determinations with the naphthalene ozonolysis mixtures. Column 3 was used for the formic and acetic acid determinations at 95°. The peaks obtained were compared with those from standard solutions, and yields were estimated by determination of peak areas with an integrator, and by peak heights. The latter did not always appear to give accurate results, however. Where peaks were obtained on the shoulders of other peaks (*e.g.*, formic acid on the shoulder of methanol), estimation was made of peak areas by cutting out and weighing, or by means of a planimeter. Most of the results are shown in Tables I and II. In addition, the yield of methyl glyoxalate (XXIIIb) was 95% from an ozonized solution of 2-methoxynaphthalene (Id) in methanol, and 70% from a similar ethanolic reaction mixture; the yield of ethyl glyoxalate (XXIIc) from an ozonized solution of 2-ethoxynaphthalene (Ie) in methanol was 100%. The standard in each case was an ozonized solution of the corresponding fumarate.

Ozonolyses of Naphthalenes with 1 Mole Equiv. of Ozone. A. **Naphthalene** (**Ia**).—A solution of 2.6 g. of naphthalene in 50 ml. methanol and 75 ml. methylene chloride was ozonized at −20°. The absorption of 1 mole equivalent of ozone was quantitative. The reaction mixture was evaporated; the residue was dissolved in a little methanol and treated with water. The precipitated naphthalene weighed 1.1 g. (42%) and melted at 72–75° (mixture melting point with known sample, 73°).

B. **2-Naphthol** (**Ic**).—A solution of 2.9 g. (0.02 mole) of Ic in 100 ml. of methanol was ozonized with 1 mole equiv. of ozone at −20°. V.p.c. of the reaction mixture showed only a trace of methyl formate. The reaction mixture was partially evaporated and poured into 500 ml. of water. Some darkening and effervescing occurred and a precipitate formed, giving a 53% yield of *o*-carboxycinnamic acid (XXVIIb), melting at 186–189°, when recrystallized from acetic acid, m.p. 196°. The compound gave a negative test for carbonyl with Brady's reagent and its melting point and infrared spectrum corresponded well with that reported by Bernatek and Frengen.[9] In another instance the cold reaction mixture was poured immediately into cold water. The yield of XXVIIb was 46%.

Anal. Calcd. for $C_{10}H_8O_4$: neut. equiv., 96. Found: neut. equiv., 101.

C. **2-Methoxynaphthalene** (**Id**).—A solution of 0.01 mole of Id in 50 ml. of a 1:1 mixture of methanol–methylene chloride was ozonized with 1 mole equiv. of ozone. V.p.c. showed only a trace of methyl glyoxalate. When the solution was poured into water, no precipitate was obtained, and evaporation or treatment with sodium hydroxide gave only red tars. The original solution was acidified with 3 drops of concentrated hydrochloric acid and refluxed for 1 hr., after which it was treated with excess 2,4-dinitrophenylhydrazine in ethanol–sulfuric acid. The DNP weighed 2.16 g. (58% yield) and melted at 192–199°, when recrystallized from benzene, m.p. 205–206°. The infrared spectrum (methylene chloride) was similar to that of the DNP of methyl phthalaldehydate, as would be expected for the DNP of XXXIII.

Anal. Calcd. for $C_{17}H_{14}N_4O_6$: C, 55.13; H, 3.81; N, 15.13; OCH_3, 8.38; mol. wt., 370. Found: C, 55.46; H, 4.08; N, 14.20, 16.13; OCH3, 8.25; mol. wt., 360.

Ozonizations with Ozone–Nitrogen and Molecular Oxygen Yields.—The procedure was as described in an earlier paper.[10] The results are shown in table form. By analogy to results with anthracene, in which 3 moles of oxygen were evolved per mole of anthraquinone in methylene chloride, and 2 moles of oxygen per mole of anthraquinone in methanol,[12] it is seen that the amount of atom attack is only 3–5% with naphthalene and 5–10% with 2-naphthol.

TABLE III

OXYGEN YIELDS USING OZONE–NITROGEN

Compound	mmoles used	Solvent	mmoles of O_3 reacted	mmoles of O_2 evolved
Naphthalene	10	CH_3OH–CH_2Cl_2, 1:1	20	0.68
Naphthalene	10	CH_2Cl_2	20	1.44
2-Naphthol	10	CH_3OH–CH_2Cl_2, 1:1	20	1.43

Acknowledgment.—The authors are grateful for grants from The National Science Foundation (G-15805), The Robert A. Welch Foundation (F-042), and The American Chemical Society Petroleum Research Fund (792A) in support of this research. They also wish to acknowledge helpful discussions with Per Kolsaker.

The Preparation of 1-Amino-1-fluoroalkylethylenes by the Addition of Active Methylene Compounds to Fluoroalkyl Cyanides

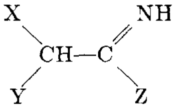
A. D. JOSEY

Contribution No. 864 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware

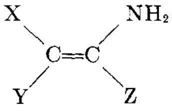
Received August 13, 1963

It has been shown that the addition of active methylene compounds to the cyano group of fluoroalkyl cyanides gives a new class of reactive intermediates, the 1-amino-1-fluoroalkylethylenes. Several reactions of these stable enamines have been studied including acylation of the acidic amino function and replacement of the latter by nucleophiles.

Addition of active methylene compounds to the cyano group have been explored to a considerable extent,[1] and while the products have often been formulated as substituted ketimines (I), it seems likely in view of more recent studies[2] that in many cases the enamine structure (II) is the preferred arrangement.



I



II

The addition of malononitrile, cyanoacetic ester, and malonic ester to the exceptionally reactive cyano group of fluoroalkyl cyanides gives stable crystalline products in yields ranging from 55–100%. The formulation of the products as primary enamines receives support from infrared spectra which disclose the $-NH_2$ group as well as the carbon–carbon double bond conjugated with the electronegative group of the active methylene compound. In addition, the ultraviolet spectra contain a single characteristic absorption maximum which shifts predictably as the electronegative groups are varied. The reaction of malononitrile with trifluoroacetonitrile

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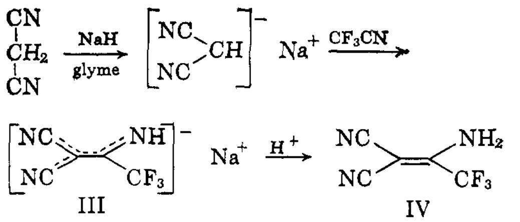
(1) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 285.

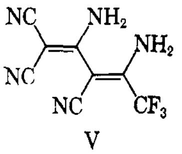
(2) S. Baldwin, *J. Org. Chem.*, **26**, 3288 (1961), and references cited therein.


(1)

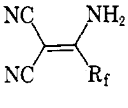
to yield 1-amino-1-trifluoromethyl-2,2-dicyanoethylene (IV) is illustrative of the type and is shown in eq. 1.

The reaction is normally conducted by generating the sodio derivative of the active methylene compound through reaction of the latter with a molar equivalent of sodium hydride in ethylene glycol dimethyl ether (glyme). The fluoronitrile is added to a cold solution of the salt, and the product is isolated by careful acidification of the solution, removal of precipitated salts, and evaporation. In a modification of this procedure, only a catalytic amount of sodium hydride is used. The success of the latter scheme is dependent on the ability of the intermediate ion (III) to extract a proton from unchanged starting material rather than from an outside source. Although a longer operating time is required, the reaction gives reasonably good yields of product.

The infrared spectra of compounds in the series show a sharp doublet in the 3500-cm.$^{-1}$ region ($-NH_2$) and strong absorption near 1650 and 1575 cm.$^{-1}$ (primary amine N–H deformation and conjugated C=C, respectively).[2,3] With the exception of the highly substituted butadiene (V) derived from malononitrile dimer and trifluoroacetonitrile, all the compounds in the series exhibit a single sharp absorption maximum in the ultraviolet near 285 mμ. Malononitrile dimer itself, which embodies a chromophore similar to that of the 1-perfluoroalkyl-1-aminoethylenes, absorbs at 276 mμ (ϵ 14,000).[4] Compound IV has λ_{max}^{EtOH} 283 mμ (ϵ 15,000) and, when one of the –CN groups is replaced by –COOEt, the maximum remains essentially unchanged. Replacement of –CN groups by –COOEt shifts the λ_{max} to 279 mμ (ϵ 13,300).

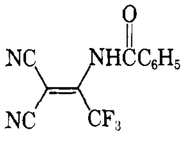

V

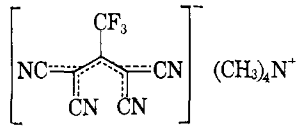
The influence of 1-perfluoroalkyl groups on the position of the absorption maximum in this structure

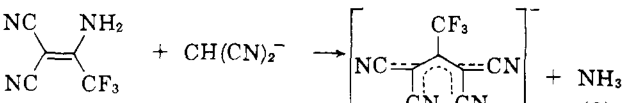


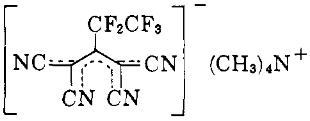
is of interest. When $R_f = CF_3$, the compound has λ_{max} 283 mμ; when $R_f = CF_2CF_3$, λ_{max} is at 287 mμ; and where $R_f = CF{\cdot}CF_2CF_3$, λ_{max} is at 289 mμ.

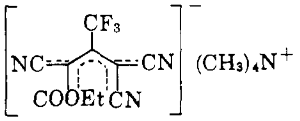
1-Amino-1-perfluoroalkyl ethylenes display none of the basic characteristics associated with free amino groups. They are, in fact, weakly acidic and readily dissolve in dilute aqueous base. Treatment of IV in pyridine solution with benzoyl chloride provided the N-benzoyl derivative (VI). However, reaction of IV in aqueous sodium hydroxide solution with tetramethylammonium chloride failed to yield the simple tetramethylammonium salt. There was isolated instead a yellow crystalline solid which was shown to have structure VII. The origin of VII lies in the reaction of IV with malononitrile anion (eq. 2) with the elimination of ammonia and the formation of the hybrid 2-trifluoromethyl-1,1,3,3-tetracyanopropenide ion. Malononitrile anion was undoubtedly present in solution through the base-catalyzed reversal of the sequence of reactions (eq. 1) which originally provided IV. Indeed, when IV was treated in an aqueous suspension with an equivalent amount of sodiomalononitrile, the former dissolved instantly and ammonia was evolved. When the solution was boiled for 15 sec., cooled, and treated with tetramethylammonium chloride, VII was isolated in 80% yield. Similar treatment of 1-amino-1-pentafluoroethyl-2,2-dicyanoethylene (XI) provided tetramethylammonium 2-pentafluoroethyl-1,1,3,3-tetracyanopropenide (VIII). It was anticipated that reaction of 1-amino-1-trifluoromethyl-2-cyano-2-carbethoxyethylene (Table I) with sodiomalononitrile would give salt IX. Actually, the only isolated product of this reaction was salt VII which was readily identified by its melting point and infrared spectrum as well as by analysis. While a variety of reasonable mechanisms can be adduced to account for this striking and unexpected transformation, a detailed study of the reaction has not been carried out.


VI

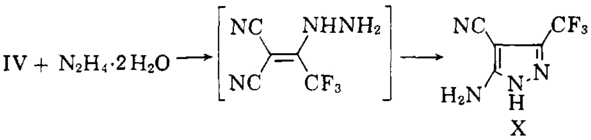

VII


(2)


VIII


IX

Further evidence for the vulnerability of the $-NH_2$ group of 1-amino-1-perfluoroalkyl ethylenes to displacement by nucleophiles is provided by reaction of the former with hydrazine. Thus, treatment of IV with hydrazine hydrate in boiling ethanol (eq. 3) provided 3-trifluoromethyl-4-cyano-5-aminopyrazole (X) in 37% yield. X presumably results from cyclization of the primary displacement product, 1-hydrazino-1-trifluoromethyl-2,2-dicyanoethylene.


X (3)

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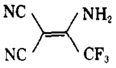
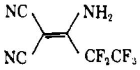
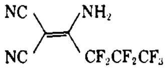
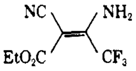
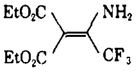
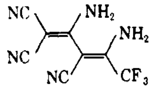
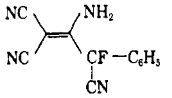
[3] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1956.

[4] R. A. Carboni, D. D. Coffman, and E. G. Howard, *J. Am. Chem. Soc.*, **80**, 2838 (1958).

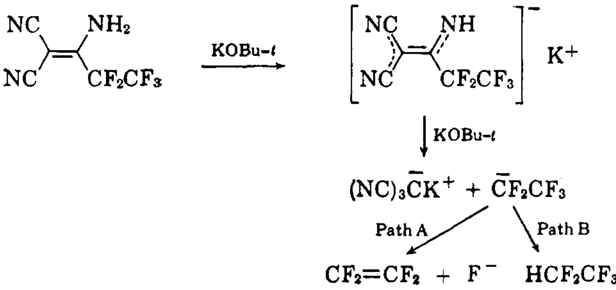
TABLE I

1-AMINO-1-FLUOROALKYLETHYLENES

Compound	M.p., °C.	Yield, %	λ_{max}^{EtOH}, mμ (ε)	Analysis, % Calcd. C	H	N	F	Found C	H	N	F
	179–180[a]	98	283 (15,000)	37.3	1.25	26.1	35.4	37.5	1.36	26.6	35.6
	201–203[a]	97	287 (13,750)	34.1	0.96	19.9	45.0	34.3	1.18	20.2	45.3
	176.5–177[a]	87	289 (13,800)	32.2	0.77	16.1	50.9	32.7	0.96	16.1	49.2
	118–120[b]	74	284 (18,200)	40.4	3.39	13.5	27.4	40.5	3.49	12.9	27.3
	125–127[c]	70	279 (13,300)	42.4	4.74	5.49	22.3	42.1	5.18	5.52	22.3
	250[d]	100	240 (40,000) 252 (25,400) 301 (6130) 330 (6160)	42.3	1.78	30.8	25.1	42.7	1.93	30.6	24.8
	149–150[a]	55	285 (11,800)	63.7	3.12	24.8	8.40	64.0	3.14	25.1	8.21

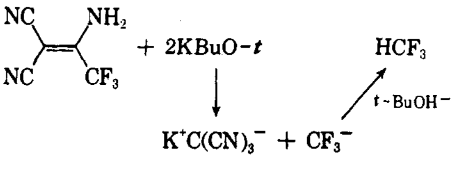
[a] Recrystallized from chloroform–acetone. [b] Recrystallized from chloroform–pentane. [c] Recrystallized from pentane.

The reaction of 1-amino-1-pentafluoroethyl-2,2-dicyanoethylene (XI) in anhydrous *t*-butyl alcohol with 2 equiv. of potassium *t*-butoxide was studied to determine if fragmentation of the molecule according to eq. 4 could be effected.



(4)

A completely concerted mechanism (path A) might be expected to yield tetrafluoroethylene, fluoride ion, and potassium tricyanomethanide, while stepwise elimination of a pentafluoroethyl carbanion might be expected in the protonic solvent to give an appreciable amount of pentafluoroethane (XII). In fact, the only gaseous product of the reaction was shown by infrared analysis to be pentafluoroethane. When IV, the trifluoromethyl analog of XI, was treated in a similar fashion (eq. 5), the sole gaseous product was fluoroform, HCF_3.



(5)

Experimental

A. 1-Amino-1-perfluoroalkylethylenes (Table I). General Procedure.—The reaction vessel was thoroughly flame-dried and allowed to cool in a nitrogen atmosphere. A solution of the active methylene compound in anhydrous ethylene glycol dimethyl ether (glyme) was added to a stirred suspension of 1 molar equiv. of sodium hydride (a commercial mineral oil dispersion was employed) in anhydrous glyme. The reaction temperature was maintained at 25° by external cooling. When the formation of the sodio derivative was complete, hydrogen evolution ceased, and a clear solution resulted. The solution was cooled to about −30° and a Dry Ice–acetone filled condenser was attached to the flask. The fluoronitrile, *ca.* 10% excess of 1 molar equiv., was condensed in a sufficiently cold receiver; then it was allowed to distill slowly into the solution of the sodio derivative. When the addition was complete, the cooling bath was removed, and the mixture was allowed to warm to 0°. Hydrochloric acid (12 *N*) was added until the mixture was just acidic to litmus paper. The precipitated sodium chloride was removed by filtration, and the filtrate was evaporated to dryness *in vacuo*. The 1-amino-1-perfluoroalkylethylenes were obtained as colorless crystalline solids, and they generally were purified by crystallization from chloroform and acetone or pentane. Those that have been prepared are listed in Table I along with some of their physical properties.

A variation of the above procedure, requiring only a catalytic amount of sodium hydride, is illustrated by the following preparation. To a solution of 6.6 g. (0.1 mole) of malononitrile in 175 ml. of glyme there was added 0.10–0.20 g. of a mineral oil dispersion of sodium hydride. The solution was cooled to −10°, and trifluoroacetonitrile (8.5 ml., *ca.* 0.1 mole) was added slowly according to the general procedure above. After the addition, the mixture was stirred for 1 hr. at −35° and worked up as above. The yield of light yellow, unrecrystallized 1-amino-1-trifluoromethyl-2,2-dicyanoethylene (IV) was 8.47 g. (52%).

B. 1-Benzamido-1-trifluoromethyl-2,2-dicyanoethylene (VI).—To a solution of 1.61 g. (0.01 mole) of IV in 5 ml. of pyridine, there was added 1.41 g. (0.01 mole) of benzoyl chloride. The mixture darkened and heat was evolved. The solution was boiled 10 min. over an open flame, and poured into ice-water. The oil which separated was washed with water several times by decantation, then taken up in methanol. On standing, the methanol solution deposited 1.31 g. (50%) of yellow crystalline 1-benzamido-1-trifluoromethyl-2,2-dicyanoethylene. Recrystallization from methanol gave yellow needles, m.p. 288–289°, $\lambda_{max}^{CH_2Cl_2}$ 270 and 338 mμ (ε 6780 and 16,600).

Anal. Calcd. for $C_{12}H_6F_3N_3O$: C, 54.3; H, 2.3; F, 21.5; mol. wt., 265. Found: C, 54.4; H, 2.3; F, 21.1; mol. wt., 264, 256 (ebullioscope, acetone).

C. **Tetramethylammonium 2-Trifluoromethyl-1,1,3,3-tetracyanopropenide (VII).**—A mixture of 1.61 g. (0.01 mole) of 1-amino-1-trifluoromethyl-2,2-dicyanoethylene and 0.88 g. (0.01 mole) of sodiomalononitrile was treated with 7 ml. of water. Solution occurred quickly. The orange-brown solution was boiled briskly for 15 sec., then there was added a solution of 2.2 g. (0.02 mole) of tetramethylammonium chloride in 8 ml. of water. A copious yellow precipitate formed immediately. The product was filtered and dried in air to provide 2.17 g. (77%) of tetramethylammonium 2-trifluoromethyl-1,1,3,3-tetracyanopropenide. Several crystallizations from water provided yellow needles, m.p. 177–179°.

Anal. Calcd. for $C_{12}H_{12}F_3N_5$: C, 50.9; H, 4.3; N, 24.7. Found: C, 50.9; H, 4.2; N, 24.7.

D. **Tetramethylammonium 2-Pentafluoroethyl-1,1,3,3-tetracyanopropenide (VII).**—A suspension of 2.11 g. (0.01 mole) of 1-amino-1-pentafluoroethyl-2,2-dicyanoethylene in 8 ml. of water was treated with 0.88 g. (0.01 mole) of sodiomalononitrile. Most of the solids dissolved quickly, and the odor of ammonia soon was apparent. The mixture was boiled for 5 min., and a solution of 2.2 g. (0.02 mole) of tetramethylammonium chloride in 7 ml. of water was added. Crystallization of the product began quickly, and the mixture was chilled in ice for 1 hr. Filtration provided 2.34 g. (70%) of bright yellow tetramethylammonium 2-pentafluoroethyl-1,1,3,3-tetracyanopropenide. Crystallization from methanol–ether provided lemon-colored prisms, m.p. 127–129°.

Anal. Calcd. for $C_6H_2F_5N_3$: C, 34.1; H, 0.96; F, 45.0; N, 19.9. Found: C, 34.3; H, 1.2; F, 45.3; N, 20.2.

E. **3-Trifluoromethyl-4-cyano-5-aminopyrazole (X).**[5]—A solution of 10.4 g. (0.065 mole) of 1-amino-1-trifluoromethyl-2,2-dicyanoethylene (IV) and 3.5 g. (0.07 mole) of hydrazine hydrate in 250 ml. of ethanol was refluxed 16 hr. The solvent was removed by rapid evaporation to leave an oil which crystallized on standing. Recrystallization from acetone–chloroform provided 4.2 g. (37%) of 3-trifluoromethyl-4-cyano-5-aminopyrazole. Two further crystallizations from chloroform gave white needles, m.p. 172–172.5°.

Anal. Calcd. for $C_5H_3F_2N_4$: C, 34.1; H, 1.7; N, 31.8. Found: C, 34.2; H, 1.6; N, 32.3.

F. **Reaction of 1-Amino-1-perfluoroalkylethylenes with Potassium *t*-Butoxide.** 1.—A solution of potassium *t*-butoxide was prepared by dissolving 1.96 g. (0.05 g.-atom) of potassium metal in 50 ml. of anhydrous *t*-butyl alcohol. 1-Amino-1-pentafluoroethyl-2,2-dicyanoethylene (5.28 g., 0.025 mole) was added in one portion. The yellow solution was heated under reflux while effluent gases were led from the top of the condenser through an infrared cell. After 16 hr. of reflux, heating was discontinued. The infrared spectrum of the gaseous product contained bands at 7.6, 8.4, 8.8, and 11.5 μ, and identified the material as pentafluoroethane (XII).[6] The yield of pentafluoroethane was not determined.

The ultraviolet spectrum of potassium tricyanomethanide shows $\lambda_{\max}^{\text{EtOH}}$ 272 mμ (ε 213), 223 (3220) with the latter appearing as a shoulder on a broad, intense absorption at lower wave lengths. The ultraviolet spectrum of the solid product of the reaction described above contained a maximum at 223 mμ (ε 3040), but the weak absorption at 272 was obscured by a strong absorption at 393 (10,900), attributable to starting material.

2.—In an experiment identical with that described in 1, except that 4 g. (0.025 mole) of 1-amino-1-trifluoromethyl-2,2-dicyanoethylene was employed, infrared analysis of the gaseous product (8.3, 8.8 μ) showed that it consisted solely of fluoroform.

Acknowledgment.—The author wishes to acknowledge valuable discussions with Dr. S. Proskow who performed some of the early experimental work in this area.

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[5] This reaction was performed by Dr. H. E. Holmquist.

[6] "Fluorine Chemistry," J. H. Simons, Ed., Academic Press, New York, N. Y., 1954, p. 472.

Reactions of *t*-Butyl Hydroperoxide with Olefins

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Received September 5, 1963

The decomposition of *t*-butyl hydroperoxide has been studied in the presence of olefins to determine the feasibility of epoxidation with it. Rates were measured at 60 and 100°. Variations in rate with olefin structure were found to be small. Epoxide yields are dependent on structure in a way that suggests that the epoxide-forming reaction is a polar process. By treating hydroperoxide with the geometric isomers of 4-methyl-2-pentene, it was shown that epoxide forms stereospecifically by a *cis* oxidation. A variety of solvents were found to accelerate the over-all reaction, although none was effective in increasing epoxide yield. It is concluded that the reaction between hydroperoxide and olefin proceeds through an intermediate complex and is generally poor for the preparation of epoxide.

The formation of epoxides from the reaction of hydroperoxides with olefins has been described[2] as part of a study of the autoxidation of olefins. The possible utility of this reaction as a synthetic method and the importance of hydroperoxide olefin interactions in hydroperoxide initiated polymerization of olefins[3-5] led us to study some further aspects of hydroperoxide epoxidation.

Experimental

Chemicals.—Olefins were Phillips pure grade. Olefins and solvents were taken from freshly opened bottles and distilled. Purity was checked by gas chromatography. *t*-Butyl hydroperoxide (Lucidol) was distilled (or redistilled) to >90% purity as determined by iodometric analysis.

Kinetics.—New glass equipment was used for kinetic experiments. Samples of 1 to 4 ml. of previously mixed reagents were introduced into small carius tubes which were then degassed with several freezing and thawing cycles and sealed at <0.1-mm. pressure. After thawing and shaking, the tubes were thermostated at 60 or 100° ± 0.02°. Tubes were removed periodically for peroxide and gas chromatographic analyses. Remaining peroxide was determined[6] by titrating aliquots which had been permitted to react in glacial acetic acid–saturated potassium iodide mixtures under carbon dioxide for ~0.25 hr., diluted with distilled water, and titrated with ~0.1 *N* thiosulfate. Gas chromatographic analyses were performed on a Perkin-Elmer Model 154C using a column containing diisodecyl phthalate on Celite (Perkin-Elmer A column), column temperature 130°, helium carrier gas flow 25 p.s.i. Constant volume sampling was achieved with a Hamilton 10-μl. syringe. Epoxide peaks thus obtained were analyzed both by per cent total peak area and by comparison with peak areas obtained from standard solutions of epoxide. The two methods gave essentially the same results implying that the amount of high boiling material, if any, was not enough to interfere with analyses by the first method. Decomposition studies as set forth in Tables I–III were performed on bulk olefin, with

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