

## CYCLOADDITION OF $\alpha$ ,N-DIPHENYLNITRONE TO ISOTHIOCYANATES

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The 1,3-dipolar cycloaddition of  $\alpha$ ,N-diphenylnitrone (N-(benzylidene)aniline N-oxide) to the multiple bond system of isothiocyanates has been examined. The stability of primary adducts and the routes of their decomposition have been discussed.

The cycloaddition of nitrones (azomethine oxides) to isothiocyanates has been so far paid little attention<sup>1-3</sup>. The cycloaddition of nitrones derived from 1-pyrroline 1-oxide to isothiocyanates has been examined in some detail<sup>4</sup>. In the present work, the cycloaddition of  $\alpha$ ,N-diphenylnitrone (N-(benzylidene)aniline N-oxide, *II*) to isothiocyanates has been investigated.

As it may be seen from Scheme 1, several products are formed by cycloaddition of compound *II* to substituted aromatic isothiocyanates *I*. The ring of the primary unstable adducts *III* and *IV* is opened with the formation of elemental sulfur, N-benzylideneaniline, N-phenylthiobenzamide, the corresponding substituted benzamidines, and 4-substituted 2,3-diphenyl-1,2,4-oxadiazolidines. With the type *III* adducts, the N—O bond appears to be interrupted with the formation of the dipolar ion (zwitterion) *V* which undergoes a further decomposition by routes *A*, *B*, and *C*. The final decomposition products of route *A* are represented by N-phenyl-N'(R<sup>2</sup>)-benzamidines *VI* which were isolated by chromatography and identified by spectral methods and elemental analysis. Furthermore, N,N'-diphenylbenzamidine was compared with an authentic specimen. A similar decomposition has been observed with adducts of nitrones to isocyanates<sup>1</sup> and adducts of aldonitrones and ketonitrones derived from 1-pyrroline 1-oxide to aromatic isothiocyanates<sup>4</sup>. However, elevated temperatures were required in the two latter cases. Routes *B* and *C* afford equal final products, namely, the azomethine *VII*, the corresponding isocyanate *VIII*, and elemental sulfur. Decompositions *B* and *C* could explain formation of the above products but no intermediate of the route *C* has been isolated. It is not therefore possible to prefer or to exclude one of the alternatives. The isomerisation *III*  $\rightarrow$  *IX* which should take place in route *C*, has been observed in the case of six-membered rings<sup>1,3</sup>; an analogous isomerisation of oxadiazolidine to triazolidinone has also been reported<sup>5</sup>.

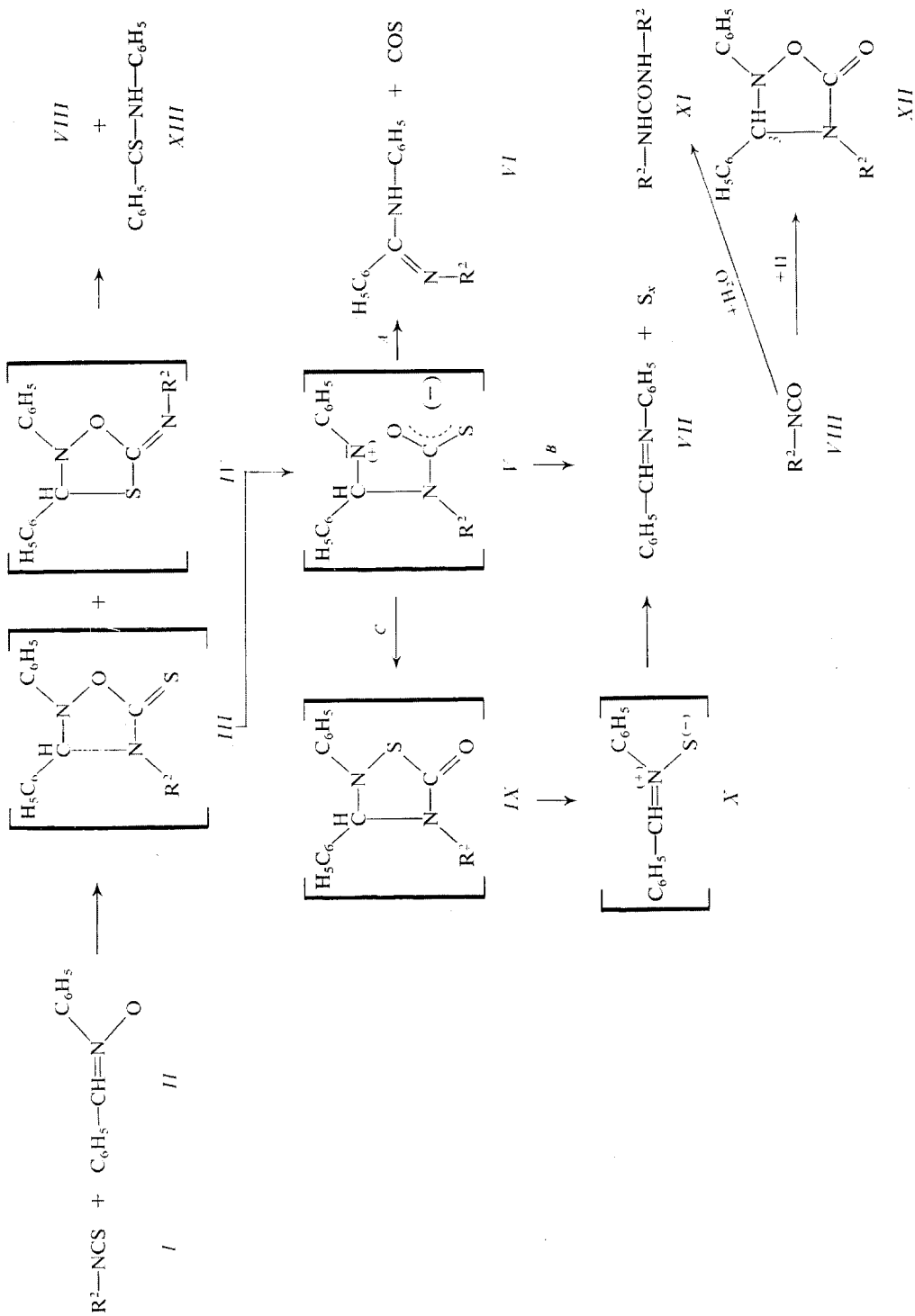
It may be inferred from the literature that aromatic isothiocyanates afford stable adducts by reaction with aliphatic<sup>4</sup> and aliphatic-aromatic nitrones<sup>8</sup>. Moreover, the ring system of 2,4-diphenyl-3,5-bis(phenylimino)-1,2,4-thiadiazolidine<sup>6</sup> and 2,4-diphenyl-5-butylimino-1,2,4-thiadiazolidine-3-thione<sup>7</sup> is relatively stable. The surprisingly low stability of rings *III* and *IV* might be due to the substituent  $R^3$  which, moreover, affects the cleavage of the N—O bond. When  $R^3$  is phenyl, the stabilisation of the positive charge on the nitrogen atom of the zwitterion *V* acts as a destabilizing factor of ring *III*. When  $R^3$  is a methyl group, the substituent effect is much weaker and the N—O bond is not heterolysed<sup>8</sup>. A similar observation was made by Black and Watson<sup>4</sup> in the case of 5,5-dimethyl-4-phenyl-1-pyrroline 1-oxide when the hydrogen atom at position 2 was replaced by the phenyl group. Such a nitrone reacted very slowly with the formation of the corresponding 1-pyrroline, *i.e.*, an analogy of the azomethine *VII*. The substituent at position 4 of the residue  $R^2$  does not markedly affect the course of the reaction ( Table I).

As decomposition products of the adduct *IV* (resulting by addition of compound *II* to the C=S bond of the isothiocyanate), N-phenylthiobenzamide (*XIII*) and the isocyanate *VIII* were obtained. The isolated compound *XIII* was identified on comparison with an authentic specimen. The isocyanates *VIII* were detected in the reaction mixture by IR spectra; their presence is also confirmed by products of subsequent reactions. Thus, by interaction with the unreacted compound *II*, stable adducts of

TABLE I  
Adducts XII

<i>XII</i> $R^2$	Formula (m.w.)	M.p., °C (yield, H)	Calculated/Found		
			% C	% H	% N
<i>a</i> $C_6H_5$	$C_{20}H_{16}N_2O_2$	167—168 <sup>a</sup>	75.93	5.10	8.85
	(316.4)	(18.5)	76.08	5.03	8.98
<i>b</i> 4- $CH_3C_6H_4$	$C_{21}H_{18}N_2O_2$	150—155	76.34	5.49	8.48
	(330.4)	(16)	76.49	5.63	8.70
<i>c</i> 4- $CH_3OC_6H_4$	$C_{21}H_{18}N_2O_3$	132—135	72.81	5.23	8.08
	(346.4)	(14)	72.56	5.39	8.22
<i>d</i> 4- $BrC_6H_4$	$C_{20}H_{15}N_2O_2Br$	156—159	60.76	3.82	7.08
	(395.3)	(20.5)	60.51	3.97	7.32
<i>e</i> 4- $O_2NC_6H_4$	$C_{20}H_{15}N_3O_4$	137—139	66.47	4.18	7.75
	(361.3)	(22)	66.19	3.93	7.97

<sup>a</sup> Lit.<sup>8</sup>, m.p. 167°C.



the type *XII* are formed. In all cases, compounds *XII* were isolated and identified on comparison with authentic adducts of substituted aromatic isocyanates with  $\alpha$ ,*N*-diphenylnitron (*II*), see Table I. For the spectral properties of adducts *XII* see Table II. When water is added into the reaction mixture, the *N,N'*-diarylureas *XI* are obtained (the adducts *XII* are not formed). The attempted cycloadditions to aliphatic isothiocyanates failed in the present case in spite of the use of elevated temperatures and excess isothiocyanates. The more reactive nitrones of the 1-pyrroline 1-oxide type are known to afford stable adducts with aliphatic isothiocyanates by reaction with the C=S bond<sup>4</sup>. With the aim to shorten the reaction time, the interaction of compounds *I* and *II* was effected in benzene at 80°C. Under these conditions, only the azomethine *VII*, the adduct *XII*, and elemental sulfur were formed.

## EXPERIMENTAL

### Materials and Methods

The reactions were performed in benzene, dioxane, tetrachloromethane, and ethylene glycol dimethyl ether as solvents.  $\alpha$ ,*N*-Diphenylnitron was prepared by condensation of phenylhydroxylamine with benzaldehyde<sup>11,12</sup>. The isothiocyanates were prepared from the corresponding amines by the thiophosgene method. The substituted phenyl isocyanates for the preparation of authentic samples were kindly supplied by Dr O. Konečný, Research Institute of Agrochemical Technology, Bratislava. The other substances were prepared by reported procedures<sup>9,10</sup>.

Thin-layer chromatography was performed on silica gel (gypsum as binder; 0.6 × 20 × 40 cm and 0.2 × 20 × 20 cm layers). The IR spectra were taken on a UR-20 apparatus (Carl Zeiss, Jena) in KBr discs or chloroform solution. The <sup>1</sup>H-NMR spectra were measured in deuterio-

TABLE II  
Spectral Properties of Adducts *XIIa–e*

<i>XII</i>	IR (cm <sup>-1</sup> ) $\nu(\text{C}=\text{O})$	<sup>1</sup> H-NMR $[\delta] \text{C}_{(3)}-\text{H}$	Mass spectrum <i>m/e</i> (rel. intensity)
<i>a</i>	1 785	6.6	271 (M-44) (36), 180 (100), 119 (7), 92 (36), 77 (71)
<i>b</i>	1 781	6.5	286 (M-44) (33), 180 (100), 194 (85), 91 (50), 77 (33)
<i>c</i>	1 778	6.46	300 (72), 285 (32), 211 (50), 210 (48), 196 (47), 180 (100), 123 (18), 108 (21), 93 (38), 77 (85)
<i>d</i>	1 780	6.76	350 (28), 180 (100), 198 (12), 196 (45), 157 (22), 93 (35), 80 (17), 77 (81)
<i>e</i>	1 789	6.85	317 (27), 205 (54), 196, 197 (23), 180 (82), 169 (30), 138 (14), 120 (24), 104, 105 (13, 5), 77 (100)

<sup>a</sup> Singlet.

acetone on a Tesla BS 487 C apparatus (hexamethyldisiloxane as internal standard). Mass spectra were recorded on a MS 902 S (AEI) apparatus (70 eV).

#### Cycloaddition of $\alpha$ ,N-Diphenylnitrone to Phenyl Isothiocyanate

Phenyl isothiocyanate (0.27 g; 0.002 mol) was added in one lot into a benzene solution of  $\alpha$ ,N-diphenylnitrone (0.394 g; 0.002 mol) and the resulting mixture kept at room temperature for 24 h under exclusion of day-light. The dark-brown solution was concentrated and the concentrate precipitated with n-hexane to deposit a red oil. The turbid supernatant afforded 122 mg of 2,3,4-triphenyl-1,2,4-oxadiazolidin-5-one (*XIIa*). The remaining oil was repeatedly chromatographed. Separation 1 was performed on 6 mm thick layers (about 500 mg of the material per one layer). The obtained two bands ( $R_F$  about 0.35 and 0.8) were scraped off and rechromatographed on 2 mm thick layers (about 100 mg of the material per one layer). The 6 mm layer was eluted with chloroform; the 2 mm layers were eluted with chloroform ( $R_F$  about 0.8) or 95 : 5 chloroform-acetone ( $R_F$  about 0.35). The upper band contained the thioamide, phenyl isothiocyanate, and elemental sulfur; the lower band contained the benzamidine, traces of the adduct *XIIa*, and elemental sulfur. The residual material consisted of decomposition products of the nitrone.

Another experiment was performed in the presence of water. The solvent was evaporated and the residual dark oil dissolved in a small amount of dry acetone to deposit 25 mg of N,N'-diphenylurea, m.p. 238–241°C.

Cycloadditions to the other substituted phenyl isothiocyanates were effected analogously. The resulting benzamidines VI exhibited melting point values in accordance with literature<sup>14–17</sup>. The cycloaddition of compound *II* to the particular aromatical isocyanates *VIII* was performed in refluxing benzene (2 h). The following yields of adducts were obtained: *XIIa*, 91%; *XIIb*, 86%; *XIIc*, 74%; *XIId*, 90%; and *XIIe*, 93% (for *XIIa* reported<sup>1</sup>, 71–100%).

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