

PII: S0040-4020(97)00918-6

Reactions of Nitrones with Sodium Iodide - Trifluoroacetic Anhydride System. Comments on the Beckmann Rearrangement of Aldonitrones and Competitive Processes of Nucleophilic Addition[†]

Józef Drabowicz,^{a,*} Andrzej Kotyński,^b Zbigniew H. Kudzin,^c Ryszard B. Nazarski,^{c,*} and Maciej K. Tasz^d

^aCenter of Molecular and Macromolecular Studies, Polish Academy of Science, Sienkiewicza 112, 90-363 Łódź, Poland ^bInstitute of Chemistry, Faculty of Pharmacy, Medical University of Łódź, Muszyńskiego 1, 90-151 Łódź, Poland ^cDepartment of Organic Chemistry, University of Łódź, Narutowicza 68, 90-136 Łódź 1, P.O. Box 376, Poland ^dChemistry Department, Marquette University, P.O. Box 1881, Milwaukee, WI 53201-1881, USA

Abstract: The systematic studies of the reaction of aldonitrones with the NaI-TFAA system were performed. The reaction engaged was recognised as a previously known process called 'the Beckmann rearrangement of nitrones'. Some mechanistic considerations on this transformation and competitive nucleophilic additions are presented in order to explain the origin of iodine release and its observed stoichiometry as well as of some products isolation. The intermediacy of C- and N-iodo species (including iodonium cations) in the presence of iodide anions, is postulated. © 1997 Elsevier Science Ltd.

INTRODUCTION

The literature contains many reports on the applications of the sodium iodide - trifluoroacetic anhydride (NaI-TFAA) reagent¹ in organic synthesis and analytical chemistry. For example this reagent was successfully used for deoxygenation of sulfoxides,¹ reduction of sulfimides to sulfides² as well as in preparative deoxygenation of quinoxaline N,N'-dioxides.³ The analytical character of this reaction (*i.e.* stoichiometric iodine evolution, short reaction time and very mild conditions) allows modification of these procedures for quantitative determination or qualitative detection of sulfoxides⁴ and nitrones (*N*-alkylideneamine *N*-oxides).⁵

Since the observed stoichiometry of iodine formation in the reaction of nitrones 1 ($\mathbb{R}^1 = H$, alkyl, aryl; $\mathbb{R}^2 = alkyl$, aryl; $\mathbb{R}^3 = H$, alkyl) with the NaI-TFAA system was the same as established for various sulfoxides 4 (Eqn. 2) and heteroaromatic *N*-oxides 5 (Eqn. 3), the same reaction type, *i.e.* reductive removal of the oxide oxygen, was initially assumed and relevant products 3 were expected.^{54,b} It should be noted here that the process depicted in Eqn. 1 would be of practical interest, since nitrone-imine transformations ($1 \rightarrow 3$), using *e.g.* triphenylphosphine,^{64,b} trimethyl(phenyl) phosphite ^{6c,d} or pentacarbonyliron,⁶ require rather drastic reaction conditions. However, no traces of the expected imine 3b ($\mathbb{R}^1 = p$ -NO₂C₆H₄, $\mathbb{R}^2 = Ph$, $\mathbb{R}^3 = H$) were found when the corresponding nitrone 1b was treated with the NaI-TFAA reagent in acetone solution. It suggested that these reaction pathways might be different. In order to recognise them, the systematic studies of the title reaction using a few model Z aldonitrones 1 ($\mathbb{R}^3 = H$) were undertaken.

[†]Dedicated to Professor A. Senning on the occasion of his 60th birthday.

^{*}E-mail: draj@bilbo.cbmm.lodz.pl and rynaz@chemul.uni.lodz.pl, respectively.

RESULTS

Upon treatment of N-(p-nitrobenzylidene)aniline N-oxide (1b) with the NaI-TFAA in an acetone solution p-nitrobenzaldehyde 7, trifluoroacetanilide 8 and small amounts of p-nitrobenzanilide 9 were isolated as the final reaction products.

$$pNO_2C_6H_4 \xrightarrow{+} N_{Ph} \xrightarrow{\text{TFAA}} pNO_2C_6H_4CHO + CF_3CNHPh + pNO_2C_6H_4CNHPh (4)$$

$$0 \qquad 0$$

$$1b \qquad 7 \qquad 8 \qquad 9$$

In order to rationalise the unexpected formation of both 8 and 9, the most reasonable first step of the reaction, *i.e.* the generation of the cation of type 2, had to be investigated. Attempted, at first, the isolation of a corresponding iminium salt 2b, supposed to be formed in the TFAA acylation of the nitrone 1b, failed. This nitrone, when treated as an ethereal suspension with twofold excess of TFAA after immediate evaporation of clear solution, yielded a colourless oil. Resulting oily product, when exposed to a sodium iodide solution, did not release any elemental iodine. Whereas treated with isopropyl alcohol or methanol, it afforded crystalline anilide 9 of analytical purity with 95% yield. This anilide was fully characterised by its spectroscopic properties (IR) and melting point; its identity was further confirmed by comparison with the authentic sample.

It is reasonable to assume that after addition of TFAA to nitrone 1 an intermediate is formed, which in absence of iodide anions collapses to the amide system(s), *e.g.* 8 and/or 9; when the iodide ions are present in the solution a faster and concurrent reaction takes place leading to the release of iodine. A semi-kinetic experiment confirmed this assumption. Namely, the amount of iodine released was found to be strongly dependent on the time interval between the additions of TFAA and NaI solutions. Thus, when the latter was added 15 or 60 seconds after the acid anhydride solution, only 20 or 4% of the expected amount of iodine was determined, respectively.

Other aldonitrones (1a-c) showed similar behaviour on treatment with TFAA, see Experimental (Table 1). When the oil, produced in the reaction of N-benzylideneaniline N-oxide (1a, $R^1 = R^2 = Ph$) with TFAA, was treated with pentane a colourless solid immediately precipitated, which was identified as the corresponding imide (N,N-diacylamine) 10a [comparison with an authentic sample (IR, mixed m.p.)]. This species reacted smoothly with isopropyl alcohol giving benzanilide 11a quantitatively.



The only exception was N-(p-nitrobenzylidene)methylamine N-oxide (1d) which afforded, after usual work-up, a crystalline compound recognised as the imide 10d [comparison with the authentic sample (IR spectrum, mixed m.p.)]. Unexpectedly, this imide was inert towards isopropyl alcohol or methanol under the standard reaction conditions.



In order to find a final product of investigated reaction, *i.e.* occurring in the presence of iodide anions, the experiment based on addition of NaI-TFAA system to acetone solution of nitrone 1c was performed. The resulting mixture was immediately analysed using GC-MS technique. Analysis of spectrum permitted to identify the product as trifluoroacetamidoalkyl trifluoroacetate 12^5 (Table 2).



DISCUSSION

The presence of anilide 9 among the products of the reaction of the nitrone 1b (Eqn. 4) suggested evidently that the process engaged is a known transformation of aldonitrones 1 into amides 11 upon treatment with acylating reagents in anhydrous solvents. Many examples of such 'chemically induced isomerization' have been reported and the reaction, *i.e.* so called Beckmann rearrangement of aldonitrones,⁷ has been briefly discussed.⁷⁻¹¹ However, it is very difficult to understand how trifluoroacetanilide 8 is formed simultaneously.

The control experiments, carried out in the absence of iodide anions under anhydrous conditions, have allowed us to isolate imides 10. It should be noted here that the compounds of type 10 have already been isolated as products of the reaction of endocyclic E aldonitrone with acetic anhydride^{6a} as well as in the reactions of acyclic Z aldonitrones with acid chlorides (or methyl chloroformate) in the presence of triethylamine.^{10,12} Under these conditions the corresponding amides 11 have not been isolated, even when the crude products have been treated with methanol. Moreover, upon treatment with benzoyl chloride no acylation of amides was observed.¹⁰ On the other hand, the chromatographic purification of the first reaction product of the nitrone 1a with acetic anhydride afforded the corresponding benzanilide 11a,⁹ in full accord with the classical Beckmann nitrone-amide rearrangement.

The facts presented above strongly suggest the need to discuss in detailed way the reaction course of the already reported reactions of nitrones 1 and structurally related heteroaromatic *N*-oxides 5, with special attention to proposal of the formation of the corresponding iminium and nitrilium salts as the reaction intermediates. Such an analysis would give a chance to propose the general rearrangement scheme, which is in full agreement with the reported experimental observations and, simultaneously, includes all possible molecular migrations.

Scheme 1

 $\mathbf{R} = \mathbf{R}^1 (Z \text{ nitrones}) \text{ or } \mathbf{R}^3 (E \text{ nitrones})$



Let us first consider the reaction course of aldonitrones 1a-d with TFAA both in the presence and in the absence of iodide anions. In the first case the corresponding imides 10a-d were isolated. However, when the

iodide anions were added to the reaction mixture amidoester 12 was obtained as the single product. It is obvious that the first step of all discussed here reactions of nitrones 1 is an O-acylation process which results in the formation of N-acyloxy iminium salts 13.¹³ In the absence of iodide anions these salts rearrange most likely to the ion pairs 14 with the nitrilium cation (Scheme 1, step al). It has been suggested^{10,12} that in such case the nitrilium cation is generated *via* the Lewis base induced abstraction of an olefinic proton (R¹ or R³ = H) from the initially formed ion pair 13 and the final departure of a carboxylate anion. Because in all experiments the trifluoroacetate anion is the only (and weak) Lewis base the formal elimination of trifluoroacetic acid from the ion pair 13 is rather slow.

Scheme 2



The possibility that the formed ion pair 14 reacts instantaneously with the generated carboxylic acid, which has been suggested for the reaction of nitrones with aroyl chlorides in the absence of bases, ¹⁰ should be ruled out from our consideration because even traces of amides 11 could not be detected (Eqn. 5). This strongly suggests that specimen 14 may be considered as an intimate ion pair. However, the ion pair 14 may be rearranged to the form of C-acyloxy imine 15 (Scheme 1, step a2); products of this type have already been isolated by Tamagaki *et al.*⁹ The imine 15 finally afforded the isolated imide 10 as the result of a well

14
$$\xrightarrow{\text{CF}_3\text{CO}_2H}$$
 $\xrightarrow{\text{CF}_3C}$ $\xrightarrow{\text{$

recognised $O \rightarrow N$ acyl shift. It can occur either in concerted way as a [1,3]-sigmatropic rearrangement (step c)¹² or via the cyclic transition state 16 (step d).¹⁰

The presence of the external, strongly nucleophilic iodide anions in the reaction mixture induce completely different reaction course (Experimental), both in the case of aldo- as well as ketonitrones 1, see Ref. 5b. This clearly indicates that the nucleophilic addition of the soft iodide anion to the soft centre of the C=N bond of the iminium salt 13 should lead to the formation of compound 19 having a new carbon-iodine bond (Scheme 2). Existence of such C-Z species 25, which are in the equilibrium with ion pairs 24 (Eqn. 6), has been postulated for some iminium systems.¹⁴ Moreover, some of them were isolated as stable products 25, as it happened in the case of endocyclic ketonitrones when Y = OAc, OBz, OTs and Z = OH.^{14a,b,15} Due to the fact that the species 19 undergo a very rapid rearrangement, their formation excludes practically the generation and further rearrangements of the nitrilium salts 14 (Scheme 1).

$$\sum_{k=1}^{X^{-}} OY + Z^{-} = \sum_{k=1}^{Z^{-}} C^{-N} OY + X^{-}$$
(6)

The C-iodo adducts 19 can be considered as the nitrogen analogues saturated precursors of the classical carbocyclic iodonium cations.^{16,17} Therefore it is reasonable to assume that they can also undergo rearrangement via a cyclic transition state (or true intermediate) 20A to form the open chain species 20B/20C. It should be noted here that this is the first proposal for the existence of such structures. In the considered interconversion $19 \rightarrow 20A$ a key role is played undoubtedly by anchimeric assistance of the iodine atom (neighbouring-group participation).^{16,18} Moreover, the leaving trifluoroacetate group as a good nucleofuge can immediately behaves as counter-anion of the formed ion pairs 20. It should be added here that such type interconversions have already been proposed^{8,19} to explain the formation of oxoaziridines (or their oxonium salts) in the reaction of cyclic nitrones with acetic anhydride⁸ or acyl(aroyl, sulfonyl) chlorides.^{8,144,b}

The above proposal is strongly supported by quantum-chemical calculations carried out for the free cations of ion pairs 20 using different semiempirical approaches (MNDO, AM1 and PM3; gas phase).²⁰ These preliminary results clearly indicate that structures having aromatic substituent on C-atom are relatively stable and simultaneously the eventual ring system 20A become substantially unsymmetrical with the C-I distance very long, what lead to the considerable amount of the open forms 20B. This is in full agreement with our knowledge about the chemistry of the classical iodonium cations.²¹

The species 20 formed in the reaction with trifluoroacetate anion the C-acyloxy N-iodo amines 21, and this process certainly occurs in the cage of an ion pair. Such conversion is well documented for the classical iodonium cations.²¹ The formed N-iodo amines 21 in the presence of iodide anions can react at least in two different ways. The first possibility is realised in the presence of an excess of TFAA (Scheme 2, path a). Alternatively, the amide 23 can be produced by the subsequent formation of the ammonium salt 22 and its reaction with iodide anions (two-step process b). Similar possibility has been considered to explain the dechlorination of the quaternary N-acyl derivatives of chloramines (Orton rearrangement).¹⁶

On the other hand, when the amount of TFAA is much smaller, and especially in the case of potentially aromatic derivatives, reactions of deoxygenation can occur. These competing reactions would afford imines **3** (path c). The driving force for such a process is related with rearomatization of such systems. The structurally related reactions of α -bromoketones with bromide anion which afford free bromine have already been observed.²¹

It should be emphasised here that the reaction sequence $1 \rightarrow \rightarrow \rightarrow 3$ (Scheme 2) constitutes the first rational explanation how compounds 6 are formed *via* deoxygenation of the heteroaromatic *N*-oxides 5^{5b} including quinoxaline *N*,*N*-dioxide^{3,5b} with the use of NaI / TFAA reducing system. It is obvious that application of these procedures for the deoxygenation of simple aldonitrones 1 (R¹ or R³ = H) would give as the final products the appropriate aldehydes, which are formed in an easy hydrolysis of the initially generated imines 3. Similar reactivity should also be true in the case of ketonitrones 1 (R¹ or R³ \neq H), however the competitive processes presented in Scheme 1, can be neglected. The much slower formation of elemental iodine, observed in these cases, ^{5b} is most probably related to the relatively severe steric crowding around the reactive centres of the corresponding intermediates.

Considering the proposed reaction mechanisms it is reasonable to expect that the observed reaction courses (Scheme 1 or 2) are strongly influenced by the conditions in which the deoxygenation is carried out. This explains why two anilides 8 and 9 (Scheme 1, steps e and f) are formed in the reaction of nitrone 1b with the NaI / TFAA system (Eqn. 4). Moreover, the isolation of aldehyde 7 clearly indicates that the formed imine 3b is rapidly hydrolysed (Scheme 2, step c).

Finally, let us consider the more general aspects of the above discussed conversions of aldonitrones 1. Important and still not very clear question is how C-acyloxy imines 15 are formed. An alternative to the twostep process a (Scheme 1) would be the sequence involving the addition-elimination on the C=N double bond of ion pair 13 leading to the formation of system 25 (Z = O-Acyl, Y = Acyl) which finally loses Acyl-OH molecule (Scheme 1, step b; see also Eqn. 6)^{6a,7a} Such a two-step process has been rejected in the case of acyclic Z nitrones.^{8,9} However, the acceptance of the formation of the constitutionally similar adducts 19 strongly suggests that conversion $13 \rightarrow 15$ should be considered in some cases due the structural effects. It should be the case of the endocyclic E nitrones, especially five-membered ones, which can very easily form compounds 25 (vide supra). Moreover, the above discussed sequence has been commonly accepted for the heterocyclic N-oxides 5.²²

The second important question related with the intermediate 15 results from the fact, that they can be converted to amides 11 on two different pathways: (i) as the result of hydrolysis of the formerly formed imides 10 (Scheme 1, step f) or (ii) directly via hydrolysis into C-hydroxy imines 18 and their subsequent tautomerization. Earlier the internal salt of type 18 has been found to rearrange to the corresponding amide 11.¹⁹ Moreover, the sequences $15 \rightarrow 18 \rightarrow 11$ have been widely accepted for the N-oxides 5.²² Therefore it is reasonable to consider that the choice of the particular pathway, *i.e.* (i) and/or (ii), is determined mainly by the stereoelectronic structure of the system 15 and reaction conditions (time, temperature).

There is generally accepted opinion that in the Beckmann rearrangement of nitrones the amides 11 are formed as the primary products which next are acylated to form imides 10 upon prolonged heating.^{7,8} The results obtained in our work and a very recent literature data (especially Ref. 10) speak strongly against such a generalisation. The presented here consideration suggests that in some cases the transformation of aldonitrones 1 into the corresponding amides 11 involves the intermediacy of their *N*-acyl derivatives 10, which only during final purification of the crude reaction products are smoothly hydrolysed to the amides 11. Such suggestion is

strongly supported by the fact that some imides 10 undergo rapid hydrolysis when they are subjected to the typical crystallisation from alcohols.

The discussion presented above clearly indicated that there is still a lot of inconsistency in the mechanistic aspects of the aldonitrones rearrangements. Therefore there is a need to carry out additional studies on this topic and to repeat at least part of the already described experiments. It is especially true in the case of older publications.

EXPERIMENTAL

Trifluoroacetic anhydride (TFAA), alcohols and solvents have been purchased from Aldrich (Milwaukee, USA). Acetone and sodium iodide were treated as previously.^{5b} Nitrones 1a,b and 1c,d have been synthesised according to Refs. 23 and 24, respectively, and were all the same purity as previously reported.^{5b}

All melting points were measured on a Boëtius apparatus and were uncorrected. Mass spectra were obtained on a LKB-2091 GC-MS instrument at 70 eV ionising energy; samples were introduced *via* a gas chromatographic system (2.7 m glass spiral column packed with 3% OV-17 silicone oil; programmed temperature from 100 to 260°C, 10°Cmin.⁻¹). ¹H-NMR spectra were taken at 80 MHz on a Tesla BS-487 spectrometer. IR spectra were measured on a Carl Zeiss UR-10 machine (Jena, Germany).

Compd.	R	R ²	2nd Solvent ^a	Product structure / N	umber	M.p. (lit.), [°C]	IR (KBr), v [cm ⁻¹]
1a	Ph	Ph	pentane	PhC(O)NPh ^b I CF ₃ C(O)	10a	77-78	1735, 1710, 1355, 1260, 1200, 1160
1a	Ph	Ph	МеОН	PhC(O)NHPh ^C	11a	163-4 (165 ^d)	
18	Ph	Ph	iPrOH	PhC(O)NHPh ^C	11a	163.5-164	
1b	pNO ₂ C ₆	H₄ Ph	iPrOH	pNO ₂ C ₆ H ₄ C(O)NHPh	° 9	216-7 (217-8 ^e)	
1¢	Ph	Me	iPrOH	PhC(O)NHMe ^C	11c	75-83 (82 ^{<i>f</i>})	
1d	pNO ₂ C ₆	H₄ Me	iPrOH	pNO ₂ C ₆ H ₄ C(O)NMe ^l CF ₃ C(O)) 10d	75-78	1735, 1712, 1600, 1525, 1370, 1350, 1300, 1210, 1175, 1155

Table 1. Rearrangements of Nitrones 1 ($R^3 = H$)

^a Used in the after-treatment. ^b Satisfactory microanalytical data (C, H, N \pm 0.3%) were obtained; ^c Identification based on the comparison with authentic sample (IR spectrum, no depression of mixed m.p.); ^d Beilstein, 12 (3), 502; ^e Beilstein, 12 (3), 505; ^f Beilstein, 9 (3), 1068.

General procedure of rearrangements

The suspension of aldonitrone 1 (2 mmol) in dry ethyl ether was treated with 1M ethereal solution of TFAA (4 mmol). The reaction mixture was stirred at room temperature for 5 minutes and the solvent was evaporated under reduced pressure. The oily residue was treated with pentane (2 ml) or appropriate alcohol (1 ml) to give product which physical properties are summarised in Table 1.

The samples for GC-MS investigations were prepared as described in Ref. 5b. The resulted acetone solution was introduced on the chromatographic column without any previous treatment. The spectroscopic features of identified compounds are collected in Table 2.

Formula / number		MS spectrum		
CF ₃ -C-NH-Ph II O	8	189 (M ^{+.}), 120 (M ^{+.} - CF ₃), 92 (PhNH), 77 (Ph), 69 (CF ₃), 51		
Ме Рһ-С-N-С-СF3 	10 c	231 (M ⁺), 105 (PhCO), 77 (Ph), 69 (CF ₃), 51		
Me Ph-CH-N-C-CF ₃ CF ₃ C(O)-O O	12	329 (M ^{+.}), 216 (M ^{+.} - CF ₃ COO), 119, 118, 97, 77 (Ph), 69 (CF ₃), 51		

 Table 2. Mass Spectra and Proposed Identification of Mixture Components

ACKNOWLEDGEMENT

One of us (J. D.) would like to thank the Polish State Committee of Scientific Research (KBN) for a partial financial support (Grant No. 3 TO9A 085 08).

REFERENCES

- 1. Drabowicz J.; Oae S. Synthesis, 1977, 404-405.
- 2. Drabowicz J.; Łyżwa P.; Mikołajczyk M. Synthesis, 1981, 890-891.
- 3. Homaidan F. R.; Issidorides C. H. Heterocycles, 1981, 16, 411-415.
- (a) Drabowicz J.; Kotyński A.; Kudzin Z. H. J. Chromatogr. 1988, 447, 225-229; (b) Ciesielski W.; Drabowicz J.; Jędrzejewski W.; Kudzin; Z. H.; Skowroński R. Talanta, 1988, 35, 969-972; (c) Ciesielski W.; Jędrzejewski W.; Kudzin Z. H.; Drabowicz J. Talanta, 1990, 37, 435-438.
- (a) Drabowicz J.; Kotyński A.; Kudzin Z. H.; Skowroński R. J. Chromatogr. 1989, 473, 287-292; (b) Ciesielski W.; Kudzin Z. H.; Tasz M.; Drabowicz J. Can. J. Chem. 1990, 68, 679-684; (c) Ciesielski W.; Kudzin Z. H.; Grabowski G. Talanta, 1995, 42, 519-526;
- (a) Schmitz E. Chem. Ber. 1958, 91, 1488-1494; (b) Bapat J. B.; Black D. St.C. Aust. J.Chem. 1968, 21, 2483-2495; (c) Arbuzov B. A.; Dianova E. N.; Vinogradova V. S.; Lisin A. F. Izv. Akad. Nauk. USSR, Ser. Khim. 1975,

695-697; (d) Black D. St.C.; Clark V. M.; Odell B. G.; Lord Todd, J. Chem. Soc., Perkin Trans 1, 1976, 1944-1950; (e) Black D. St.C.; Johnstone L. M. Aust. J. Chem. 1984, 37, 95-107, 577-585.

- 7. (a) Kröhnke F. Ann. 1957, 604, 203-207; (b) Zinner G. Chem.-Ztg. 1978, 102, 58-60.
- Lamchen M. Nitrone Rearrangements. In Mechanisms of Molecular Migrations; Thyagarajan B. S., Ed.; Interscience: New York, Vol. 1, 1968; pp. 36-43.
- 9. Tamagaki S.; Kozuka S.; Oae S. Tetrahedron, 1970, 26, 1795-1804.
- 10. Heine H. W.; Zibuck R.; VandenHeuvel W. J. A. J. Am. Chem. Soc. 1982, 104, 3691-3694.
- Breuer E. Nitrones and Nitronic Acid Derivatives: Their Structure and Their Roles in Synthesis. In Nitrones, Nitronates and Nitroxides, Patai S.; Rappoport Z., Eds.; Wiley: Chichester, 1989; pp. 165-166, 254-257.
- 12. Coates R. M.; Cummins C. H. J. Org. Chem. 1986, 51, 1383-1389.
- 13. Heistand II R. H.; Stahl M. A.; Heine H. W. J. Org. Chem. 1978, 43, 3613-3615.
- (a) Alazard J.-P.; Khemis B.; Lusinchi X. Tetrahedron, 1975, 31, 1427-1436; (b) Cherest M.; Lusinchi X. Tetrahedron, 1982, 38, 3471-3478; (c) Cherest M.; Lusinchi X. Bull. Soc. Chim. Fr.II, 1984, 227-232.
- 15. Barton D. H. R.; Basu N. K.; Day M. J.; Hesse R. H.; Pechet M. M.; Starratt A. N. J. Chem. Soc., Perkin Trans. 1, 1975, 2243-2251.
- Jones R. A. Y. Physical and Mechanistic Organic Chemistry, Cambridge University Press: Cambridge, 1979, Chapts. 7, 9 and 14.
- 17. Carey F. A.; Sundberg R. J. Advanced Organic Chemistry, Part A: Structure and Mechanisms, 3rd ed., Plenum: New York, 1990; pp. 351-359.
- March J. Advanced Organic Chemistry. Reactions, Mechanisms, and Structure, 4th ed., Wiley: New York, 1992; pp. 308-312.
- 19. Baiocchi L.; Picconi G.; Palazzo G. J. Heterocycl. Chem. 1979, 16, 1479-1481.
- 20. Nazarski R. B. unpublished results.
- House H. O. Modern Synthetic Reactions, 2nd ed., Benjamin, Menlo Park, 1972, Chapt. 8, and references cited therein.
- Traynelis V. J. Rearrangement of O-Acylated Heterocyclic N-Oxides. In Mechanisms of Molecular Migrations; Thyagarajan B. S., Ed.; Interscience: New York, Vol. 2, 1969; pp. 1-42.
- 23. Wheeler O. H.; Gore P. H. J. Am. Chem. Soc. 1956, 78, 3363-3366.
- 24. Dicken C. M.; DeShong P. J. Org. Chem. 1982, 47, 2047-2051.

(Received in UK 8 July 1997; revised 6 August 1997; accepted 7 August 1997)