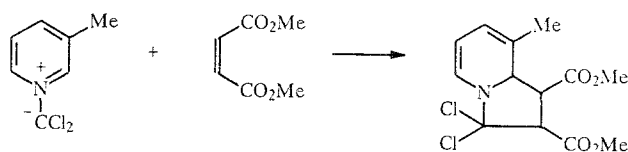
These reactions are facilitated when electron-withdrawing substituents are introduced into the aryl isocyanate ring and electron-donating substituents are introduced into the N-oxide ring. This behavior demonstrates that the N-oxide reacts with its HOMO and the dipolarophile reacts with its LUMO.

The oxazolo[2,3-b]pyridines formed decompose to give 2-substituted derivatives at 150°C.

The reaction in the case of asymmetrical 3-picoline N-oxide leads to isomeric compounds III and IV [25]:

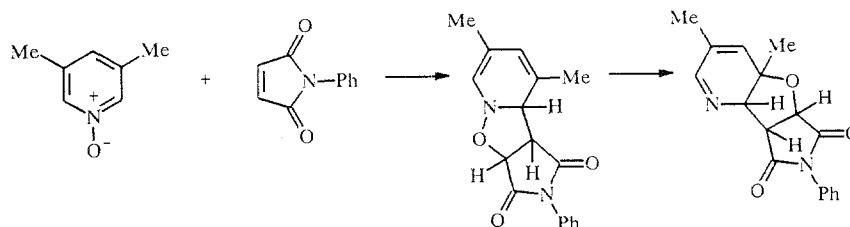


Although the formation of isomer IV is favored sterically, the observed reaction product ratio does not conform to this hypothesis. The formation of the sterically hindered cycloadduct by attack at the oxygen atom and C₍₂₎ is attributed to efficient secondary orbital interactions between the protons of the methyl group of the N-oxide and aromatic ring of the isocyanate [25]. Secondary orbital effects also play a significant role in the 1,3-dipolar cycloaddition of pyridinium N-ylids. Thus, the reaction of 3-picoline dichloromethyl-N-ylid with dimethyl maleate leads to the predominant formation of the sterically hindered cycloadduct [28]:



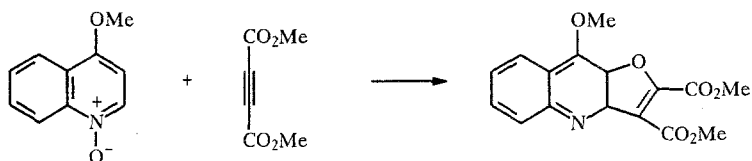
However, the steric hindrance in the case of 2,3-dimethylpyridine N-oxide is so great that attack occurs exclusively at the oxygen atom and C₍₆₎ [25].

The formation of furo[2,3-b]pyridines upon the reaction of 3,5-dimethylpyridine N-oxide with phenylmaleimide has permitted study of the stereochemistry of this reaction [27]. The endo isomer formed as the result of a [1,5]-sigmatropic shift of the primary exo cycloadduct is the only reaction product:

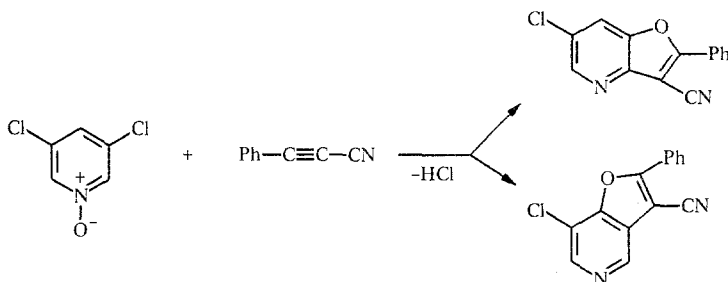


The formation of the sterically disadvantageous exo cycloadduct in the first reaction step is also attributed to secondary orbital effects between the protons of the N-oxide methyl groups and aromatic ring of phenylmaleimide.

Similar transformations were also found in the reactions of aromatic N-oxides with some acetylenic dipolarophiles. Thus, 4-methoxyquinoline N-oxide reacts with dimethyl acetylenedicarboxylate to give furo[2,3-b]quinoline [18]:



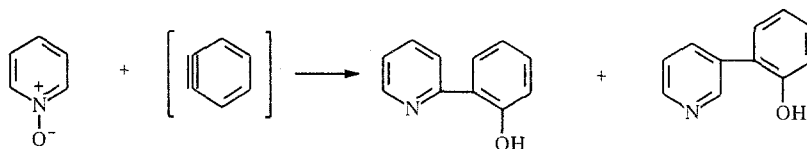
The reaction of 3,5-dihalopyridine N-oxides with phenylcyanoacetylene leads to two isomeric condensed systems, namely, furo[2,3-b]pyridine and furo[2,3-c]pyridine [8]:



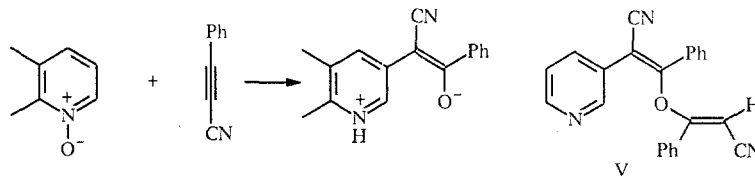
These reactions permit us to obtain condensed heterocycles, which were previously difficult to synthesize.

5. FORMATION OF 3-SUBSTITUTED DERIVATIVES

The formation of 3-substituted derivatives is encountered only when using acetylenic dipolarophiles. A special mechanism is characteristic for this transformation. Thus, the cyclization of N-ylid structure IIb may lead to the three-membered ring in IIg. This intermediate may be formed directly from primary cycloadduct II by a [3,5]-sigmatropic shift. The subsequent cleavage of the $C_{(2)}-C$ bond leads 3-substituted compounds represented by two tautomers IIh \rightleftharpoons IIj. An example may be found in the reaction of pyridine N-oxide with dehydrobenzene [9], which gives an $\sim 1:4$ mixture of 2- and 3-substituted derivatives in 26% overall yield:



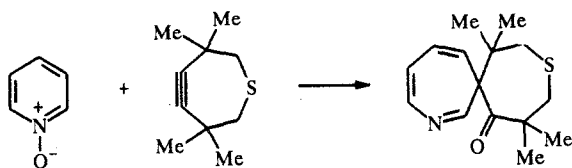
The formation of 3-substituted derivatives (in a mixture with other compounds) is observed in the reactions of pyridine N-oxides with phenylacetylene [19]:



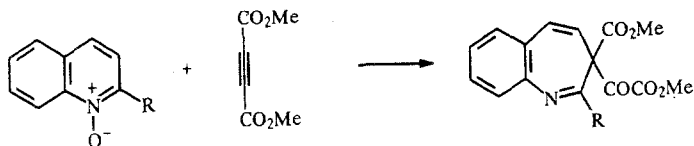
This reaction is complicated by the formation of a 1:2 adduct with tentative structure V [8].

6. FORMATION OF 3H-AZEPINES

An alternative stabilization for structure IIg is ring expansion to give 3H-azepine derivatives IIIi. This pathway is found in the reaction of N-oxides with strained cycloalkynes [29]. One of the driving forces for this reaction is a reduction in strain in the cycloalkyne molecule.



2-Substituted N-oxides react analogously with acetylenic dipolarophiles [30-32]:

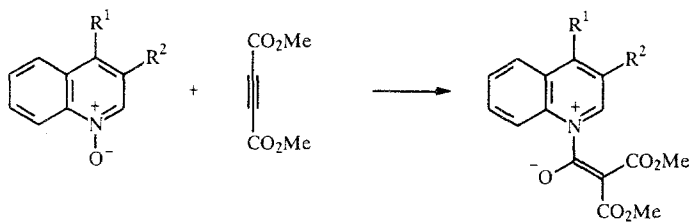


However, the introduction of substituents such as a methoxy group or chlorine atom at C₍₄₎ of the N-oxide completely alters the reaction course. In this case, furo[3,2-b]quinolines are formed, while benzazepines are not obtained [18].

7. FORMATION OF N-SUBSTITUTED COMPOUNDS

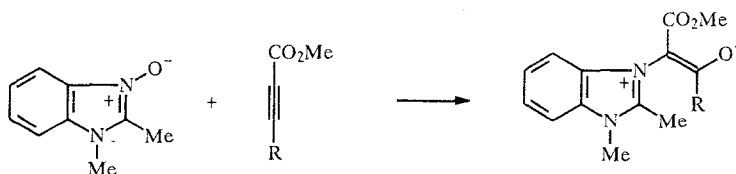
The most general pathway for the reactions of aromatic N-oxides with acetylenes is the formation of N-betaines and N-ylids. The major factor accounting for this pathway is the presence of strong electron-withdrawing groups in the dipolarophile molecule, which are capable of stabilizing negative charge in ions II ℓ and II m . Thus, for example, esters of acylenedicarboxylic acid are more active in such reactions than esters of propiolic acid [33]. Initially formed cycloadduct II undergoes bond rearrangement of the 4-isoxazoline ring [34] with formation of a [1,2]-condensed system III. Cleavage of the C₍₂₎-C bond gives a dipolar ion, which may be represented by two resonance forms, namely, ylid II ℓ and betaine II m .

Good correlation with the electronic properties of the substituents is found in the reactions of 3- and 4-substituted quinoline N-oxides with dimethyl acylenedicarboxylate [7, 18, 35]:

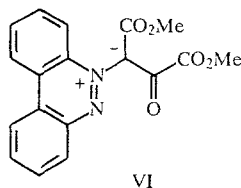


R¹, R²=H, Br, Cl, OMe, Me, NO₂, 2-quinoly1

Isoquinoline N-oxide reacts analogously [36]. Imidazole N-oxides also are rather active relative to acetylenic dipolarophiles [37-39]:



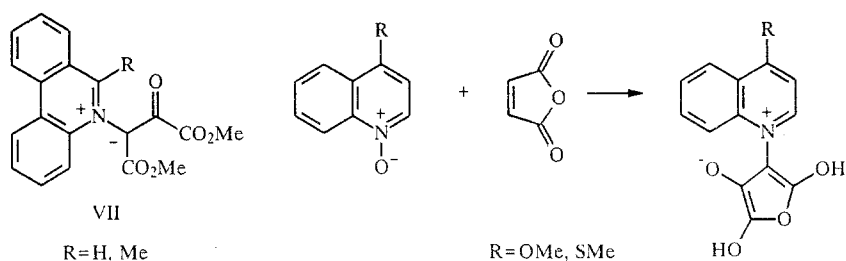
R=H, Me, CO₂Me



On the other hand, benzo[*c*]cinnoline reacts with dimethyl acetylenedicarboxylate to form 1:1 adduct VI in yields of only 2-7% [40]. The second nitrogen atom in the heterocycle leads to deactivation in this reaction.

The presence of substituents at C₍₂₎ of the N-oxide reduces the activity of these compounds as a result of steric hindrance. Thus, 6-methylphenanthridine 5-oxide, in contrast to phenanthridine 5-oxide, does not react with methyl propiolate but both compounds react readily with more reactive dimethyl acetylenedicarboxylate [33] to form N-ylids VII.

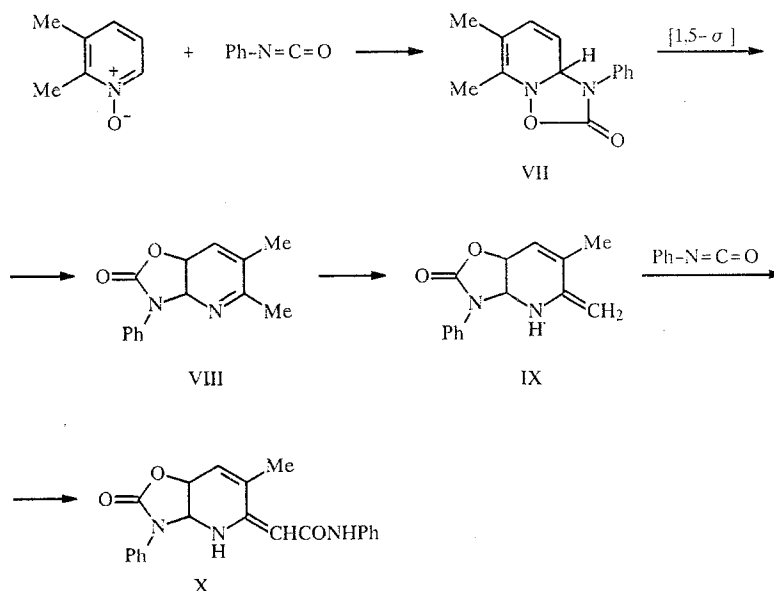
The formation of N-substituted betaines was once thought to be characteristic only for acetylenic dipolarophiles. However, we have recently shown that such systems are formed upon the reaction of activated quinoline N-oxides with maleic anhydride [41]:



We should note that the maleic anhydride fragment is converted into an aromatic furan ring. The structure of the isolated adducts was indicated by PMR and IR spectroscopy and qualitative reactions [41].

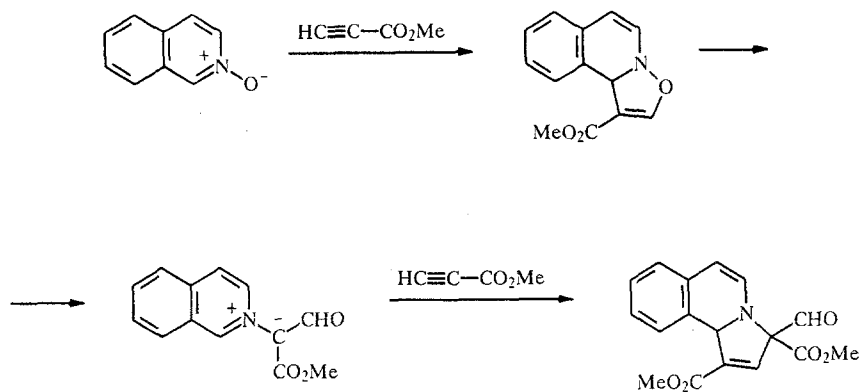
8. FORMATION OF 1:2 AND 1:3 ADDUCTS

In some cases, the 1:1 adducts may react with excess dipolarophile to give 1:2 and 1:3 adducts [25, 42]. The reaction of 2,3-dimethylpyridine with two moles of phenyl isocyanate has been studied in greatest detail [25]. The reaction rate increases only slightly with decreasing polarity of the solvent. This finding excludes an ionic mechanism and permits us to consider this transformation as a sequence of pericyclic reactions:



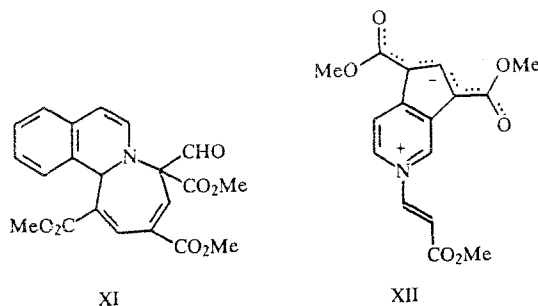
Initial cycloadduct VII rearranges to 1:1 adduct VIII as the result of a [1,5]-sigmatropic shift, which is followed by a [1,3]-hydrogen shift. Although 1:1 adduct IX may be isolated under certain conditions, 1:2 adduct X is usually formed. In this case, there is [2+2]-cycloaddition of a second phenyl isocyanate molecule to IX with subsequent cleavage of the C—N bond of the four-membered ring.

Isoquinoline N-oxide reacts with two or three moles of methyl propiolate to give the formation of the corresponding adducts [42]:



The addition of a second dipolarophile molecule leads to an N-ylid and a stable cycloadduct. The 1:3 cycloadduct has structure XI.

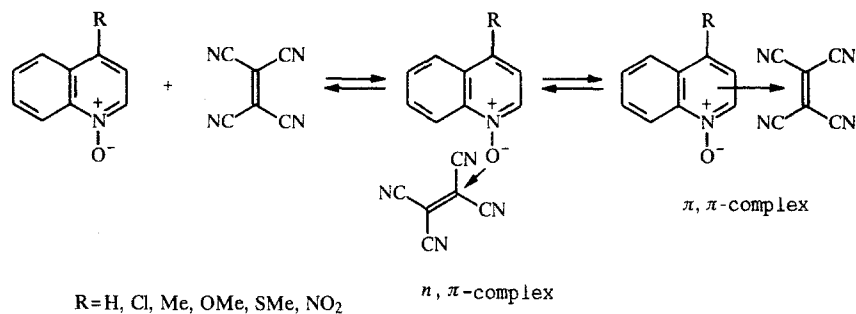
The reaction of pyridine N-oxide with methyl propiolate proceeds through a complex mechanism and leads to the formation of eight compounds, of which five were characterized [43]. The major reaction product, XII, is formed in 23% yield upon the addition of three moles of methyl propiolate to one mole of the N-oxide. The 1:1 and 1:2 adducts are formed in 2.3 and 8% yield, respectively.



9. FORMATION OF CHARGE TRANSFER COMPLEXES

A specific feature of aromatic N-oxides, in contrast to other dipoles, is that these compounds may act as π -donors as well as n-donors. On the other hand, some dipolarophiles are strong π -acceptors. Thus, the possibility of a donor-acceptor interaction must also be taken in the reactions of aromatic N-oxides with dipolarophiles. In this case, the charge transfer complexes formed either precede some of the previously described 1,3-dipolar cycloaddition reactions or are the final reaction products. An example of the first type of complexes may be the charge transfer complex of pyridine N-oxides with phenyl isocyanate [26]. These complexes precede cycloaddition reactions, leading to oxazolo[2,3-b]pyridines (see Section 4) and exist only in solution in equilibrium with their components. The complexation equilibrium constants for N-oxides are higher than for nonoxide heterocycles and increase with increasing donor capacity of the N-oxides (with the introduction of methyl substituents). New charge transfer bands appear in the vicinity of 450 nm in the electronic spectra of such charge transfer complexes and are an indication of their formation. It is interesting that the electron-withdrawing site in the phenyl isocyanate molecule is not the aromatic ring, but rather the N=C bond.

In the case of a stronger π -acceptor, namely, tetracyanoethylene (TCE), the charge transfer complexes with N-oxides are so stable that they do not undergo further chemical reaction. Such complexes were also initially studied for the simplest N-oxides, namely, pyridine and alkylpyridine N-oxides [44, 45]. These charge transfer complexes could not be isolated as solids. Studies were subsequently carried out on more reactive polycyclic N-oxides, containing strong electron-donating substituents such as methoxy and methylmercapto groups [46]. In this case, solid nonstoichiometric charge transfer complexes were also obtained. A good correlation was found between the complex formation constants, position of the charge transfer bands, yields, and relative TCE content relative to substituent properties for 4-substituted quinoline N-oxides:



The question concerning the donor site is fundamental for aromatic N-oxides, which are ambident donors. Such sites may be either the oxygen atom of the N-oxide group (n-site) or aromatic π -system (π -site). This question is resolved largely on the basis of UV and IR spectral data. The weaker charge transfer complexes of N-oxides with TCE existing only in solution are presumably n, π -complexes [41]. On the other hand, solid charge transfer complexes of quinoline and isoquinoline N-oxides are π , π -complexes [46].

Weaker π -acceptors such as p-benzoquinone and bromanil may participate as partners in complexation in reactions with some aromatic N-oxides [47].

* * *

Thus, aromatic N-oxides display dual reactivity relative to activated unsaturated systems.

1,3-Dipolar cycloaddition is realized in reactions with typical dipolarophiles. The effects of electronic and steric factors in the reagents on the nature of the reaction have not been studied sufficiently. Nevertheless, the reported reactions may be considered as variants of unusual pathways for the synthesis of substituted pyridine derivatives.

On the other hand, aromatic N-oxides behave as ambident donors in complexation with π -acceptors. The study of such reactions also holds promise since many of the stable charge transfer complexes are used in the manufacture of materials for the electronics industry. Thus, for example, solid charge transfer complexes quinoline N-oxides with TCE are either dielectrics or semiconductors with valuable electrophysical properties [48].

LITERATURE CITED

1. E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).
2. D. V. Ioffe and L. S. Éfros, *Usp. Khim.*, **30**, 1325 (1961).
3. I. Kuruts, Isomerization of Cyclic Nitrones [in Russian], Chemical Sciences Candidate's Dissertation, Leningrad (1978).
4. G. Wittig and G. Steinhoff, *Ann.*, **676**, 21 (1964).
5. T. Hisano, K. Harano, T. Matsuoka, T. Suzuki, and Y. Murayama, *Chem. Pharm. Bull.*, **38**, 605 (1990).
6. M. Ungureanu and D. J. Zugravescu, *An. Sti. Univ. Jasi*, No. 1, 29 (1974).
7. M. Yoshida, Y. Ishiguro, T. Yamamori, M. Aoyama, T. Endo, H. Noda, K. Funakoshi, S. Saeki, and M. Hamana, *Heterocycles*, **12**, 167 (1979).
8. Y. Ishiguro, M. Yoshida, K. Funakoshi, S. Saeki, and M. Hamana, *Heterocycles*, **20**, 193 (1983).
9. R. A. Abramovitch and I. Shinkai, *J. Am. Chem. Soc.*, **96**, 5265 (1974).
10. R. A. Abramovitch, G. Grins, R. B. Rogers, M. J. L. Atwood, M. D. Williams, and S. Grider, *J. Org. Chem.*, **37**, 3383 (1972).
11. H. Seidl and R. Huisgen, *Tetrahedron Lett.*, No. 30, 2023 (1963).
12. M. Hamana, K. Funakoshi, and Y. Kuchino, Abstracts of Papers of the 90th Annual Meeting of the Pharmaceutical Society of Japan, Sapporo (1970), p. 38.
13. V. I. Ivanskii, Chemistry of Heterocyclic Compounds [in Russian], Vyssh. Shkola, Moscow (1978), p. 279.
14. F. A. Mailey and L. R. Ocone, *J. Org. Chem.*, **33**, 3343 (1968).
15. M. Hamana, K. Funakoshi, H. Shigyo, and Y. Kuchino, *Chem. Pharm. Bull.*, **23**, 346 (1975).
16. A. M. Nour El-Din and A.-R. M. Tawfik, *J. Chem. Eng. Data*, **32**, 125 (1987).
17. A. M. Nour El-Din, A.-R. M. Tawfik, and M. Ramadan, *Rev. Roum. Chim.*, **33**, 183 (1988).

18. Y. Ishiguro, K. Funakoshi, S. Saeki, T. Endo, and M. Hamana, *Heterocycles*, **20**, 158 (1983).
19. T. Hisano, T. Matsuoka, K. Tsusumi, K. Muraoka, and M. Ichikawa, *Chem. Pharm. Bull.*, **29**, 3706 (1981).
20. M. Hamana, *Khim. Geterotsikl. Soedin.*, No. 9, 1155 (1973).
21. M. Hamana and M. Yamazaki, *Chem. Pharm. Bull.*, **11**, 411 (1963).
22. T. Hisano, K. Harano, T. Matsuoka, F. Suematsu, and N. Ohizumi, *Chem. Pharm. Bull.*, **33**, 1869 (1985).
23. K. Harano, F. Suematsu, T. Matsuoka, and T. Hisano, *Chem. Pharm. Bull.*, **32**, 543 (1984).
24. T. Matsuoka, M. Shinada, F. Suematsu, K. Harano, and T. Hisano, *Chem. Pharm. Bull.*, **32**, 2077 (1984).
25. T. Matsuoka, K. Harano, H. Kubo, and T. Hisano, *Chem. Pharm. Bull.*, **34**, 572 (1986).
26. K. Harano, R. Kondo, M. Murase, T. Matsuoka, and T. Hisano, *Chem. Pharm. Bull.*, 966 (1986).
27. T. Hisano, K. Harano, T. Matsuoka, H. Yamada, and M. Kurihara, *Chem. Pharm. Bull.*, **35**, 1049 (1987).
28. A. F. Khlebnikov and R. R. Kostikov, *Khim. Geterotsikl. Soedin.*, No. 6, 856 (1987).
29. A. Krebs, H. Colberg, U. Hopfner, H. Kimling, and J. Odenthal, *Heterocycles*, **12**, 1153 (1979).
30. R. A. Abramovitch and I. Shinkai, *Accounts Chem. Res.*, **9**, 192 (1976).
31. H. Noda, T. Yamamori, M. Yoshida, and M. Hamana, *Heterocycles*, **4**, 453 (1976).
32. Y. Ishiguro, K. Funakoshi, S. Saeki, M. Hamana, I. Ueda, and S. Kawano, *Heterocycles*, **20**, 1545 (1983).
33. R. M. Acheson, A. S. Bailey, and J. A. Selby, *Chem. Commun.*, No. 20, 2066 (1967).
34. J. E. Baldwin, R. G. Pudnsery, A. R. Quereshi, and B. Sklarz, *J. Am. Chem. Soc.*, **90**, 5325 (1968).
35. Y. Ishiguro, K. Funakoshi, S. Saeki, M. Hamana, and I. Ueda, *Heterocycles*, **14**, 179 (1980).
36. R. Huisgen, H. Seidl, and J. Wulff, *Chem. Ber.*, **102**, 915 (1961).
37. S. Takahashi and H. Kano, *J. Org. Chem.*, **30**, 1118 (1965).
38. S. Takahashi and H. Kano, *Chem. Pharm. Bull.*, **14**, 1219 (1966).
39. S. Takahashi and H. Kano, *Chem. Pharm. Bull.*, **16**, 527 (1968).
40. S. R. Challand, C. W. Ress, and R. Storr, *Chem. Commun.*, No. 10, 837 (1973).
41. A. V. Ryzhakov and L. L. Rodina, *Zh. Org. Khim.*, **25**, 1577 (1989).
42. S. Kano, T. Yokomatsu, Y. Inasha, and S. Shibuya, *Heterocycles*, **19**, 2143 (1982).
43. R. A. Abramovitch, D. Kishore, M. Konieczny, and Z. Danter, *Heterocycles*, **25**, 13 (1987).
44. A. M. Nour El-Din, *Spectrochim. Acta*, **41A**, 1101 (1985).
45. V. S. Troilina, V. N. Sheinker, A. D. Garnovskii, and O. A. Osipov, *Zh. Fiz. Khim.*, **50**, 2436 (1976).
46. A. V. Ryzhakov and L. L. Rodina, *Khim. Geterotsikl. Soedin.*, No. 4, 488 (1991).
47. A. V. Ryzhakov, *Reactions of Aromatic N-Oxides and Ethylene System π -Systems* [in Russian], Chemical Sciences Candidate's Dissertation, Leningrad (1990).
48. T. V. Bezdvornyykh and A. V. Ryzhakov, *Abstracts of the All-Union Conference on the Electronics of Organic Materials* [in Russian], Dombai (1990), p. 123.