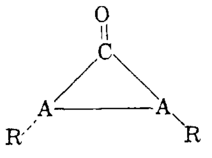
A Stable Cyclopropanone (*trans*-2,3-Di-*t*-butylcyclopropanone)

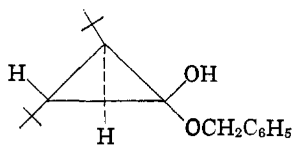
Sir:

Our investigations on diazacyclopropanones[1] (Ia) have provided a number of indications that the alkyl groups on nitrogen are not in the plane of the ring and that a substantial difference in stability exists between the ditertiary derivatives and those possessing smaller alkyl groups. Recently this has also been observed in the α-lactam series in the stability of 1,3-di-*t*-butylaziridinone (Ib).[2] Upon extension of this concept to cyclopropanones, we find that 2,3-di-*t*-butylcyclopropanone (Ic) may be prepared and is an isolable compound of moderate stability.[3] We regard this finding with interest and feel that it may point the way to the preparation of other small-ring compounds which have heretofore appeared to be too unstable or reactive for isolation.

Reaction of α-bromodineopentyl ketone with the potassium salt of *p*-chlorophenyldimethylcarbinol results in the formation of 2,3-di-*t*-butylcyclopropanone in 20–40% yield: mp 24–26° (*Anal.* Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.70, H, 12.08); carbonyl band in the infrared (CCl_4) at 1822 cm^{-1};[4] nmr (CCl_4) δ 0.96 (singlet, 18 H), 1.55 (singlet, 2 H); ultraviolet (isooctane) λ_{max} 354 mμ (ϵ 33); major species in the mass spectrum at 70 ev: *m/e* (relative intensity), 168 (1.7, parent ion), 125 (75), 83 (100), 70 (90), 69 (91), 57 (90), 55 (90), 41 (90). The cyclopropanone is moderately stable in the absence of nucleophiles (50% destruction in 6 hr at 150° in carbon tetrachloride). It decomposes readily in air, but under anhydrous conditions is stable to oxygen. Chemical evidence in support of the cyclopropanone structure is found in catalytic hydrogenation with platinum in dioxane to dineopentyl ketone (45% yield) and in conversion by benzyl alcohol to a hemiketal (II, 65% yield): mp 102–103° (*Anal.* Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.2; mol wt, 276. Found: C, 78.04; H, 10.35; mol wt, 279 (osmometric)); infrared (CCl_4) hydroxyl at 3570 cm^{-1}, no carbonyl absorption, nmr (CCl_4) δ 0.97 and 1.02 (two sharp peaks of equal area; integrated area from δ 0.8 to 1.6 is 20 H, 9 for each of two different *t*-butyl groups and 2 for the cyclopropyl hydrogens), 2.8 (singlet, 1 H), 4.4–4.8 (AB quartet from the two magnetically nonequivalent benzylic hydrogens), 7.1 (singlet, 5 H). These nmr data permit the assignment of *trans* stereochemistry to the two *t*-butyl groups of the cyclopropanone.



Ia, A = N
b, A = CH, N
c, A = CH



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[1] F. D. Greene and J. C. Stowell, *J. Am. Chem. Soc.*, **86**, 3569 (1964).

[2] J. C. Sheehan and J. A. Beeson, *ibid.*, **89**, 362, 366 (1967).

[3] See W. B. Hammond and N. J. Turro, *ibid.*, **88**, 2880 (1966), and references cited therein for information on cyclopropanones containing smaller substituents.

[4] A direct indication of the intermediacy of the cyclopropanone under Favorskii conditions is seen in the buildup and disappearance of this band upon subjection of the bromo ketone to *t*-butoxide in *t*-butyl alcohol.

[5] James Flack Norris Fellow, 1966.

Photolysis of Benzene Vapor at 1849 A[1]

Sir:

In two recent publications[2,3] it has been suggested that benzvalene (the tricyclic valence isomer of benzene) is a major product of the photolysis of benzene vapor at 1849 A. These suggestions were based upon the appearance of a highly structured ultraviolet absorption[2,3] centered near 2400 A and of a product[2] eluting near benzene in gas chromatography. Because of our interest[4] in benzvalene and our desire to find a more efficient preparation than that afforded by the photolysis of liquid benzene at 2537 A,[5] we have reinvestigated the 1849-A vapor photolysis. We find that benzvalene is not present in detectable quantities. Fulvene is the predominant volatile product and is responsible for the structure and most of the density of the optical absorption. Smaller amounts of other volatile products, however, make an appreciable contribution to the absorption.

In our studies, mixtures of benzene vapor (0.05 to 3 torr) and nitrogen (1 atm) in a 10-cm silica cell[6] were irradiated with a mercury resonance lamp[7] for 1 to 12 min at room temperature. The resulting absorption spectra were measured with a Cary Model 14 spectrophotometer against a benzene blank and corrected for nonvolatile absorption on the cell windows.[8]

A typical spectrum, obtained after 7% consumption of the benzene from an initial pressure of 2 torr, is shown as curve A of Figure 1. Spectra obtained at other benzene pressures and at conversions from 1 to 15% exhibit an identical fine structure. Curve A is almost indistinguishable from a spectrum reported by Shindo and Lipsky[3] and is quite similar to that of Foote, *et al.*[2]

Gas chromatography of the photolysis mixtures on columns coated with didecyl phthalate, Apiezon L, and a polar Ucon show the presence of two reaction products eluting near benzene. (In the run corresponding to curve A the amounts of these products were 2.4 and 0.4% of the residual benzene.) The retention volumes of the major product are the same as those of

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 3698 (1966).

[3] K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

[4] L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Am. Chem. Soc.*, **87**, 675 (1965), and subsequent publications.

[5] K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, **89**, 1031 (1967).

[6] A Pyrocell No. 2005, 10-cm cylindrical cell of S18-260 silica, to which inlet and outlet ports fitted with Teflon stopcocks were attached.

[7] The Suprasil discharge tube, in the form of a flat helix, was placed 1 cm from one end of the cell.

[8] Identical spectra were obtained when 2537-A radiation was excluded (irradiated LiF filter[9]). No absorption at all was produced with 2537 A alone (Corning 7910 filter).

[9] J. L. Weeks, S. Gordon, and G. M. A. C. Meaburn, *Nature*, **191**, 1186 (1961).