Tetrahedron Letters No. 48, pp 4935 - 4940, 1972. Pergamon Press. Printed in Great Britain.

SOME NOVEL REACTIONS OF ALKYNES WITH CATIONOID ELECTROPHILES IN NITROALKANE SOLUTIONS

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(Received in UK 4 September 1972; accepted for publication 1 November 1972)

Electrophilic addition of strongly polarized ("cationoid") complexes $X^+ Y^-$ (X^+ - inorganic or stable organic cation, Y^- - anion of a strong acid) to alkenes had been described recently /1/. Further studies in our laboratory have been aimed at the use of these reagents in Ad_E- reactions with alkynes /2/. Since CH_3NO_2 has been extensively used as the most suitable solvent for the reactions with alkenes we tried to use the same solvent as the reaction medium for the alkyne series. Surprisingly, we discovered that CH_3NO_2 (or other nitroalkanes) could not be used as the inert solvent but should be considered as an active reagent, capable of acting as a nucleophile after the addition of X^+ to the triple bond /3/. This reaction course seems to be quite general for various X^+ (X^+ - proton, alkyl, alkoxyalkyl or acyl cations) provided Y^- is an anion of low nucleophilicity (such as BF_4^- or SbF_6^-). The structure of the end products may differ considerably depending on the nature of the reagents. Typical examples will be discussed below.

<u>X^+ = proton</u>. The interaction of the strong inorganic acids such as HBF_4 or FSO_3H with mono- or di-substituted alkynes in primary or secondary nitroalkanes proceeds smoothly with the formation of nitrogen-containing adducts containing one molecule of nitroalkane per one molecule of alkyne.

The results of the foregoing reactions are summarized in Table I (I-V). Typical procedure is as follows: a solution of decyne-5 (0.69 g, 5 mmoles) in 2 ml of CH_3NO_2 was added at -25°C to a freshly prepared solution of HBF_4 (0.44 g, 5 mmoles) in 5 ml of CH_3NO_2. The reaction mixture was held for 5 min

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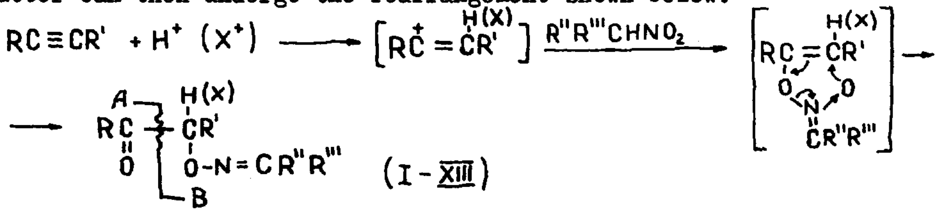
at -25°C and decomposed by ice cold bicarbonate solution. After the usual treatment, the product I was isolated by distillation (yield 0.7 g (70%), b.p. 56-57°/0.5 mm, n_D^{21} 1.4421).

All the adducts I-V were shown to possess the α-(alkylideniminoxy)ketone structure, RCO-CH(R')ON=CR"R'" on the basis of the following evidence: 1) IR-spectra showed the absorption characteristics of >C=O (1710-1715 cm^{-1}) and >C=N-O- (1060 cm^{-1}) groups; 2) p.m.r.-spectra revealed characteristic signals of deshielded protons of the O-substituted oxime group, -O-N=CR"R"' (see Table I) with the expected values of chemical shifts and spin-spin coupling constants /4a/; 3) mass-spectra revealed the presence of two main peaks, A and B, corresponding to the fragmentation shown in the Scheme 1; 4) the reduction of I-V by $NaBH_4$ (ethanol, 20°C, 12 hrs) gives corresponding secondary alkohols R CHOH-CH(R')ON=CR"R"' (IR-, p.m.r.-data); 5) the hydrolysis of the adducts I-III (aqueous phthalic acid, 90°C, 2 hrs) gives, with good yields, the corresponding carbonyl compounds, R"R"' CO (identified as dimedone derivatives for I and II or as the 2,4-dinitrophenylhydrazone for III).

The formation of the compounds I-V may be rationalized as the result of protonation of the triple bond followed by the reaction with the nitro-group of the nitroalkane, with the intermediate formation of vinylnitronic ester. The latter can then undergo the rearrangement shown below:



(1)

Proof of the site of protonation was additionally given by the use of DBF_4 instead of HBF_4. P.m.r.-spectra of the monodeutero-analogs Ia or IIa show the disappearance of the deshielded α-carbonyl proton triplet (δ 4.28); their mass-spectra reveal the presence of one deuterium atom in the fragment B (m/e 115 for Ia or 129 for IIa). The postulated rearrangement may be considered as another mode of O-alkylnitronic ester stabilization /4/ via a 3-2 sigmatropic process /5/.

Table I

N	RCOC(R')(X)ON=CR"R"'					Yield /10/	P.m.r.-data*) for			Mol. weight	Mass-spectra data**)		
	R	R'	X	R"	R"'		X	R"	R"'		M^+	A^+	B^+
I	n-C_4H_9	n-C_4H_9	H	H	H	70	4.28(t,6.7)	7.0 (AB,	6.38 8.0)	199	–	85	114
II	-"-	-"-	H	H	CH_3	83	4.23(t,6.7)	6.63 (AX_3,	1.75 6.0)	213	213	85	128
III	-"-	-"-	-"-	CH_3	CH_3	80	4.15(t,6.5)	1.80 (s)	1.75 (s)	227	227	85	142
IV	-"-	-"-	-"-	-$(CH_2)_5$-		68	4.14(t,6.5)	2.0-2.5(m)		267	-	85	182
V	-"-	H	-"-	H	H	65	4.38(s)	7.0 (AB,	6.38 8.0)	143	143	85	58
VI	n-C_4H_9	n-C_4H_9	CH_2OCH_3	H	H	65	3.56 3.33 (AB, 10.0) 3.17(s)	7.0 (AB,	6.41 8.0)	243	-	85	158
VII	-"-	-"-	-"-	H	CH_3	47	3.57 3.34 (AB, 10.0) 3.17(s)	6.70 (AX_3,	1.86. 6.0)	257	-	85	172
VIII	-"-	H	-"-	H	H	54	3.63(d,4.5) 3.20(s)	7.0 (AB,	6.41 8.0)	187	187	85	102
IX	-"-	-"-	-"-	H	CH_3	64	3.36(d,4.5) 3.07(s)	6.47 (AX_3,	1.67 6.0)	201	201	85	116
X	C_6H_5	H	$(CH_3)_3C$	H	CH_3	60	0.93(s)	6.53 (AX_3,	1.88 6.0)	233	233	105	128
XI	n-C_4H_9	n-C_4H_9	CH_3CO	H	H	30	2.01(s)	7.18 (AB,	6.55 8.0)	241	241	85 (43)	156 (198)
XII	-"-	-"-	n-C_4H_9CO	H	CH_3	50	0.8-2.2(m)	6.80 (AX_3,	2.01 6.0)	297	297	85	212
XIII	-"-	-"-	-"-	CH_3	CH_3	31	-"-	1.93 (s)	1.82 (s)	311	-	85	226

*) P.m.r.-spectra were recorded on a DA-60-IL (Varian) with HMDS as internal standard; chemical shifts (δ) are given in p.p.m.; coupling constants (J, figures in brackets)- in c/s; s-singlet, d-doublet, t-triplet, m-multiplet.

**) Mass-spectra were recorded on CH-6 (Varian); main fragments; A RCO; B CR'(X)ON=CR"R"'

X^+ = alkyl or alkoxyalkyl cations. We have found that alkyl and alkoxyalkyl cation (generated by the metathesis reaction, RHal + $AgBF_4$ $\longrightarrow$ RBF_4 + AgCl /6/) are able to alkylate alkynes in nitroalkane media with the formation of nitrogen-containing adducts. The use of the stabilized cations such as $CH_3OCH_2^+$ is preferable. Representative examples are listed in Table I (VI-X). The adducts formed (VI-X) belong to the same type of α-alkylideniminoxy)-ketones (cf.spectral data for VI-X with that of I-V, Table I). Their formation may be represented by Scheme 1 with X^+ = alkyl or alkoxyalkyl cations. A typical procedure is as follows: a solution of $C_6H_5C\equiv CH$ (0.25 g, 2.5 mmoles) and $(CH_3)_3CCl$ (0.46 g, 5 mmoles) in 2 ml of $C_2H_5NO_2$ was added to a stirred solution of $AgBF_4$ (0.73 g, 3.75 mmoles) in 5 ml of $C_2H_5NO_2$ at -65°C. The mixture was held at -65°C for 30 min and decomposed in the usual way. The product X was isolated in 60% yield by TLC on SiO_2, m.p. 75-77°C.

X^+ = acyl cations. The formation of nitrogen-containing adducts has also been observed on acylation of alkynes by acyl cationoids in nitroalkane media. Acyl cationoids may be prepared by any of the usual methods /6/. Typical examples of the products obtained by the reaction of decyne-5 with RCO^+Y^- are given in the Table I (XI-XIII). The structures of the adducts XI-XIII were deduced from the similarity of their p.m.r. - spectral parameters and mass-spectral fragmentation pattern to those of I-X. The formation of XI-XIII evidently follows the same reaction pattern as was postulated above (Scheme 1) with X^+ = acyl cation. However, yields of these adducts were substantially lower than those of I-X. Further studies have shown that the formation of XI-XIII is always accompanied by the formation of the corresponding β-diketones (XX or XXI). Moreover we have shown that the acylation of monosubstituted alkynes proceeds with the exclusive formation of β-diketones. Some data on the scope of this reaction are presented in Table 2. A typical procedure is as follows: solution of CH_3COCl (1.17 g, 15 mmoles) and hexyne-1 (0.82 g, 10 mmoles) in 5 ml of abs. CH_3NO_2 was added at -25°C to the stirred solution of $AgBF_4$ (2.9 g, 15 mmoles) in 5 ml of CH_3NO_2. The reaction mixture was held for 5 min at -25°C and worked up in the usual way. The product, octane-2,4-dione (XIV), was isolated by distillation, with a yield of 64%, b.p. 43-44°/1 mm, n_D^{19} 1.4525, Cu-chelate (yield 80%) m.p. 143°C.

The structure of the β-diketones XIV-XXI corresponds to the addition of acyl cation and hydroxyl anion to the starting alkyne. Special experiments have shown that the use of the water-free procedure /7/ for neutralization of

Table 2

Alkyne	Acylating agent	Product	Yield /10/
$n\text{-}C_4H_9C\equiv CH$	CH_3COBF_4	$n\text{-}C_4H_9COCH_2COCH_3$ (XIV) *)	64
-"-	$(CH_3)_3CCOBF_4$	$n\text{-}C_4H_9COCH_2CO\ C(CH_3)_3$ (XV)	65
-"-	$n\text{-}C_4H_9COBF_4$	$n\text{-}C_4H_9COCH_2COC_4H_9\text{-}n$ (XVI)	35
-"-	$n\text{-}C_4H_9COSbF_6$	-"-	56
$(CH_3)_3CC\equiv CH$	$(CH_3)_3CCOBF_4$	$(CH_3)_3CCOCH_2COC(CH_3)_3$ (XVII)	26
$C_6H_5C\equiv CH$	CH_3COBF_4	$C_6H_5COCH_2COCH_3$ (XVIII)	45
-"-	$(CH_3)_3CCOBF_4$	$C_6H_5COCH_2COC(CH_3)_3$ (XIX)	44
$n\text{-}C_4H_9C\equiv CC_4H_9\text{-}n$	CH_3COBF_4	$n\text{-}C_4H_9COCH(n\text{-}C_4H_9)COCH_3$ (XX)	25
-"-	CH_3COSbF_6	-"-	73
-"-	$n\text{-}C_4H_9COSbF_6$	$n\text{-}C_4H_9COCH(n\text{-}C_4H_9)COC_4H_9\text{-}n$ (XXI)	30
$n\text{-}C_4H_9C\equiv CH$	CH_3COBF_4	$n\text{-}C_4H_9C(OBF_2)=CHCOCH_3$ **) (XXII)	28
-"-	$(CH_3)_3CCOBF_4$	$n\text{-}C_4H_9C(OBF_2)=CHCOC(CH_3)_3$ (XXIII)	22
$C_6H_5C\equiv CH$	$(CH_3)_3CCOBF_4$	$C_6H_5C(OBF_2)=CHCOC(CH_3)_3$ (XXIV)	30

*) All β-diketones (XIV-XXI) were identified as Cu - chelates and/or by direct comparison with authentic samples.

**) Products XXII-XXIV were prepared in $(CH_3)_2CHNO_2$ solution and purified by chromatography on SiO_2 (XXII and XXIII) of by crystallization (XXIV, m.p. 91-92°). Their identity was proved by ^{19}F n.m.r.-spectra and by hydrolysis to their respective β-diketones.

the reaction media has no effect on the yields of β-diketones. Hense we are forced to suggest that the formation of β-diketones in the reaction under study is probably due to the intermediate formation of an acyl-alkyne-nitroalkane adduct. The vinylnitronic ester structure is proposed for the latter (see above) but further study is required before a precise mechanism of its transformation to the end-products can be advanced. It was also discovered that the use of primary nitroalkanes as the reaction solvents is essential for the preparation of β-diketones. Thus, the reaction of decyne-5 with $n\text{-}C_4H_9COSbF_6$ in $C_2H_5NO_2$ gives β-diketone XXI (see Table 2), while the same reaction in $(CH_3)_2CHNO_2$ proceeds with exclusive formation of the adduct XIII (see Table I). At the same time acylation of terminal alkynes (e.g. hexyne-1) with $RCOBF_4$ in $(CH_3)_2CHNO_2$ do not give either β-diketones or nitrogen-containing adducts but

BF_2-enolates of β-diketones as the only isolable products (see Table 2, XXII-XXIV).

These novel reactions appear to be important, both for preparative applications and for the study of the Ad_E-mechanism. The unusual nucleophilic activity /8/ of nitroalkanes in these reactions should evidently be ascribed to the "hot" nature /9/ of the intermediate vinyl cations. Our preliminary data show that other solvents of low nucleophilicity such as aromatic hydrocarbons, sulfur dioxide, vinyl halides and nitriles are also active nucleophiles in the course of the addition of cationoid electrophiles to the triple bond.

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3. Nitromethane is widely used as the inert solvent for different Ad_E-reactions with alkenes or for S_E-reactions in aromatic series although there are some data indicating its ability to react with cationoid intermediates (see the study of Ph_3CCl ionization in CH_3NO_2 solution, Y.Pocker, J.Chem. Soc. 1958, 240).
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7. The reaction mixture is decomposed by the addition of dry $(C_2H_5)_3N$ and the product is isolated by extraction with petroleum ether and purified by distillation.
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