[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The sym-Triphenylcyclopropenyl Cation, a Novel Aromatic System[1]
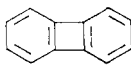
BY RONALD BRESLOW AND CHIN YUAN

RECEIVED MARCH 19, 1958

The synthesis of the sym-triphenylcyclopropenyl cation (VIII) is reported. Derivatives, both covalent and ionic, have been prepared, and the cation has been ring-opened with base to a known ketone. Studies on the equilibrium between the ion and a covalent ether derivative, investigated with the aid of ultraviolet spectroscopy, help to establish the rather high stability of this new aromatic system.

Valence theory, both in the molecular orbital and in the valence bond approach, predicts that certain ring systems should be "aromatic," in the sense that their cyclic conjugation should lead to stability which is considerably greater than might be expected by analogy with simple linear conjugated compounds. Molecular orbital theory, as in the simple LCAO method applied by Hückel, makes the further prediction that only certain cyclic conjugated systems will be aromatic, while others, such as cyclobutadiene, will not be associated with large delocalization energy (i.e., extra stability due to conjugation) and may also be unfavorable for other reasons.[2] The prediction that the three monocarbocyclic six π-electron conjugated systems—cyclopentadienyl anion, benzene and cycloheptatrienyl cation—should be aromatic has been well supported by experiment, and more complex systems, such as polycyclic hydrocarbons, support, in their chemical behavior, the prediction of stability based on molecular orbital calculations.[3] A particularly interesting correlation has been furnished by Roberts, who has demonstrated that a derivative of cyclobutadienoquinone (I) is stable,[4] as predicted by simple LCAO calculations.[5] The strain in this system should be about as great as that in cyclobutadiene, suggesting that it is not only the ring strain in cyclobutadiene which has led to the failure of all attempts to prepare it. Another striking correlation is the existence of biphenylene (II), predicted by LCAO calculations to be stable.[3,5]

I II

These considerations all suggest that derivatives of cyclopropene should be of theoretical interest, as the simple LCAO treatment predicts[5] aromaticity for the cyclopropenyl cation (III) but not for the anion (IV). We have found that certain derivatives of cyclopropene may be prepared conveniently by reaction of acetylenes with diazo compounds,[6,7] and we wish to report here that, utilizing this route, we have prepared the sym-triphenylcyclopropenyl cation, a stable derivative of the simplest possible aromatic ring.


III IV

Reaction of diphenylacetylene with phenyldiazoacetonitrile yields 1,2,3-triphenylcyclopropenyl cyanide (V). This compound (Fig. 1, A) shows the strong absorption maxima in the ultraviolet at about 305 and 320 mμ, and the pair at 225 and 230 mμ, which we have found in 1,2-diphenylcyclopropenedicarboxylic acid (VI),[6] and in the related monocarboxylic acid[8] (Fig. 1, C); apparently this is characteristic of 1,2-diphenylcyclopropenes. That it is rather different from the spectrum of cis-stilbene (λ_{max} 280 mμ, ϵ_{max} 13,500) must be due partly to the strain, and perhaps partly to electronic interactions in the small ring, reflecting extra "unsaturated" character.[9] Triphenylcyclopropenyl cyanide exhibits an extra band at 287 mμ, which must be due to the phenyl at C-3, as the same spectrum (Fig. 1, A) is found for 1,2,3-triphenylcyclopropenyl methyl ether (VII) (vide in-

(1)
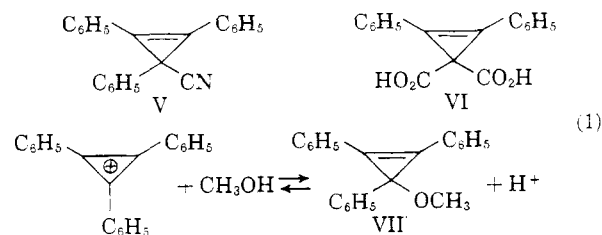
fra). The absorption is at longer wave length than is expected for an isolated benzene ring, again suggesting some special interaction such as might arise from extra "unsaturated" character of the

(1) For a preliminary report of some of these results, see R. Breslow, THIS JOURNAL, 79, 5318 (1957).

(2) Valuable discussions of aromaticity and of the valence bond and molecular orbital methods are contained in G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, and in C. A. Coulson, "Valence," Oxford Press, London, 1952.

(3) A table of some of the correlations which have been found is included in B. Pullman and A. Pullman, "Les Théories Électroniques de la Chimie Organique," Masson and Cie., Paris, 1952, p. 226.

(4) J. Smutny and J. D. Roberts, THIS JOURNAL, 77, 3420 (1955). A more recent synthesis of diphenyldimethylenecyclobutene by A. T. Blomquist and Y. C. Meinwald, ibid., 79, 5317 (1957), also demonstrates in striking fashion the stability of this type of strained system.

(5) Cf. (a) J. D. Roberts, A. Streitwieser and C. M. Regan, ibid., 74, 4579 (1952), and J. D. Roberts, Record Chem. Progress, 17, 106 (1956). The "stabilities" predicted are of course only the extra stabilities due to delocalization, and do not include such factors as angle strain. Furthermore, the correlations found are particularly interesting since the Hückel LCAO method makes several simplifying assumptions which cast doubt on the quantitative correctness of its conclusions. It has been suggested (J. A. Pople, J. Phys. Chem., 61, 6 (1957)) that one of these assumptions, the neglect of electronic interactions, is particularly serious for ions.

(6) R. Breslow and R. Winter, Am. Chem. Soc. Meeting Abstracts, New York, N. Y., 1957, p. 18-P.

(7) The first published report of the synthesis of a cyclopropene in this manner, which has only recently come to our attention, appears to be that of I. A. D'yakonov and M. I. Komendantov, Vestnik. Leningrad. Univ., 11, No. 22, Ser. Fiz. i Khim. No. 4, 166 (1956); cf. C. A., 52, 2762 (1958).

(8) Unpublished observation of M. Battiste.

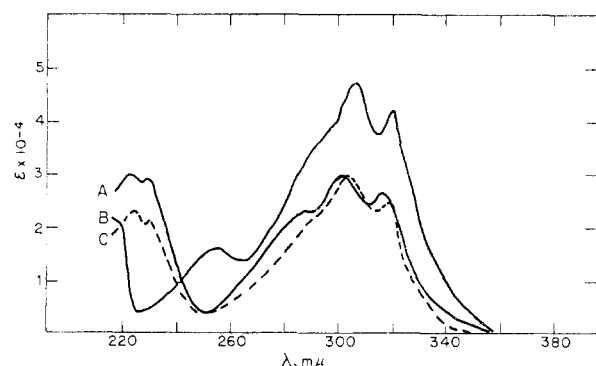(9) R. J. Mohrbacher and N. H. Cromwell, THIS JOURNAL, 79, 401 (1957).

Fig. 1.—Ultraviolet spectra: A, covalent 1,2,3-triphenyl-cyclopropenes; B, the *sym*-triphenylcyclopropenyl cation; C, 1,2-diphenylcyclopropenecarboxylic acid and -dicarboxylic acid.

three-membered ring or from homoallylic conjugation of the isolated phenyl with the stilbene system.[10]

The cyanide is soluble in non-polar solvents and gives no precipitate with ethanolic silver nitrate, so it is not ionic. The possibility of a structure in which cyanide ion is bound in a tight symmetrical complex to the triphenylcyclopropenyl cation is ruled out by the nuclear magnetic resonance spectrum of the compound, which reveals the presence of two types of phenyl rings in the ratio of two to one, supporting a simple covalent structure.

Treatment of the covalent cyanide with boron trifluoride etherate containing some water[11] (which therefore contains fluoroboric, hydroxyfluoroboric and boric acids) leads to a white high-melting solid which is apparently a mixed fluoroborate–hydroxyfluoroborate of the *sym*-triphenylcyclopropenyl cation (VIII); the nuclear magnetic resonance spectrum reveals that there is now only one type of phenyl ring, as expected. This cation has been further characterized by conversion to its picrate. Both the fluoroborate–hydroxyfluoroborate and the picrate are insoluble in the usual non-polar solvents but both are soluble in methanol and ethanol and, to some extent, acetonitrile. The presumption that these compounds are ionic is supported by the bright yellow color of the picrate, for such color is characteristic of ionic picrates as contrasted to covalent picric acid ethers. Furthermore, there seems to be no reasonable way to bind a fluoroborate ion covalently.
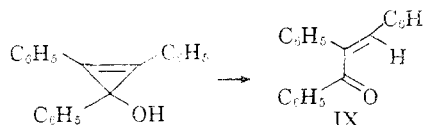

VIII
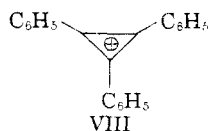
When the fluoroborate–hydroxyfluoroborate is treated with potassium cyanide under mild conditions triphenylcyclopropenyl cyanide is re-formed, showing that no rearrangement of the carbon skeleton has occurred. Furthermore, the fluoroborate–hydroxyfluoroborate reacts with methanol to form

(10) E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4073 (1956).

(11) This procedure is based on a known method for preparing the cycloheptatrienyl cation (M. Dewar and R. Pettit, *ibid.*, 2026 (1956)).

1,2,3-triphenylcyclopropenyl methyl ether (VII). Reaction of the cation with aqueous alkali, however, leads to ring opening, the product being the higher-melting isomer of the two benzylidene desoxybenzoins (IX).[12] The formation of this compound, identical with authentic material, furnishes clear support for the structures assigned in our series.[13]

IX

The covalent triphenylcyclopropenyl methyl ether (VII) promises to be a convenient source of salts of the triphenylcyclopropenyl cation (VIII), which it can furnish on acid treatment. As an example, we have prepared the bromide salt of VIII by treating the ether with hydrogen bromide. This cyclopropenyl bromide is clearly a salt, as revealed by its physical and chemical properties, rather than being covalent as is, for instance, triphenylmethyl bromide. This fact is evidence that there is special stability in the triphenylcyclopropenyl cation as compared to the triphenylmethyl cation, although both species have the positive charge conjugated with the three benzene rings. The ionization of triphenylmethyl bromide should be partly favored by steric effects, as the three bulky phenyl groups move further apart when the central carbon becomes trigonal in the ionization (B strain).[14] In the triphenylcyclopropenyl case, however, this B strain effect is not present, and in fact one would expect steric factors to operate strongly *against* the cation, as in a small ring a trigonal carbon should be more strained than would be a tetrahedral carbon.[15] Another factor operating against the cyclopropenyl cation is the increased electronegativity of carbons in small rings, which results from the greater s-character of the exocyclic bonds due to altered hybridization.[16] This would of course strengthen the bond in the covalent bromide and thus favor it relative to the cation. For these reasons, then, it is rather striking that *sym*-triphenylcyclopropenyl bromide is ionic while triphenylmethyl bromide is covalent.[17]

A better measure of the stability of the ion is found in our ultraviolet spectral studies. As expected, the *sym*-triphenylcyclopropenyl cation has a different spectrum (Fig. 1,B) from that of the covalent compounds, such as the methyl ether. It is striking, however, that the two major bands of the cation occur in the same regions as those of the co-

(12) E. Knoevenagel and R. Weissgerber, *Ber.*, **26**, 441 (1893).

(13) This irreversible ring opening by water explains our earlier observation (ref. 1) that alcohol solutions of the cation suffer slow decomposition.

(14) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

(15) This kind of effect, I strain," must be responsible for the low acidity of nitrocyclopropane (G. S. Hammond in M. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 440).

(16) J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5030 (1951).

(17) One factor which favors the triphenylcyclopropenyl case over the triphenylmethyl one, however, is the lesser crowding of the phenyls in the cation of the former, with consequent greater planarity and conjugation.

valent compounds, although the intensities are much higher for the cation. Work on other derivatives of the cyclopropenyl cation should establish whether this is a coincidence or whether there is some fundamental connection between the spectra of these rather different electronic systems. In alcohol solvent either the cation or the ether will be present, depending on the pH (equation 1). We find that in ethanol the transition occurs at about 1 N acid, while in a mixed acetonitrile–ethanol solvent (nine to one) it occurs at 10^{-4} N acid. We also find that picrate ion is converted to picric acid in these same regions of acidity, suggesting that the pK of the *sym*-triphenylcyclopropenyl cation with ethanol as base is about the same as the pK of picric acid; thus the pK_a of the triphenylcyclopropenyl cation might be near 1 in water (solubility and ring-opening difficulties prevent our titrating our compound in water). At any rate, triphenylmethyl methyl ether shows no cation formation even with 1 N hydrochloric or sulfuric acid in the acetonitrile–ethanol, revealing again the greater stability of the *sym*-triphenylcyclopropenyl cation.

Although further work will be needed to determine how much of the stability of the *sym*-triphenylcyclopropenyl cation is contributed by the phenyls, and how much by the cyclopropenyl aromatic system, it is interesting that the simple molecular orbital calculations indicate[18] that the three phenyls should increase the stabilizing delocalization energy of a simple cyclopropenyl cation, 2.0β, to 4.3β (corrected for DE of the appropriate covalent cyclopropene).[19] The increase in delocalization energy on ionization of a covalent cycloheptatriene derivative to the cation is, by the same type of calculation, only 2.0β; the fact that this species has a[20] pK_a in water of 4.75 shows, however, that it is more stable than our cation. This discrepancy might be a reflection of the strain factors discussed earlier, but it is more likely to reflect a quantitative failure of the simplified molecular orbital theory, since it should be realized that the assumptions made in the simple calculations, *e.g.*, that π–σ overlap and altered hybridization can be ignored, could introduce serious errors, especially in small ring compounds. We feel, however, that our finding of aromaticity in a cyclopropenyl cation is strong support for the qualitative correctness of the molecular orbital calculations.

Experimental[21]

α-Phenyldiazoacetonitrile.—α-Amino-α-tolunitrile was prepared by a modification of the method of Zelinsky.[22] A mixture of KCN (30 g.), NH₄Cl (25 g.), benzaldehyde (50 g.) and methanol (100 ml.) in H₂O (200 ml.) was left at room temperature for 7 hr. The oily product was collected and the methanol was removed *in vacuo* at room temperature. The residue was then taken up in ether and saturated with gaseous HCl. The white product, α-amino-α-tolunitrile hydrochloride, was collected, washed, and recrystallized from ethanol–ether with the acid of HCl; yield 10 g. (13%), m.p. 166–172° (reptd.[22] 173°).

(18) Private communication from J. D. Roberts and S. L. Manatt.

(19) The increase in delocalization energy when a covalent triphenylmethyl compound ionizes is only, by the simple LCAO calculation, 1.8 β (A. Streitwieser, THIS JOURNAL, **74**, 5288 (1952)).

(20) W. Doering and L. Knox, *ibid.*, **76**, 3202 (1954).

(21) M.p.'s uncorrected.

(22) N. Zelinsky and G. Stadnikoff, *Ber.*, **39**, 1722 (1906).

The hydrochloride (10 g.) was dissolved in 250 ml. of H₂O and the solution was extracted with ether to remove non-basic impurities. A layer of ether (100 ml.) was added, the mixture was then cooled to 0°, and a solution of NaNO₂ (6 g.) was added dropwise with good stirring. After five minutes the ether layer was removed and quickly washed with 10% Na₂CO₃ solution, while the aqueous layer was returned to the ice-bath with a fresh portion of ether. After a further 5 minutes this was collected and washed and the combined ether layers were dried over Na₂SO₄. When the ether was removed *in vacuo* from a portion of this solution the residue showed, in the infrared, very strong absorption at 4.82 μ (the diazo group) together with the cyanide peak at 4.5 μ, but the α-phenyldiazoacetonitrile was too unstable to be further characterized, and the ether solution was therefore used directly.

1 2,3-Triphenylcyclopropenyl Cyanide (V).—The above ether solution was mixed with 13 g. of diphenylacetylene and the resulting solution was heated on the steam-bath. When the ether had boiled away a vigorous evolution of N₂ ensued; the reaction was over in about two minutes, with concurrent disappearance of the band at 4.82 μ in the infrared. The residue was then chromatographed on alumina, the excess diphenylacetylene eluting with petroleum (30–60°), the product with 50% benzene–petroleum. After recrystallization from benzene–petroleum ether 1,2,3-triphenylcyclopropenyl cyanide showed m.p. 145–146°, yield 1.3 g. (7.5%).[23]

Anal. Calcd. for C₂₂H₁₅N: C, 90.07; H, 5.15; N, 4.77; mol. wt., 293. Found: C, 90.22; H, 5.43; N, 4.91; mol. wt. (Rast, in camphor), 286.

The compound was insoluble in water, and soluble in benzene, ether, chloroform and methanol. Its methanol solution gave no precipitate with ethanolic AgNO₃. In the infrared the compound showed absorption at 4.5 μ (—C≡N) and its ultraviolet spectrum in ethanol exhibited peaks at 319 mμ (30,000), 303 mμ (33,700), 287 mμ (22,500), 230 mμ (28,700) and 223 mμ (29,600). The n.m.r. spectrum of the compound (CS₂, infinite dilution) showed two peaks, one at −33.6 cycles/sec. and the second of half the intensity at −25.2 cycles/sec. (Varian V-4012 A magnet, 7050 gauss field, 30 megacycles/sec. probe; frequencies referred to benzene capillary and increasing field).

The *sym*-Triphenylcyclopropenyl Cation (VIII).—The above cyano compound (0.53 g.) was refluxed vigorously for 7 minutes in 3 ml. of BF₃-etherate containing 3 drops of H₂O. Dilution with 50 ml. of ether precipitated a white solid which was collected, washed with ether, and dried.

sym-Triphenylcyclopropenyl fluoroborate–hydroxyfluoroborate (mixed salt) showed m.p. 300° dec. after recrystallization from acetone–ether; yield 0.50 g. (78%).

Anal. Calcd. for C₂₁H₁₅BF₄: C, 71.21; H, 4.27; F, 21.46. Calcd. for C₂₁H₁₆BF₃O: C, 71.62; H, 4.58; F, 16.18. Found: C, 71.03, 71,18; H, 4.56, 4.38; F, 17.80, 18.31.

The substance was insoluble in ether, benzene, chloroform, hot 2-butanone and water. It dissolved in warm acetone and in methanol. In concentrated sulfuric acid solution (in which its ultraviolet spectrum is unchanged, *vide infra*) there is a single slightly broadened band at −40 cycles/second in the n.m.r.

The fluoroborate–hydroxyfluoroborate (110 mg.) in warm ethanol was treated with saturated ethanolic picric acid. On cooling, *sym*-triphenylcyclopropenyl picrate separated as a yellow crystalline solid; yield 150 mg. (98%), m.p. 180–188°. The compound was purified by recrystallization from ethanol containing picric acid, followed by a final digestion of the dry substance with hot benzene to remove excess picric acid; m.p. 194–197°.

Anal. Calcd. for C₂₇H₁₇N₃O₇: C, 65.45; H, 3.46; N, 8.48. Found: C, 65.50, 65.67; H, 3.55, 3.59; N, 8.59, 8.71.

The compound was insoluble in benzene, ether, chloroform or water. It was soluble in methanol, ethanol and hot dioxane.

sym-Triphenylcyclopropenyl fluoroborate–hydroxyfluoroborate (50 mg.) was dissolved in acetone and an excess of KCN in water was then added. Isolation and chromatography yielded 1,2,3-triphenylcyclopropenyl cyanide (V) (17 mg., 57%) identical in all respects with the authentic compound. A sample of the fluoroborate–hydroxyfluoroborate was sus-

(23) This yield has been improved to 25% over-all in later work.

pended in 10% NaOH in H₂O, and an ether layer was added. When the solid had disappeared the ether was collected and the aqueous solution re-extracted. The infrared spectrum of the residue after removal of the ether revealed that it consisted of an essentially pure **benzylidene desoxybenzoin (IX)**; when crystallized from ethanol it furnished the compound, m.p. 101–102°, identical with that of the authentic high-melting isomer prepared according to the procedure of Knoevenagel.[10] The mixed melting point was undepressed. The highly characteristic infrared spectrum of our sample was identical with that of the authentic material in every detail, as was its ultraviolet spectrum.

sym-Triphenylcyclopropenyl fluoroborate–hydroxyfluoroborate (200 mg.) was dissolved in methanol (50 ml.) and then 2 ml. of 10% Na₂CO₃ solution was added, followed by 20 ml. of water. The excess methanol was removed *in vacuo* and the neutral material isolated by ether extraction. Trituration of the residue, after evaporation of the ether, with methanol afforded **1,2,3-triphenylcyclopropenyl methyl ether (VII)**, m.p. 69–70° after recrystallization from warm methanol; yield 120 mg. (99%).

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.55; H, 6.08. Found: C, 88.65, 88.70; H, 6.16, 6.14.

The methyl ether is very soluble in ether, benzene and chloroform.

A solution of the above compound in diethyl ether was treated with gaseous HBr. A white solid precipitated immediately, which could be purified by crystallization from methanol–ether with the addition of HBr. **sym-Triphenylcyclopropenyl bromide**, m.p. 269–271° dec., is a colorless salt-like crystalline compound, insoluble in ether, benzene (hot or cold) and chloroform, whose solution in methanol gives an instantaneous precipitate with AgNO₃ solution.

Anal. Calcd. for $C_{21}H_{15}Br$: C, 72.64; H, 4.36; Br, 23.01. Found: C, 72.30; H, 4.46; Br, 23.05.

Ultraviolet Spectra.—The fluoroborate–hydroxyfluoroborate, the methyl ether, and the bromide all show, in ethanol solvent, essentially the same spectrum (due to the covalent ether): λ_{max} 317 mμ (27,000), 302 mμ (30,000) (23,000), 230 mμ (29,000) and 223 mμ (30,000) (Fig. 1,A). The picrate shows an additional band at 360 mμ (17,600) due to picrate ion, and higher intensity at the 230 and 223 mμ bands.

In acetonitrile containing ethanol (10%) the spectra are as above, as they are when HCl is added up to a concentration of 10^{-5} N. At greater than 10^{-4} N HCl in 10% ethanol–acetonitrile the methyl ether, bromide, fluoroborate–hydroxyfluoroborate, and picrate show a change to 320 mμ (42,000) and 307 mμ (47,000). The band at 287 mμ is not evident, and the two bands at 230 and 223 mμ are replaced by strong end absorption. In addition, a new band at 255 mμ (16,000) appears. The same spectrum (Fig. 1,B) is found for solutions in concentrated H₂SO₄. In the picrate the band at 360 mμ is suppressed, and the strong absorption of covalent picric acid at lower wave lengths is added to the cation spectrum. The same change from picrate ion to covalent picric acid is found, at 10^{-4} N HCl in 10% ethanol-acetonitrile, for authentic solutions of picric acid. Except in the region of 10^{-4} N acid these spectra are not affected by added acid or base. In ethanol solvent the same spectroscopic behavior is observed, except that the transition now occurs at about 1 N acid (as does that for the picrate ion). The spectrum of trityl methyl ether is unchanged in 10% ethanol in acetonitrile on addition of HCl or H₂SO₄ to a concentration of 1 N.

NEW YORK 27, N. Y.

Studies in Organic Peroxides. XXII. The Thermal Decomposition of *t*-Butylperoxy Isobutyrate

BY NICHOLAS A. MILAS AND ALEKSANDAR GOLUBOVIĆ[1]

The purification and study of the decomposition of *t*-butylperoxy isobutyrate in the pure state, in benzene and in water are reported. The decomposition of this peroxyester is a first-order reaction and is unique in that it produced mainly a polymeric compound (dimethylpolyglycolid) the formation of which can be explained on the basis of an intermediate diradical which is stabilized by the charge distribution between two carbon and two oxygen atoms. Tentative structures of the polyglycolids have been proposed and compared with that of the dimethyldiglycolid.

In the industrial production of *t*-butylperoxy isobutyrate using essentially the method published from this Laboratory[2a] it was observed[2b] that under certain conditions this perester decomposed slowly into a white, non-peroxidic solid, the structure of which was unknown. We undertook to study the thermal decomposition of pure *t*-butylperoxy isobutyrate and to attempt to elucidate the structure of the solid formed during the decomposition.

Since this peroxyester has not been reported previously in the literature it was necessary to prepare it in the pure state and study its decomposition under specified conditions. The commercial product,[2] containing about 75% of the peroxyester, was purified using special methods which are described in the Experimental part. Pure *t*-butylperoxy isobutyrate is a clear colorless liquid, m.p. –45.7°.

The stability of this peroxyester was studied at various temperatures by following the peroxide

(1) Lucidol Research Assistant.

(2) (a) N. A. Milas and D. Surgenor, THIS JOURNAL, **68**, 642 (1946); N. A. Milas, U. S. Patent 2,567,615, Sept. 11, 1951; (b) Lucidol Division, Wallace and Tiernan, Inc.

content iodimetrically. At 0° the peroxyester is stable for an indefinite period of time and even at room temperature its decomposition is imperceptibly small. The pure peroxyester decomposes at 40° to the extent of 1.26% in 5 hours and at 50°, 9.12% in 4 hours. At 70° the rate of decomposition seems to be approximately of the first order as shown in Table I. At 80° the decomposition is very rapid and reaches 76.66% in 1 hour, while at 90° it proceeds explosively.

TABLE I

DECOMPOSITION OF *t*-BUTYLPEROXY ISOBUTYRATE AT 70°

Time, hr.	Decomposition, %	k
1	13.37	0.1436
2	27.77	.1627
3	37.97	.1592
4	44.77	.1485
5	47.05	.1272
	Mean	0.1482

The decomposition also was measured in boiling benzene under an efficient reflux and the results are shown in Table II.