Cyclopropyldiazomethane

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CYCLOPROPYLDIAZOMETHANE (I) has been cited as an intermediate in various carbenic and cationic decompositions.[1] However, until (I) has been prepared and subjected to the requisite reaction conditions, all postulates of its intermediacy lack total cogency. Attempted preparations of (I) from *N*-nitroso-β-amino-ketones,[2] and from cyclopropylcarboxyaldehyde tosylhydrazone[3] have been unsuccessful. Product instability under conditions necessary to decompose the precursor appeared to be the problem. Preparation of the skeletal isomers of (I), diazocyclobutane,[4] and allyldiazomethane,[5] from the *N*-nitrosourea and *N*-nitrosourethane, respectively, as well as our own work in this area,[6] suggested that (I) should be preparable from a nitrosourethane precursor.

$$\mathrm{RCN} \rightarrow \mathrm{RCH_2{\cdot}NH_2} \rightarrow \mathrm{RCH_2{\cdot}NH{\cdot}CO_2Et}$$

$$\rightarrow \mathrm{RCH_2{\cdot}N(NO)CO_2Et} \rightarrow \underset{\text{(I)}}{\mathrm{RCH{:}N_2}}$$

$$\rightarrow \underset{\text{(II)}}{\mathrm{RCH_2{\cdot}CO{\cdot}Ph}} \rightarrow \underset{\text{(III)}}{\mathrm{RCH_2{\cdot}CH(OH){\cdot}Ph}}$$

R = cyclopropyl

Reduction of cyclopropyl cyanide with lithium aluminium hydride, followed by reaction of the product amine with ethyl chloroformate[7] afforded cyclopropylmethylurethane. The latter, characterized by satisfactory elemental analysis, i.r., and n.m.r. spectra, was nitrosated according to the method of White.[8] The *N*-nitrosourethane thus obtained was characterized by relation of its n.m.r. to that of the urethane.[9]

A freshly prepared solution of sodium (56 mmoles) in triethylene glycol (30 ml.) was contained in a vessel evacuated to 1—2 Torr; the glycol solution was cooled (−25°) and *N*-nitrosourethane (32 mmoles) was slowly added. Product (I) distilled and was collected in a first trap at −78°. After completion of addition, pressure was reduced to 0·25 Torr; the trap was warmed to −20°, and (I) was collected in a second trap at −78°. A final distillation afforded (I), a red–orange liquid possessing a strong garlic odour. Upon warming from −78°, (I) rapidly decolorized, with considerable gas evolution and obvious exothermicity. Dilution with precooled $CDCl_3$ permitted i.r. determination (plastic cell); a strong band, *ca.* 2070 cm.$^{-1}$, was observed.[10] As the solution warmed, frothed, and bleached, this band rapidly decayed.

When (I) was treated with precooled benzaldehyde,[4] immediate bleaching was accompanied by evolution of 24% of theoretical nitrogen content (based on *N*-nitrosourethane). Gas chromatography (Carbowax 20M, 185°) of the residue showed the presence of benzaldehyde and α-cyclopropylacetophenone, (II) (13% based on *N*-nitrosourethane). Traces of an unidentified component were also present. Compound (II) was purified by gas chromatography. Its infrared spectrum (CCl_4) showed a strong peak at 5·95μ.

Its nuclear magnetic resonance spectrum (CCl_4) showed peaks at: multiplet, 7·90—7·69 δ, 2·0 protons (*ortho*-aromatic); multiplet, 7·49—7·12 δ, 2·9 protons (aromatic); doublet, 2·78 δ, J = 6·5 c./sec., 1·8 protons (methylene); multiplet centred at *ca.* 1·10 δ, 1·2 protons (methine); multiplet, 0·80—0·00 δ, 4·0 protons (cyclopropyl). A 2,4-dinitrophenylhydrazone was prepared, m.p. 155—156° (from ethanol). Reduction of (II) with lithium aluminium hydride gave the alcohol (III), identical (i.r. and n.m.r.) with an authentic sample.[11]

Preliminary low-temperature n.m.r. studies, and decomposition experiments have given results in accord with reasonable expectations for (I).

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[3] G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, 1965, **87**, 935. Footnote 5 states, ". . . cyclopropyldiazomethane . . . formed in less than 5% . . . by pryolysis of lithium salts of *p*-tosylhydrazones."

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