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ALKYL DIAZOTATES, VII. ALKYLATION WITH TRIETHYLOXONIUM TETRAFLUOROBORATE, FORMATION OF AZOXYALKANES (1)

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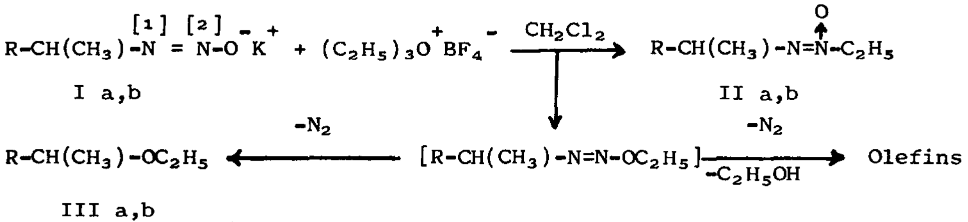
We studied the title reaction as a means of generating alkyl diazoethers, which are of mechanistic interest in the alcoholysis of diazoalkanes. The major products of our reactions, however, were unsymmetrical azoxyalkanes. Since such compounds are difficult to obtain by other means (3), and our findings may be of general applicability, we present this communication.

Triethyloxonium tetrafluoroborate (4) reacted with butane-2-diazotate, Ia, or 1-phenylethane-1-diazotate, Ib, (5) in CH_2Cl_2 at ca. -20°. Slow nitrogen evolution (6) ceased after 1-2 hrs. and was 37-39% of the theoretical yield.

The major nitrogen-loss products from Ia were 1- and 2- butenes (7). Ether IIIa was formed in less than 1% yield. N-(2-butyl)-N'-ethyldiazine N'-oxide, IIa, was isolated either by gc at 82° (8) or by tlc (9, 10). Its yield, based on diazotate precursor, was 48%. (gc analysis, bromobenzene standard).



$$R\text{-}CH(CH_3)\text{-}\overset{[1]}{N}=\overset{[2]}{N}\text{-}O^-K^+ + (C_2H_5)_3O^+BF_4^- \xrightarrow{CH_2Cl_2} R\text{-}CH(CH_3)\text{-}N=\overset{O}{\overset{\uparrow}{N}}\text{-}C_2H_5$$

I a,b → II a,b

$$R\text{-}CH(CH_3)\text{-}OC_2H_5 \xleftarrow{-N_2} [R\text{-}CH(CH_3)\text{-}N=N\text{-}OC_2H_5] \xrightarrow[-C_2H_5OH]{-N_2} \text{Olefins}$$

III a,b

(a, R= C_2H_5; b, R= C_6H_5)

From Ib, we isolated styrene (7.3 %) and α-phenyldiethyl ether, III b (15.3%) by gc at 121° (8, 10). Identification was by spectral comparison with authentic materials; yields were determined by gc. N-(1-phenylethyl)-N'-ethyldiazine N'-oxide, IIb, was isolated either by gc at 225° (8) or by tlc (9). Its yield was 46% (gc analysis, *n*-hexadecane standard).

IIa* and IIb* were identified as follows. *IIa.* The mass spectrum showed a base peak at (m/e) 29; M^+ at 130 (0.18%); M-17 (24.79%); M-16 (1.80%). Ir (neat) showed strong absorptions at 1500 and 1320 cm^{-1}, characteristic of azoxyalkanes (11). Uv (ethanol) showed λ_{max} 220 nm (log ϵ=3.72) and an inflection at 280 nm (log ϵ=1.62), again characteristic of simple azoxyalkanes (11). Nmr (CCl_4) showed a quartet, J=7, (centered) at 4.07δ ($-CH_2-N(O)=$) and three high-field lines of what is probably a sextet at 3.85δ ($>CH-N=$), 3 protons; a triplet, J=7, at 1.46δ ($\underline{CH_3}-CH_2-N(O)=$) superimposed on a multiplet for ($CH_3-\underline{CH_2}-CH<$), 5 protons; and a doublet, J=6, at 1.05δ ($\underline{CH_3}-CH-N=$) superimposed on a crude triplet at 0.87δ ($\underline{CH_3}-CH_2-CH<$), 6 protons. Not only are the nmr data consistent with IIa, but the chemical shift of the ($-CH_2-N(O)=$) absorption establishes that it is the ethyl group which is bonded to the azoxy nitrogen atom (3, 12, 13).

IIb. The mass spectrum showed a base peak at (m/e) 161, M-17; M^+ at 178 (8.44%); M-16 (11.42%). Ir (neat) showed strong absorptions at 1490 and 1320 cm^{-1} (11). The uv spectrum (cyclohexane) was dominated by a phenyl absorption at 208 nm. Nmr (CCl_4) showed a multiplet at 7.12δ (aryl), 5 protons; a quartet, J=6.8, at 5.00δ ($>CH-N=$), 1 proton; a quartet, J=7.5, at 4.01δ($-CH_2-N(O)=$), 2 protons; a doublet, J=6.8, at 1.38δ ($\underline{CH_3}-CH<$) and a triplet, J=7.5, at 1.37δ ($\underline{CH_3}-CH_2$), 6 protons. Note the similarity of the azoxymethylene resonance shift to that of IIa and of model compounds (3, 12, 13).

IIa and IIb probably arise by direct alkylation of N[2] of the diazotate system, I. Such a process is analogous to the formation of nitrones by the alkylation of oximate salts (14). Nitrogen-loss products probably arise by O-alkylation of I, followed by a collapse of the resulting diazoethers. *Aryl* diazotates can be alkylated on O to give aryl diazoethers, or on N[1] of the diazotate to give nitrosamines (15). Nitrosamine formation was not observed from Ia and was specifically excluded (16) in the alkylation of Ib. Differences in the site of N-alkylation of the aliphatic and aromatic diazotates may have to do with steric hindrance to N[1] attack in the aliphatic series, particularly when R=*sec*-alkyl.

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*Satisfactory C, H, and N microanalyses were obtained.

We are continuing our studies of these and related reactions.

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References

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(2) American Cyanamid Company Educational Awardee, 1969-1970.

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(5) See R. A. Moss, J. Org. Chem., **31**, 1082 (1966) for the general diazotate synthesis. The diazotates were prepared in ether. Ether was removed under vacuum and replaced with CH_2Cl_2. Three equiv. of the oxonium salt were used in the subsequent reaction.

(6) Dissolution of the diazotate may be the limiting factor.

(7) Identified by gc on a 15', 0.25", 30% hexanedione on 45/60 Gas Chrom P column. Overall yield was not determined; the olefin distribution was approximately 1:1:1 among the three linear butenes. Much isobutene was present. Control experiments suggest its origin in a reaction of triethyloxonium tetrafluoroborate and excess potassium *t*-butoxide used in generation of the diazotate (5).

(8) 10', 0.25," 5% Carbowax 20M on 45/60 Gas Chrom R column. An SE-30 column (5 ft., 20%) could be used at a lower temperature.

(9) ChromAR Sheet 1000, ether-pentane eluent, 1:10 (IIa) or 1:5 (IIb).

(10) Diethyl, ethyl *t*-butyl, and di-*t*-butylcarbonates, formed during the generation of I, are also present; see reference (5).

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(16) By gc comparison of crude reaction product with authentic N-(1-phenylethyl)-N-ethylnitrosamine, prepared by nitrosation (HNO_2 or N_2O_4) of N-(1-phenylethyl)ethylamine.