Fluorination of Diazo-ketones with Fluoroxytrifluoromethane

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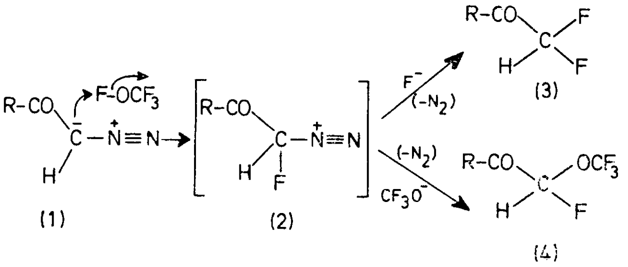
Summary Fluorination of diazo-ketones with CF_3OF produces a mixture of αα-difluoro-ketones and α-trifluoromethoxy-α-fluoro-ketones by the initial electrophilic attack on the diazo-group followed by nucleophilic attack with F^- or CF_3O^-.

It is possible to consider fluoroxy-compounds as 'pseudohalogen' derivatives of fluorine.[1] Their reactions with double bonds exhibit characteristics which are typical of electrophilic additions.[2] The α-fluorocarbocation initially formed is captured either by CF_3O^- or F^- ($CF_3O^- \rightleftharpoons COF_2 + F^-$).

Halogens or pseudohalogens are known to react readily with aliphatic diazo-compounds.[3] The mechanism is considered to involve initial electrophilic attack on the diazoalkane. In order to confirm the 'pseudohalogen' nature of CF_3OF, we examined its reaction with some α-diazo-ketones. We obtained mixtures containing mainly αα-difluoroketones[4] and α-trifluoromethoxy-α-fluoro-ketones, hitherto unknown compounds. This result can be explained by nucleophilic attack of the diazo-alkane upon the fluorine, followed by nucleophilic attack upon intermediate (**2**) (or its α-keto-α-fluorocarbonium ion), either by F^- or CF_3O^-.



a; R = Ph (3) : (4) = 58 : 42
b; R = $PhCH_2$ (3) : (4) = 62 : 38
c; R = cyclohexyl (3) : (4) = 66 : 34

For instance, α-diazoacetophenone, prepared from benzoyl chloride (0·02 mol) was treated in $CFCl_3$ with CF_3OF (1·5 mol. equiv.) at −75 °C. After work-up (aqueous $NaHCO_3$), *ca.* 2·5 g of crude oil was obtained. Compounds (**3a**) and (**4a**) form 85% of the crude mixture, in the ratio of 58:42, as shown by ^{19}F n.m.r. spectroscopy. The overall yields, from benzoyl chloride, of pure analytical samples (**3a**) and (**4a**) were 14 and 10%, respectively. I.r., n.m.r. and mass spectra are consitent with the structures given.

(*Received, 6th April* 1976; *Com.* 371.)

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[3] G. A. Olah and J. Welch, *Synthesis*, 1974, 896.

[4] For other preparations of α-difluoro-ketones see: S. Nakanishi, R. L. Morgan, and E. V. Jensen, *Chem. and Ind.*, 1960, 1136; J. Cantacuzène and J. Leroy, *Tetrahedron Letters*, 1970, 3277; P. Crabbé, A. Cervantes, A. Cruz, E. Galeazzi, J. Iriarte, and E. Velarde, *J. Amer. Chem. Soc.*, 1973, **95**, 6655; T. B. Patrick and E. C. Hayward, *J. Org. Chem.*, 1974, **39**, 2120; C. Wakselman and M. Tordeux, *J.C.S. Chem. Comm.*, 1975, 956.