Tetrahedron Letters No.37, pp. 3215-3218, 1970. Pergamon Press. Printed in Great Britain.

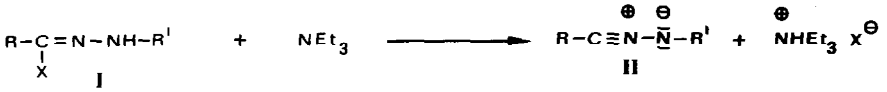
NEW FEATURES OF THE REACTION BETWEEN NITRILIMINES AND ARYLACETYLENES

S. Morrocchi, A. Ricca and A. Zanarotti

Istituto di Chimica, Politecnico di Milano - Italy

(Received in UK 19 May 1970; accepted for publication 9 July 1970)

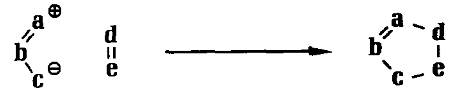
On reaction with NEt_3, *α-halogenophenylhydrazones* (I) lose HX with release of the corresponding nitrilimines (II) [1] :



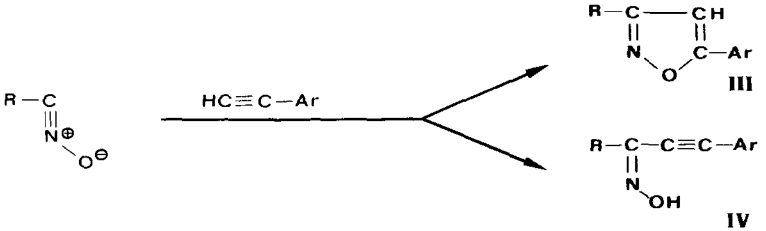
$$\underset{\substack{|\\X}}{R-C}=N-NH-R' \ (\mathrm{I}) + NEt_3 \longrightarrow R-C\equiv\overset{\oplus}{N}-\overset{\ominus}{\underline{N}}-R' \ (\mathrm{II}) + \overset{\oplus}{N}HEt_3 \ X^{\ominus}$$

When (II) is produced "in situ" in the presence of different dipolarophilic substances, the corresponding cyclic products have been isolated in variable amounts, and the reaction occurs according to the general scheme of 1,3-dipolar cycloaddition [1,2] :

Scheme 1



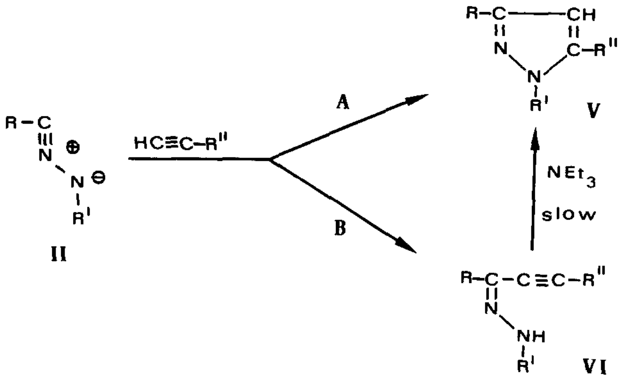
With the co-operation of P. Gruenanger and others, we gave evidence that the reaction between nitrile oxides and arylacetylenes, which had been previously framed into scheme 1, takes place through two parallel reactions [3]; their behaviour is largely influenced by the nature of the nitrile oxide and acetylenic compound [4]. Hence the reaction must be represented as follows :



where acetylenic oximes (IV) are formed in addition to isoxazoles (III).

By analogy with the reaction observed for nitrile oxides and since acetylenic phenylhydrazones are fairly stable compounds [5] and, once formed, may be easily isolated, we have re-examined the reaction between nitrilimines and arylacetylenes and obtained not only pyrazoles (V), but also the corresponding acetylenic phenylhydrazones (VI) :

Scheme 2



We prepared two α-halogenophenylhydrazones I_a and I_b (I_a : R = phenyl, R' = 2,4-dibromophenyl, X = bromine ; I_b : R = R' = phenyl, X = chlorine) and converted them "in situ" with an excess of acetylenic compound, into the corresponding nitrilimines (II_a) and (II_b), by treatment with NEt_3 either at room temperature or at 80°C for 90 minutes.

In the reactions with arylacetylenes, we always isolated acetylenic phenylhydrazones from the crude reaction product, by chromatography on column (SiO_2). The results obtained are reported in Table 1 .

TABLE 1

Nitrilimines (II)		Arylacetylenes	Pyrazoles (V)		Phenylhydraz.(VI)		Reaction temperature
R	R'	R''	m.p.	Yield	m.p.	Yield	
C_6H_5	$C_6H_3Br_2$	C_6H_5	V_a 141°C	23 %	VI_a^6 168°C	32 %	25°C
C_6H_5	$C_6H_3Br_2$	p-CH_3O-C_6H_4	V_b oil	< 10	VI_b 130°C	38	25°C
C_6H_5	C_6H_5	C_6H_5	V_c 137°C	58	VI_c 154°C	17	80°C
C_6H_5	C_6H_5	p-CH_3O-C_6H_4	V_d oil	43	VI_d 132°C	20	80°C
C_6H_5	C_6H_5	p-$(CH_3)_2N$-C_6H_4	V_e oil	20	VI_e 136°C	20	80°C
C_6H_5	C_6H_5	p-NO_2-C_6H_4	V_f 142°C	50	VI_f 185°C	<10	80°C

The structures of the isolated compounds were determined by Mass Spectroscopy, N.M.R., I.R. and U.V. analyses; the relating data are reported in Table 2.

U.V. spectra of compounds (VI) run in ethanol with traces of alkali vary with time

(3 - 9 hrs) changing into those of pyrazoles (V).

TABLE 2

	N.M.R. (CDCl$_3$)	I.R. νcm^{-1}	U.V.(mμ)			N.M.R. (CDCl$_3$)	I.R. νcm^{-1}	U.V.(mμ)	
			λ_{max}^{EtOH}	logϵ				λ_{max}^{EtOH}	logϵ
V$_a$	$-\underset{\|}{CH}$ S 6.83δ	1610 1545 970	250	4.567	VI$_a$	>NH S 9.28δ	>NH 3235 −C≡C− 2189	249 271 278	4.376 4.438 4.458
V$_b$	S 6.81δ	1615 1585 970	254	4.470	VI$_b$	S 9.20δ	3225 2173	250 288	4.358 4.424
V$_c$	S 6.81δ	1600 1545 970	251	4.505	VI$_c$	S 8.70δ	3262 2180	246 268 279	4.338 4.238 4.268
V$_d$	S 6.73δ	1615 1555 970	256	4.558	VI$_d$	S 8.69δ	3280 2190	248 283 290	4.396 4.397 4.420
V$_e$	S 6.72δ	1610 1545 970	272	4.472	VI$_e$	S 8.73δ	3225 2173	242 300 325	4.326 4.382 4.326
V$_f$	S 6.90δ	1590 1540 970	265	4.344	VI$_f$	—	3220 2180	290	4.378

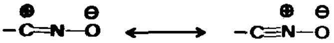
As shown from the data of table 1 and contrary to what has been reported[1], compounds (V$_c$) and (VI$_c$) have been isolated in the reaction between (I$_b$) and phenylacetylene under the same condition described by Huisgen and others. (VI$_c$) could not be isolated by the German Authors owing to an unlucky choice of operating conditions; in fact we observed that phenylhydrazone (VI$_c$) remains unaltered on heating to 130 - 150°C under mechanical pump vacuum, while it cyclizes entirely when eluted with benzene on alumina (Woelm, basic, activity I) with formation of the pyrazole (V$_c$).

Furthermore, by heating in the presence of NEt$_3$ to 80°C for 90 minutes, phenylhydrazone (VI$_c$) partially changes into (V$_c$); this suggests that under these conditions, at least a part of the pyrazole obtained does not derive from a cycloaddition reaction, but *via* B of scheme 2[7].

The analogous behaviour of nitrile oxides and nitrilimines leads us to assume that, at least when the 1,3 - dipolar reagent is a nitrilium betaine, the general scheme of the reaction with arylacetylenes should not be formulated according to scheme 1 only, but must be represented as follows :

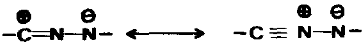
Nitrilium betaines

Nitrile oxides



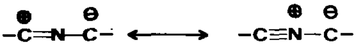
$$\overset{\oplus}{-C}{=}N{-}\overset{\ominus}{O} \longleftrightarrow -C{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{O}$$

Nitrile imines

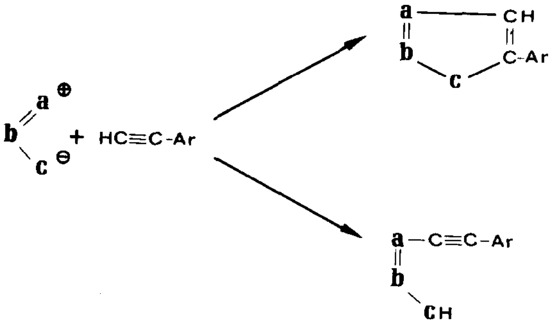


$$\overset{\oplus}{-C}{=}N{-}\overset{\ominus}{N}- \longleftrightarrow -C{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{N}-$$

Nitrile ylides



$$\overset{\oplus}{-C}{=}N{-}\overset{\ominus}{C}- \longleftrightarrow -C{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{C}-$$



We are continuing our investigations in order to check the validity of our forecasts concerning nitrile ylides and simultaneously to examine the behaviour of other 1,3 -dipolar reagents.

REFERENCES

1) R. Huisgen, M. Seidel, G. Wallbillich and H. Knupfer, Tetrahedron 17, 3 (1962).

2) J.S. Clovis, A. Eckell, R. Huisgen and R. Sustmann, Chem. Ber. 100, 60 (1967).

3) S. Morrocchi, A. Ricca, A. Zanarotti, G.Bianchi, R.Gandolfi and P. Gruenanger, Tetrahedron Letters 39, 3329 (1969).

4) S. Morrocchi, A. Ricca, A. Selva and A. Zanarotti, Rend. Acc. Lincei, February (1970).

5) By exchange with 2,4-dinitrophenylhydrazine, acetylenic oximes yield dinitrophenylhydrazones, see ref. (3).

6) The same compund (VI_a) has been previously obtained by a different way by P.Gruenanger and M.R. Langella (Gazz. Chim. Ital. XC, 229 (1960)). The isomeric pyrazolic structure attributed to it by the Authors should be revised. We thank Prof.P. Gruenanger for a sample of (VI_a) supplied for the comparison.

7) This behaviour, previously neglected, should cause variation of the values of the relating kinetics carried out on nitrilimines, where arylacetylenes are involved.
A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey and E. Splinder, Chem. Ber. 100, 2192 (1967).