302 (24,400), 343 (15,900), 420 (17,200), 706 (61); ir (Nujol) 2230 cm^{-1} (C≡N), 1595, 1572 (C=C), 760 (*o*-benzo).

Anal. Calcd for $C_{22}H_8N_4$: C, 80.48; H, 2.46; N, 17.05. Found: C, 80.33; H, 2.43; N, 17.03.

The polaragraph was carried out in a 0.1 *M* $LiClO_4$ solution of acetonitrile and was measured against a saturated calomel electrode.

Synthesis of the Radical Salt 11.—Under an atmosphere of N_2 a mixture of 50 mg of **8** and 250 mg of tetra-*n*-butylammonium iodide were fused at 115°. After 10 min the melt was cooled and was extracted with four 15-ml portions of benzene. The residue was dissolved in tetrahydrofuran. After filtering of this solution, ether was added giving 40 mg of a purplish black precipitate. This precipitate was recrystallized from tetrahydrofuran–ether affording 7 mg of analytically pure purple-black powder, **11**, mp 197–199°. The original benzene extract afforded, after concentration and fractional crystallization, another 8 mg of less pure **11**: mp 196–200°; electronic spectrum, λ_{max} (chloroform) 274 mμ (ϵ 134,200), 292 (109,200), 328 (37,500), 341 (39,260), 409 (22,380), 433 (19,820), 553 (28,150), 594 (55,200), 740 (15,520), 820 (22,500), 1130 (2520), and about 3.5 μ (in KBr); ir (KBr) 2180 (C≡N), 1580 (C=C), 736 cm^{-1}.

Anal. Calcd for $C_{98}H_{96}N_{14}$: C, 80.08; H, 6.58; N, 13.34. Found: C, 79.62; H, 6.31; N, 13.58.

Registry No.—**1,** 16408-95-0; **6,** 16408-96-1; **7,** 16408-97-2; **8,** 16408-98-3; **9,** 16408-99-4; **11,** 12259-94-8.

Acknowledgment.—We wish to thank Dr. R. Nicholson (Michigan State University) for the polarographic determination and Dr. P. Manoharan (Michigan State University) for the esr results.

Reactions of the Cyclobutylcarbinyl Radical

LEONARD KAPLAN

Department of Chemistry, University of Chicago, Chicago, Illinois

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The occurrence of a 1,2-alkyl shift in a hydrocarbon monoradical has not been demonstrated.[1] We have unsuccessfully approached this problem by attempting to use the relief of ring strain accompanying ring expansion of the cyclobutylcarbinyl to the cyclopentyl radical as a driving force for such a rearrangement. The exothermicity of this reaction, estimated[2] to be about 25 kcal/mol, is very much larger than the 7 kcal/mol available in previously studied neopentyl systems. Also, if products resulting from reaction of the cyclopentyl radical[4] had been observed, it would have been unlikely that they formed by fragmentation to the 4-penten-1-yl radical followed by cyclization to the cyclopentyl radical[5,6] since reaction of CH_2=CH-$(CH_2)_3I$ with benzoyl or di-*t*-butyl peroxide in benzene does not yield any detectable cyclopentane, cyclopentene, cyclopentyl benzoate, or cyclopentylbenzene, all of which are formed to a significant extent when cyclopentyl iodide is allowed to react under the same conditions.[4]

Reaction of cyclobutylcarbinyl iodide (I) at room temperature and cyclobutylcarbinyl chloride (II)[7] at 148° with triphenyltin hydride in benzene resulted in formation of methylcyclobutane (III) with no detectable cyclopentane.

Reaction of I, which is thermally stable at all temperatures used, with approximately equimolar amounts of benzoyl peroxide (114 and 76°) or di-*t*-butyl peroxide (167 and 133°) in benzene yielded complex mixtures of products which contained no detectable cyclopentane or cyclopentene. Use of only 5 mol % peroxide revealed the reason for the failure of our approach. With both peroxides, a 2:1 mixture of 5-iodo-1-pentene and I resulted. Thus, I apparently opened to 5-iodo-1-pentene in a radical-chain process by way of the cyclobutylcarbinyl and 4-penten-1-yl radicals. We estimate[8] the cyclobutylcarbinyl radical → 4-penten-1-yl radical fragmentation to be less favorable than rearrangement to cyclopentyl radical by about 19 kcal/mol in ΔH and about 15 kcal/mol in ΔF.

The complete trapping, before fragmentation, of the cyclobutylcarbinyl radical by Ph_3SnH is in accord with our earlier conclusion that Ph_3SnH is a very good radical-trapping agent.[9]

Experimental Section

Benzene, cyclopentane, cyclopentene, benzoyl peroxide, di-*t*-butyl peroxide, 5-chloro-1-pentene, cyclopentyl chloride, and cyclopentyl iodide were commercial materials.

Cyclobutylcarbinyl chloride,[10] triphenyltin hydride,[11] and 5-iodo-1-pentene[12] were prepared by use of literature procedures.

Cyclobutylcarbinyl iodide was prepared by use of a procedure reported for cyclopropylcarbinyl iodide.[13] Cyclobutylcarbinyl chloride (1.06 g, 0.010 mol) and 1.5 g (0.010 mol) of sodium iodide were refluxed in 7.5 ml of acetone for 17 hr. The resulting mixture was filtered and the solvent removed from the filtrate. Ether was added to the heterogeneous residue and then removed from the resulting liquid phase. Cyclobutylcarbinyl iodide was obtained from the liquid residue by separation from unreacted chloride by use of preparative gas chromatography. It, as did the cyclobutylcarbinyl chloride prepared as indicated above, contained no detectable amount of the cyclopentyl isomer. Its nmr spectrum (CCl_4) consisted of a multiplet at τ 6.8 (2 H) and complex absorption between τ 7.0 and 8.6 (7 H).

Anal. Calcd for C_5H_9I: C, 30.64; H, 4.63; I, 64.73. Found: C, 30.72; H, 4.56; I, 64.89.

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[1] For reviews, see C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 407, and R. Kh. Freidlina in "Advances in Free-Radical Chemistry," Vol. I, G. H. Williams, Ed., Academic Press Inc., New York, N. Y., 1965, p 211.

[2] Calculated assuming that D(cyclobutylcarbinyl–H) = D($CH_3CH_2CH_2$–H) and using known[3] values of the heat of formation of cyclobutane, cyclopentane, H·, and the cyclopentyl and *n*-propyl radicals.

[3] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[4] L. Kaplan, *J. Org. Chem.*, **32**, 4059 (1967).

[5] In the course of a study of ring-size effects in the neophyl rearrangement, Wilt observed the formation of some phenylcyclopentane and 1-phenylcyclopentene in the decarbonylation of (1-phenylcyclobutyl)acetaldehyde and presented arguments which he felt supported an elimination-addition mechanism.[6]

[6] J. W. Wilt, L. L. Maravetz, and J. F. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966).

[7] Reaction of II with Ph_3SnH at 148° resulted in the gradual accumulation of III over a period of about 28 hr. At this point the remaining II was very rapidly converted into cyclopentene. When the reaction was run for 20 min at 205°, the essentially exclusive product was cyclopentene. 5-Chloro-1-pentene did not give cyclopentene under these conditions. At both temperatures, the final reaction mixture was heterogeneous. The precipitated gray solid was found to convert II into a mixture of cyclopentene and cyclopentyl chloride under the reaction conditions.

[8] Calculated assuming that D(CH_2=$CHCH_2CH_2CH_2$–H) = D($CH_3CH_2CH_2$–H) and using known[3] values of the thermodynamic parameters of cyclopentane, 1-pentene, H·, and the cyclopentyl and *n*-propyl radicals.

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Registry No.—Cyclobutylcarbinyl radical, 16447-31-7; cyclobutylcarbinyl iodide, 16408-62-1.

Acknowledgment.—We are grateful to Professor W. D. Walters for a sample of methylcyclobutane.

The Reaction of Triethyl *trans*-1,2,3-Tricyanocyclopropane-1,2,3-tricarboxylate with Base. Formation of a Substituted Cyclopropane Anion Radical

ANTHONY J. PAPA[1a]

Fabrics and Finishes Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

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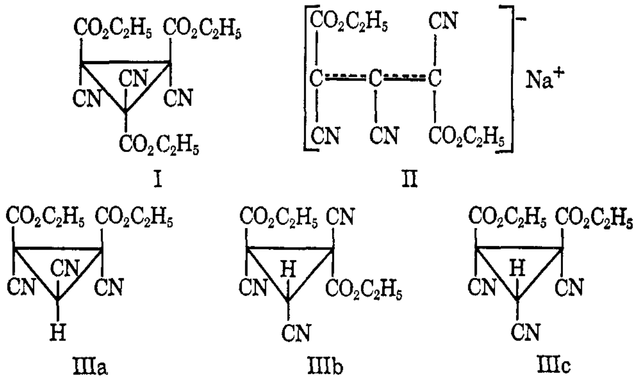
In the synthesis of triethyl *trans*-1,2,3-tricyanocyclopropane-1,2,3-tricarboxylate (I) by reaction of ethyl sodiocyanoacetate and ethyl bromocyanoacetate according to the general procedure of Felton,[1b] we obtained, in addition to I, two other compounds, sodium 1,2,3-tricyano-1,3-dicarbethoxypropenide (II) and diethyl 1,2,3-tricyanocyclopropane-1,2-dicarboxylate (IIIa–c) (21 and 6% yield, respectively) (Chart I).

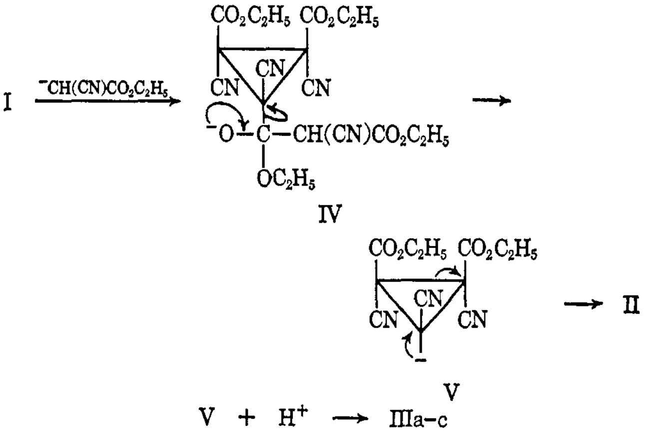
CHART I



Compounds II and IIIa–c were characterized and identified as follows. The yellow salt II gave the correct elemental analysis and was soluble in water and insoluble in nonpolar solvents. The infrared spectrum showed the presence of conjugated nitrile,[2] exhibiting a strong, sharp absorption peak at 4.51 μ and a less intense peak at 4.47 μ. The absorption bands at 5.88 and 6.78 μ are assigned to C═O and C═C stretching vibrations, respectively. The ultraviolet spectrum of II showed $\lambda_{\max}^{C_2H_5OH}$ 425 mμ (ε 22,203) and 218 (13,192). These ultraviolet absorption features are similar to those reported for pentacyanopropenides.[3]

Assignment of structures IIIa–c is based primarily on analysis of spectral data. The proton nmr spectrum exhibited signals centered at δ 4.55 (two protons, quartet), 4.54 (two protons, quartet), 3.58 (one proton), and 1.45 ppm (six protons, triplet). The two low-field signals are attributed to the ester methylene protons, the 3.58-ppm signal to the cyclopropyl proton,[4] and the 1.45-ppm triplet to the ester methyl protons. Absorption bands in the infrared spectrum at 3.29 (cyclopropyl C—H),[5] 5.73 (C═O), and 4.44 μ (C≡N) and elemental analysis also indicate structures IIIa–c. The spectra are compatible with the structures IIIa–c for the cyclopropane derivative.

Regan[6] has observed propenide formation in the reaction of diethyl 2,2,3,3-tetracyanocyclopropane-1,1-dicarboxylate with ammonia. It would appear that formation of compound II results from base-catalyzed ring opening of I and that this type of ring opening could be general for highly negatively substituted cyclopropane derivatives with at least one carbalkoxy group. These results are consistent with the initial involvement of a Haller-Bauer[7] type of cleavage reaction. The transformations involved in the derivation of II and IIIa–c might be rationalized by initial formation of pentasubstituted cyclopropyl carbanion (V), which is formed by the elimination of diethyl cyanomalonate from intermediate IV, which, in turn, results from the nucleophilic addition of ethyl cyanoacetate anion to an electron-deficient ester carbonyl of I. Rearrangement of V would lead to the propenide (II) while proton capture would give IIIa–c. This rationalization is supported by the fact that compound II and its potassium salt were formed upon treatment of I with ethyl sodiocyanoacetate and potassium acetate in anhydrous 1,2-dimethoxyethane in 78 and 51% yield, respectively. Moreover, reaction of I with ethyl sodiocyanoacetate gave IIIa–c in 4–8% yield. On the other hand, the strongly basic sodium hydride gave an 11% yield of II and no cyclopropane product could be detected after 1 week at room temperature. These products are identical with those isolated in the original reaction as evidenced by comparison of infrared and ultraviolet absorption spectra and mixture melting point determinations.



That the cyclopropane derivative (IIIa–c) did not arise from a mechanism involving protonation of II was demonstrated by treating II with *p*-toluenesulfonic acid in ethanol. Only 1,2,3-tricyano-1,3-dicarbethoxy-

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[1] (a) Address correspondence to the author at the Union Carbide Corp., Research and Development Department, South Charleston, W. Va. (b) D. G. I. Felton, *J. Chem. Soc.*, 515 (1955).

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