Chemical Communications

NUMBER 22/1968 20 NOVEMBER

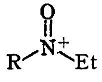
Direct Alkylation of Nitroso-compounds to Nitrones

By J. E. BALDWIN* and R. G. PUDUSSERY
(*Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania,* 16802)

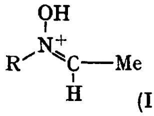
and B. SKLARZ and M. K. SULTAN
(*Chemistry Department, University of Birmingham, Edgbaston, Birmingham* 15, *England*)

PREPARATIVE routes to aliphatic nitrones commonly involve condensations of hydroxylamines with carbonyl-containing species.[1,2] These reactions are often complicated by self condensation of the product under the necessarily basic conditions employed.[3,4] Such difficulties might be avoided by direct alkylation of a nitroso-monomer,[5] to a cation (I), which by prototropic shift would yield the nitrone salt (II), as we have now proved.

The low basicity of the nitroso-nitrogen atom requires powerful alkylating agents and we have discovered that the oxonium salts are adequate in this respect. Thus when 2-methyl-2-nitrosopropane was stirred in the dark with triethyloxonium fluoroborate until the blue colour was discharged (4 days), it was transformed into the highly crystalline fluoroborate salt (II; R = Bu^t). This hygroscopic substance, $C_6H_{14}NOBF_4$,† m.p. 75—80°; ν_{max} ($CHCl_3$) 2500—2000 (H-bonded OH), 1100—1030 cm.$^{-1}$ (fluoroborate); λ_{max} (EtOH) 232 mμ (ϵ 1280), titrated as a monobasic acid. The n.m.r. spectrum (dichloromethane) showed τ 8·40 (9H, s), 7·53 (3H, d, J 5·5), 1·58 (1H, q, J 5·5 c./sec.), and 1·17 (1H, br s), in complete agreement with the formulation. The mass spectrum yielded only one ion (*m/e* 115) from the parent nitrone. Chemical proof of structure was obtained by hydrolysis with dilute mineral acid to acetaldehyde (2,4-dinitrophenylhydrazone), and also by oxidative cleavage with periodate[6] to 2-methyl-2-nitrosopropane and acetaldehyde. 2,4,4-Trimethyl-2-nitrosopentane (III; X = NO) when treated with triethyloxonium fluoroborate in methylene dichloride gave only a dark oil. However, when the reaction was carried out in the presence of solid calcium carbonate, chromatographic work-up gave 2,2,4-trimethylpentene, 2,4,4-tetramethyl-2-nitropentane and finally in low yield a chromatographically homogeneous oil breaking down on high-vacuum distillation. It had ν_{max} 1585 cm.$^{-1}$, λ_{max} (EtOH) 235 mμ (6600), and τ 9·05 (9H, s), 8·45 (6H, s), 8·08, 8·0 (5H, s and d,

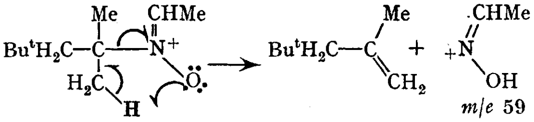


(I)



(II)

$Me_3C{\cdot}CH_2{\cdot}CMe_2X$ (III)



(IV)

---

† Satisfactory analysis has been obtained.

J 6 c./sec. respectively), and 2·92 (1H, AX q, J 6 c./sec.) consistent with its formulation as N-ethylidene-1,1,3,3-tetramethylbutylamine N-oxide [(III); X = N(O):CHMe]. The mass spectrum contained a peak at m/e 59 (18·5% of base peak at 57) with composition C_2H_5NO by accurate mass measurement. This is ascribed to the decomposition (IV). Treatment with dilute acid gave acetaldehyde (2,4-DNP) and the hydroxylamine (III; X = NH·OH, picrate) and periodate gave the nitroso-compound. The reduction product from treatment with borohydride gave a blue colour with Tetrazolium Blue and did not absorb at 1585 cm.$^{-1}$

A small amount of the same nitrone [III; X = N(O):CHMe] was obtained by alkylating the nitroso-compound with ethyl bromide and silver fluoroborate[7] in the presence of calcium carbonate.

Previous transformations of nitroso-compounds to nitrones have involved a nucleophilic attack on the nitroso-compound.[1,2,5] This alternative method may be of value in cases where the nitroso-compound is available.

(*Received, August* 19*th*, 1968; *Com.* 1146.)

---

[1] G. R. Delpierre and M. Lamchen, *Quart. Rev.*, 1965, **19**, 329.

[2] J. Hammer and A. Macaluso, *Chem. Rev.*, 1964, **64**, 473.

[3] F. H. Banfield and J. Kenyon, *J. Chem. Soc.*, 1926, 1612.

[4] R. F. C. Brown, V. M. Clark, I. O. Sutherland, and Sir Alexander Todd, *J. Chem. Soc.*, 1959, 2109.

[5] Readily available from the amines, *cf.* J. E. Baldwin, A. K. Qureshi, and B. Sklarz, *Chem. Comm.*, 1968, 373.

[6] A. K. Qureshi and B. Sklarz, *J. Chem. Soc.* (*C*), 1966, 412.

[7] H. Meerwein, V. Hederich, and K. Wunderlich, *Arch. Pharm.*, 1958, **291/63**, 541.