97–98°, was added a solution of 0.020 g. of *p*-toluenesulfonic acid monohydrate in 3 ml. of isopropenyl acetate, and the mixture was refluxed for 2 hr. Then *ca.* 10 ml. of the isopropenyl acetate was removed by distillation and replaced by 10 ml. of hexane. The resulting mixture was allowed to stand overnight in the refrigerator, whereupon a precipitate formed. Another 10 ml. of hexane was added, and the 0.181 g. of solid, m.p. 118–120°, was collected by decantation and washed with hexane. Chromatography of the supernatant liquid on 10 g. of acid-washed alumina afforded (with 3:17 acetone–hexane) an additional 0.161 g. of III, m.p. 116–118°, for a total yield of 0.342 g. (74%). The analytical sample was prepared by recrystallization from ether–hexane and had m.p. 119.5–120.0°; $\lambda_{\max}^{\mathrm{EtOH}}$ 247 mμ (ϵ 13,700); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.73, 5.96, and 6.12 μ; n.m.r., 1.71 ($\mathrm{C}H_3\mathrm{C}{=}\mathrm{C}$), 2.04 ($\mathrm{C}H_3\mathrm{COO}$), and a quartet at 4.89 p.p.m. ($H\mathrm{COAc}$).

Anal. Calcd. for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.16; H, 7.08.

Lithium–Ammonia Reduction of III.—To 150 ml. of liquid ammonia was added *ca.* 0.12 g. (3 cm. of $^1/_8$-in. wire) of lithium. To the resulting blue solution was added 0.516 g. (1.84 × 10^{-3} mole) of diacetate III, m.p. 119–120°, dissolved in 12 ml. of anhydrous tetrahydrofuran (distilled from lithium aluminum hydride). The mixture was magnetically stirred for 5 min. and then crystalline ammonium chloride was added, discharging the dark blue color. The mixture was allowed to evaporate, and the residual material was washed thoroughly with three 150-ml. portions of anhydrous ether. Evaporation of the ether yielded 0.377 g. of oily product, which v.p.c. analysis (silicone SE-30 column at 200°) indicated to contain one major component (at least 80% of the material detected by the column) and five minor components. The major component was collected from the chromatograph and exhibited $\lambda_{\max}^{\mathrm{film}}$ 5.81 μ. This material decolorized potassium permanganate solution, and, when it was treated with ethanolic sodium hydroxide, strong ultraviolet absorption at 245 mμ developed, consistent with XII → XIII.

The v.p.c.-purified XII yielded a red 2,4-dinitrophenylhydrazone (prepared with heating), m.p. 177.5–178.5°. This derivative was compared with the 2,4-dinitrophenylhydrazone, m.p. 178.5–179.5° (lit.[19] m.p. 177°), of 1-methyl-$\Delta^{1,9}$octalone-2 (XIII) prepared from ethyl vinyl ketone and the pyrrolidine enamine of cyclohexanone,[20] and these were found to be identical in all respects. The mixture melting point was 178.5–179.5°.

One of the minor components of the reduction mixture (the second fraction, eluted directly after XII) was judged from its spectral properties [$\lambda_{\max}^{\mathrm{film}}$ 5.97 and 6.15 μ; $\lambda_{\max}^{\mathrm{EtOH}}$ 249 mμ (ϵ 9500); lit.[21] $\lambda_{\max}^{\mathrm{EtOH}}$ 249 mμ (ϵ 12,500)] to be XIII.

Lithium–Ammonia Reduction of I.—A solution of 0.200 g. (7.5 × 10^{-4} mole) of diacetate I in 4.9 ml. of dry tetrahydrofuran was added to a magnetically stirred solution of 0.05 g. of lithium in 60 ml. of liquid ammonia over a 4-min. period. The resulting solution was stirred for 8 min. before solid ammonium chloride was added to discharge the blue color. The ammonia was evaporated, and the mixture was partitioned between saturated sodium chloride solution and ether. The ether extracts were dried over magnesium sulfate and stripped to afford 0.084 g. of a light yellow oil (74% of the theoretical amount of XIV). V.p.c. analysis showed only one constituent after material of very low retention time (presumably solvent). The product peak had an infrared spectrum with $\lambda_{\max}^{\mathrm{film}}$ 5.82 (strong), 5.99 (weak), and 6.15 μ (weak), and other bands consistent with XIVcontaining a small amount of XV. On the basis of v.p.c. peak areas, the yield of XIV + XV was 55–60%. The crude product exhibited $\lambda_{\max}^{\mathrm{EtOH}}$ 238 mμ (ϵ 1600), which indicated that, of the mixture of XIV and XV contained therein, *ca.* 12% was XV [lit.[20] $\lambda_{\max}^{\mathrm{EtOH}}$ 239 mμ (ϵ 17,400)].

Treatment of the product with base caused isomerization of XIV to XV, as indicated by an increase in absorption at 238 mμ. When the reduction product was treated with 2,4-dinitrophenylhydrazine reagent under the nonisomerizing conditions of Wilds and Nelson,[9] a yellow derivative with m.p. 163.0–163.5° was obtained; $\lambda_{\max}^{\mathrm{KBr}}$ 6.14, 6.27, 6.53, 6.66, 7.49, and 7.60 μ (lit.[9] m.p. 173.0–173.5° for the 2,4-DNP of XIV). When the reduction product was derivatized under the isomerizing conditions of Wilds and Nelson,[9] a mixture of 2,4-dinitrophenylhydrazones was obtained in 42% yield. The pure, red 2,4-DNP derivative of XV was separated by thin layer chromatography on silica gel G with chloroform and had m.p. 168–169° (lit. m.p. 168°,[22] 168–170°,[20] 180–181°[9]). The infrared spectrum of this derivative ($\lambda_{\max}^{\mathrm{KBr}}$ 6.18, 6.27, 6.57, 6.66, 7.51, and 7.66 μ) was identical with that of a red 2,4-DNP, m.p. 179–180°, of XV prepared by reaction of the pyrrolidineenamine of cyclohexanone with methyl vinyl ketone.[20]

Acknowledgment.—This investigation was supported by Public Health Service Research Grant AM-05014. The authors are grateful to Professor K. L. Williamson for determining and discussing the n.m.r. spectra.

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Hydrolysis of Alicyclic Perhalo Olefins[1]

Richard F. Stockel, Michael T. Beachem, and Frederic H. Megson

Research and Development Department, Organic Chemicals Division, American Cyanamid Company, Bound Brook, New Jersey

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The reaction of several cyclic fluoro olefins (I) with hydroxide ion in solvents such as diglyme, dimethylformamide, and dimethyl sulfoxide gave high yields of salts of the corresponding 3-hydroxyperhalo-2-cycloalken-1-ones. The hydrogen analogs (II) of these salts were found to be extremely strong acids. The mechanism of the reaction and physical properties of the products are discussed.

In the course of preparing organofluoro compounds, we studied the reaction of several cyclic fluoro olefins (I)[2] with potassium hydroxide and observed unusual solvent effects.

Although no reaction was reported to occur between 1,2-dichlorohexafluorocyclopentene-1 (Ic) and potassium hydroxide in aqueous dioxane,[6] we found that 4 equiv. of base were consumed in diglyme or aprotic dipolar solvents, such as dimethyl sulfoxide. The product was the potassium salt of IIc. The same salt was also obtained by treating 1-chloro-2-methoxyhexafluorocyclopentene-1 (If) or 1-chloro-2-phenoxyhexa-

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[1] Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[2] All of these compounds are known except Ig and Ih. These are prepared by the standard method of adding 1 equiv. of the anion to the appropriate olefin. See ref. 3–5.

[3] J. D. Park, J. R. Dick, and J. R. Lacher, *J. Org. Chem.*, **28**, 1154 (1963).

[4] J. D. Park, M. L. Sharrah, and J. R. Lacher, *J. Am. Chem. Soc.*, **71**, 2337 (1949).

[5] R. F. Stockel, M. T. Beachem, and F. H. Megson, *Can. J. Chem.*, **42**, 2880 (1964).

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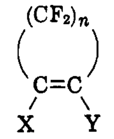
TABLE I

SPECTROSCOPIC RESULTS

Compd. (K • salts)	Infrared, μ[a]	Ultraviolet λ_{max}, mμ (ε) (solvent)[b]	N.m.r.[c] (internal std. $CFCl_3$)
IIe[d]	5.91, 6.03 (w), 6.25–6.40 (br), 6.75 (w)	329 (24,386) (ethanol)	Triplet and quintet (intensity 2:1) at ϕ 120.7 and 134.5 (methanol), J = 11.3 c.p.s.
IIc	5.89, 5.99 (w), 6.15–6.35 (br), 6.68 (w)	273 (28,656) (ethanol)	Singlet at ϕ 125.6 (methanol)
IId	5.85, 5.95 (w), 6.10–6.32 (br), 6.66 (w)	272 (32,569) (ethanol)	Doublet and quintet (intensity 4:1) at ϕ 126.2 and 171.0 (methanol), J = 9.1 c.p.s.
IIa	5.60, 5.88 (m), 6.05–6.30 (br), 6.64 (w)	243 (14,372) (water)	Singlet at ϕ 119.3 (methanol)
IIb	5.53, 5.86 (m), 6.03–6.28 (br), 6.61 (w)	243 (20,529) (water)	Doublet and triplet at ϕ 118.5 and 128.2 (water),[e] J = 20 c.p.s.
IIf[f]	5.88, 5.98 (w), 6.15–6.36 (br), 6.68 (w)	. . .	. . .

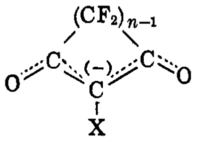
[a] Mineral oil mulls on a Perkin-Elmer Model 317 spectrophotometer. [b] Beckman DU spectrophotometer manually operated. [c] Varian HR-60 operating at 56.4 Mc. Compounds were measured as 10% solutions in the indicated solvents. For an explanation of the shielding value, ϕ, see G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959). [d] For this material the carbon and hydrogen values were high and chlorine was low. [e] $CFCl_3$ was used as an external standard. [f] The dimethylammonium salt of IIc.



Ia, X = Y = Cl; n = 2
b, X = Y = F; n = 2
c, X = Y = Cl; n = 3
d, X = Y = F; n = 3
e, X = Y = Cl; n = 4
f, X = Cl; Y = OCH_3; n = 3
g, X = Cl; Y = OC_6H_5; n = 3
h, X = F; Y = OCH_3; n = 3

fluorocyclopentene-1 (Ig) with potassium hydroxide under similar conditions.

The other alicyclic fluoro olefins also gave salts of the fluoro acid II when treated with alkali, alkaline earth, or quarternary ammonium hydroxides in diglyme.



IIa, X = Cl; n = 2
b, X = F; n = 2
c, X = Cl; n = 3
d, X = F; n = 3
e, X = Cl; n = 4

The hydrolysis of 1,3,3-triethoxy-2-chloro-4,4-difluorocyclobutene-1 under strongly acidic conditions was reported[7] to give 3-keto-2-chloro-4,4-difluorocyclobutenol (IIa) which was characterized by conversion to the known 2-chloro-3-ethoxy-4,4-difluorocyclobutenone.

We obtained quantitative conversions to the desired acids by simply passing aqueous solutions of the potassium salts through a cation-exchange resin in the hydrogen ion form. The resulting acids were low-melting solids that could be dissolved in water and organic solvents, but analytical samples were not obtained because of their hygroscopicity.

Since the addition of sulfuric acid to aqueous solutions of the acids did not alter their ultraviolet spectra, we believe that these acids are completely dissociated in water. Furthermore potentiometric titrations carried out in aqueous hydrochloric acid indicated that the fluorinated acids are as strong as hydrochloric acid.

A potentiometric titration of the acid IIc in pyridine, using tributylethylammonium hydroxide as the titrant, gave an indicated purity of 97.3% on the anhydrous basis. The estimated limit of error for this value is ±0.5%.

A conductimetric[8] titration of IIc in pyridine, using tributylethylammonium hydroxide as the titrant, showed that it is a stronger acid than either HBr or H_2SO_4, and has approximately the same acidity as perchloric acid in pyridine.

Discussion

It is well known that certain solvents can greatly enhance the rates of bimolecular nucleophilic substitution reactions.[9] Some of the factors involved in this effect are a reduction in the effective hydrogen bond with the anions, an increase in the polarizability of the leaving group, an increased solubility and/or a difference in basicity; any one of these factors may be important in enhancing the rate of reaction.

The reaction of ethoxide ion with 1,2-dichlorotetrafluorocyclobutene-1 gives 1-ethoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene.[3] Further reaction with methoxide ion gives 1,3-dimethoxy-3-ethoxy-2-chloro-4,4-difluorocyclobutene.

In contrast to the 1,2-dichlorofluorocycloalkenes the corresponding four- and five-membered perfluorocycloalkenes behave somewhat differently[4,5] in that the introduction of the second alkoxide ion gives the 1,2-dialkoxyperfluorocycloalkene. Chart I summarizes the mechanisms[10] for the reaction of the two types of cycloalkenes with alkoxide ion.

The differences can be ascribed to steric factors and the reactivities of intermediates III and IV. The vinylic chlorine atom in III is considerably more bulky than the vinylic fluorine in IV. In addition, a vinylic fluorine is much more reactive toward nucleophilic substitution than a vinylic chlorine.[11]

When the nucleophile is hydroxide ion, both types of cyclic perhalo olefins give exclusively the same type of

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(7) J. D. Park, S. Cohen, and J. R. Lacher, *J. Am. Chem. Soc.*, **84**, 2919 (1962).

(8) Both the potentiometric and conductimetric titrations were performed on a Precision-Dow Recordomatic titrator modified by addition of a conductance bridge.

(9) For an excellent review see A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(10) For a discussion of the mechanism see E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlov, and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 3557 (1962), in addition to ref. 3–5.

(11) E. F. Silversmith and D. Smith, *J. Org. Chem.*, **23**, 427 (1958), and references cited therein.

CHART I

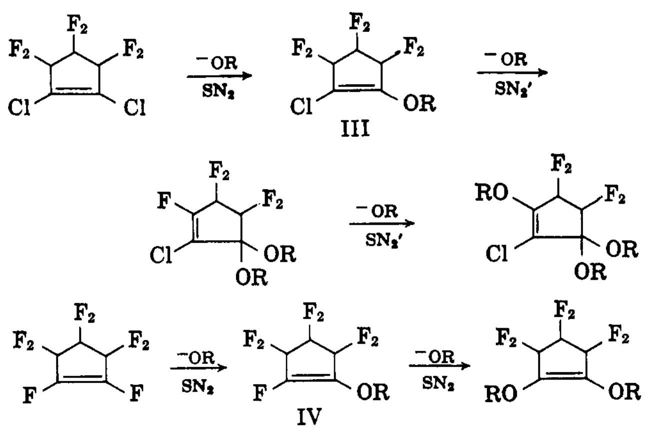
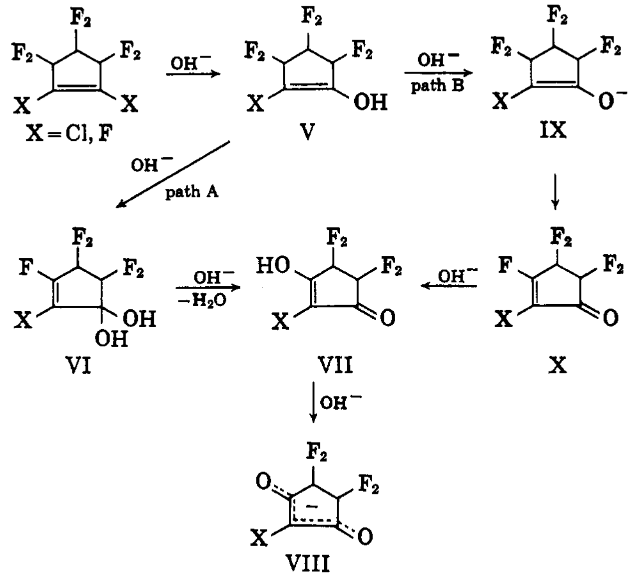


CHART II



product. Chart II gives two plausible reaction paths for reaction with hydroxide ion.

Via path A the intermediate V can react further with 3 equiv. of hydroxide ion to give VI, VII, and VIII. This sequence is analogous to the reaction sequence of alkoxide ion with the 1,2-dichlorofluorocycloalkenes.

However, path B is also possible, and it may explain why the reactions with hydroxide ion are different from those with alkoxide ion. In the latter case the formation of enolate anion IX is not possible.

Thus far intermediate X has not been detected, although amine salts of the enolate anion IX have been prepared by a different method.[12]

Ordinarily vinyl ethers are susceptible to mild acid cleavage; however, 1-chloro-2-ethoxyhexafluorocyclopentene-1 is completely inert to both Brønsted and Lewis acids.[13] Since amine salts[14] effectively cleave ethers, 1-chloro-2-methoxyhexafluorocyclopentene-1 was treated with HI in dimethylformamide, thereby generating dimethylammonium iodide *in situ*.[15] Methyl

TABLE II

Compd.	Time, hr.	Temp., °C.	% yield	M.p., °C.	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found	Cl, % Calcd.	Cl, % Found	F, % Calcd.	F, % Found	K, % Calcd.	K, % Found
IIe	2 then 15	50 Room temp.	92.7[a]	114–115[b]	$C_{16}H_{10}ClF_6NO_2$	48.31	48.28	3.02	2.53	3.52	3.50	8.91	8.82	...	...	...	...
IIc	15	75	90	276–278 dec.	$C_5ClF_4KO_2$	24.75	24.87	0.00	0.24	...	...	14.61	14.70	...	...	16.11	16.42
IId	24	75 (sealed tube)	86.0	199–201 dec.	$C_5F_5KO_2$	26.55	26.45	0.00	0.21	...	...	...	...	...	...	17.28	16.88
IIa	24	75 (sealed tube)	80.9	190–192 dec.	$C_4ClF_2KO_2$	24.94	25.09	0.00	0.33	...	...	18.41	18.27	...	...	...	...
IIb	24	50 (sealed tube)	62.5	146–148 dec.	$C_4F_3KO_2$	27.27	27.81	0.00	0.34	...	...	...	...	32.31	31.84	...	...
IIf	4[c] 8[d]	104 155 (autoclave)	81.0[c] 61.8[d]	149–151	$C_7H_8ClF_4NO_2$	33.68	33.84	3.22	3.68	5.61	5.91	...	...	...	...	...	...

[a] As the N-methylquinolinium salt. [b] This is the melting point for the N-methylquinolinium salt of the acid IIc from the reaction of 1-chloro-2-methoxyhexafluorocyclopentene-1 with HI in DMF. [c] As the dimethylammonium salt. [d] As the dimethylammonium salt of the acid IIc from the reaction of 1-chloro-2-methoxyhexafluorocyclopentene-1 with KF·2H₂O in dimethylformamide.

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(12) This work will be reported in a subsequent paper.

(13) R. A. Shepard, H. Lessoff, J. D. Domijan, D. B. Hilton, and T. F. Finnegan, *J. Org. Chem.*, **23**, 2011 (1958).

(14) N. Prey, *Ber.*, **74**, 1219 (1941); **75**, 350 (1942).

(15) When an aqueous HI solution was refluxed in dimethylformamide, a quantitative yield of the ammonium salt was obtained.

iodide was isolated and the dimethylammonium salt (IIf) of IIc was obtained in good yield.

In another experiment designed to replace the chlorine in 1-chloro-2-methoxyhexafluorocyclopentene-1 with fluorine in dimethylformamide, the dihydrate of potassium fluoride was inadvertently used. Once again the product was the corresponding dimethylammonium salt IIf.

In both cases a possible explanation for the formation of the salt involves the decomposition of dimethylformamide to give dimethylamine, which acts as a nucleophile and forms the 1-amino derivative.[16] Vigorous hydrolysis of the latter gave the observed product.

Spectroscopic Studies

The spectroscopic results for the potassium salts are reported in Table I. The fluorine n.m.r. spectra are consistent with the proposed structures in both the correct multiplet observed and the expected ratios.

In each case the infrared absorption spectrum contains three bands characteristic of the O=C=C=C=O system. Actually, four bands should be present due to the two C=O and two C=C bonds[17]; however, one of these centered around 8 μ is not observed owing to C–F absorption. The doublet found at the highest frequency is due to crystal splitting.

An analogy can be made between these fluorinated salts and certain metal chelates of acetylacetonates.[17] Of course, the exact position of the various bands is affected by the substituents on the ring and by the size of the ring as indicated in Table I.

The ultraviolet absorption spectra show a bathochromic shift with increasing ring size and a definite increase in absorptivity when a chlorine atom is replaced by a fluorine atom,[18] but the λ_{max} remains unchanged.

Experimental[19]

General Procedure for Hydrolysis.—Potassium hydroxide (4 moles) was added to diglyme (350 ml.) and the olefin (1 mole) was slowly added thereto while vigorously stirring. The reaction was fairly exothermic. In the sealed-tube reactions the exotherm appeared to be sufficient to effect mixing of the solution.

The solution was then cooled and filtered to remove inorganic salts, and the filtrate was concentrated to dryness under vacuum. The residue was dissolved in hot isopropyl alcohol, treated with activated charcoal, and filtered. Upon evaporating the solvent the salt was obtained as a solid precipitate. Alternatively, the salt could also be obtained by adding ethyl ether to a concentrated solution in isopropyl alcohol.

General Procedure for Preparing the Acid Form.—The potassium salts were eluted with a known quantity of distilled water through Dowex 50W-M8, an ion-exchange resin in hydrogen ion form.

In the case of IIc the aqueous solution was concentrated to near dryness and sublimed at 90–100° (1–2 mm.). This gave a very hygroscopic acidic material[20] which was soluble in both water and polar organic solvents.

The analyses and melting points of the acid forms were variable, probably owing to the amount of water present. The infrared curves of the acid forms are similar to those of the potassium salts, with the exception of two bands at *ca.* 2.78 and 3.00 μ which are characteristic of the hydroxyl group.

Acknowledgment.—The authors wish to acknowledge the assistance of Dr. J. E. Lancaster for the fluorine n.m.r. spectra, Dr. W. M. Banick for the nonaqueous titrations, Mr. A. Ferri for the ultraviolet spectra, Mr. N. B. Colthup for the infrared interpretation, and Mr. J. J. Kobliska for the analyses. The authors are also grateful to Professor W. Bailey, University of Maryland, for helpful discussions during this work.

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[16] C. O. Parker, *J. Am. Chem. Soc.*, **81**, 2183 (1959).

[17] N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964, pp. 244–246.

[18] W. W. Robertson and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5252 (1950).

[19] See Table II for experimental details, yields, and analytical results.

[20] In a recent publication [E. D. Weil and J. Linder, *J. Org. Chem.*, **28**, 2218 (1963)] the chlorine analog of this compound was reported. These authors have observed broad bands between 6.1 and 6.4 μ and acidities similar to those of the compound we have prepared.

A New High-Temperature Free-Radical Source

GEORGE A. MORTIMER

Plastics Division, Monsanto Company, Texas City, Texas

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A new free-radical initiator, azobisisobutanol diacetate, has been prepared from azobisisobutyronitrile in good yield in three steps: (1) methanolysis to convert the nitrile groups to ester functions; (2) reduction of the diester to a diol; and (3) acetylation. Thus, it is more easily synthesized than other azo compounds having similar free-radical-generating properties and may be easily tagged with C^{14} if desired. Steady production of free radicals at 167° was demonstrated.

Azobisisobutyronitrile has been widely used in the laboratory as a thermal initiator for polymerization because its decomposition rate is independent of the medium and therefore accurately known. Labeled with C^{14}, it has been used to trace initiator residues in polymers because the radicals formed upon elimination of nitrogen do not undergo any further fragmentation. Despite these advantages, its usefulness is limited by the fact that above about 80° its rate of decomposition is too fast for kinetic experiments. This report describes the preparation and initiating characteristics of a new initiator which has the same advantages but decomposes thermally about 100° higher than azobisisobutyronitrile.

The major objective of this work was to provide an easily prepared, free-radical initiator useful for kinetic work at approximately 150–200°. Azoisobutane yields free radicals at a useful rate in this temperature range,[1] but its synthesis is not facile. The procedure of Kooy-

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[1] J. B. Levy and B. K. W. Copeland, *J. Am. Chem. Soc.*, **82**, 5314 (1960).