Anal. Calcd. for this mixture: C, 78.98; H, 14.18; O, 6.84. Found: C, 78.96; H, 13.91; O, 7.17.

Acknowledgment. We are indebted to Mr. D. R. McAdams of these laboratories for mass spectroscopic analyses and to Dr. Earl S. Huyser for helpful suggestions concerning certain aspects of mechanism.

BATON ROUGE, LA.

[CONTRIBUTION NO. 2735 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY,
CALIFORNIA INSTITUTE OF TECHNOLOGY]

Small-Ring Compounds. XXXVII. Free Radical Decarbonylation of Some Cyclopropanecarboxaldehydes[1]

DAVID I. SCHUSTER[2] AND JOHN D. ROBERTS

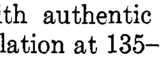
Received August 2, 1961

The di-*t*-butyl peroxide initiated decarbonylations of cyclopropanecarboxaldehyde and 1-methyl- and 1-phenylcyclopropanecarboxaldehyde have been studied. The first of these did not undergo decarbonylation to a measurable extent, while the substituted aldehydes reacted without ring opening to give methyl- and phenylcyclopropane, respectively.

Cyclopropyl radicals have been generated under a variety of conditions, and the extent of ring opening has been determined in each case. Only unrearranged cyclopropyl products were reported from photochemical chlorination[3] and vapor-phase nitration[4] of cyclopropane, brominative decarboxylation of silver cyclopropanecarboxylate,[5] and decomposition of biscyclopropanecarboxylic acid peroxide in carbon tetrachloride.[6] Exclusively open-chain products, structurally derived from the allyl radical, were formed in the Kolbe electrolysis of potassium cyclopropanecarboxylate[7] and the photolysis of methyl cyclopropyl ketone,[8] while mixtures of allyl and cyclopropyl chloride were obtained on thermal chlorination of cyclopropane.[3] Apparently, products in which the intermediate cyclopropyl radical has maintained its structural identity are obtained exclusively when the radical is generated at temperatures below 175–200° while at higher temperatures varying amounts of ring opening occur. The results of the photolysis of methyl cyclopropyl ketone[8] have been interpreted in terms of a concerted ring-opening reaction in which cyclopropyl radicals do not appear to be involved as intermediates.

It is relatively difficult to generate cyclopropyl radicals as compared with other hydrocarbon radicals.[9] For example, Trotman-Dickenson and Steacie[9a] report cyclopropane to be less reactive toward methyl radicals than a large number of other hydrocarbons studied. Only benzene was less reactive than cyclopropane.

As part of a study of a number of small-ring radicals as generated by the free radical decarbonylation of the corresponding aldehydes, we have studied the decarbonylation of the aldehydes I (R = H, CH_3, and C_6H_5) initiated by di-*t*-butyl peroxide. Because of the volatility of cyclopropanecarboxaldehyde and 1-methylcyclopropane carboxaldehyde under the usual decarbonylation conditions (130–140°), the reactions were carried out in diphenyl ether. The decarbonylation of 1-phenylcyclopropanecarboxaldehyde was run without solvent. The homogeneity and identity of the products were determined by means of vapor-phase chromatography, infrared spectroscopy, NMR, and by comparison with authentic samples. The extents of decarbonylation at 135–145°, calculated as a maximum value on the assumption that all the noncondensable gas evolved was carbon monoxide, were: 15% for cyclopropanecarboxaldehyde, 59% for 1-methylcyclopropanecarboxaldehyde and 97% for 1-phenylcyclopropanecarboxaldehyde. However, infrared analysis of the gas evolved with cyclo-



I

---

(1) Supported in part by the Petroleum Research Fund of the American Chemical Society and the National Science Foundation. Grateful acknowledgment is hereby made to the Donors of the Petroleum Research Fund.

(2) National Science Foundation Predoctoral Fellow, 1956–1960.

(3) J. D. Roberts and P. H. Dirstine, *J. Am. Chem. Soc.*, **67**, 1281 (1945).

(4) H. B. Hass and H. Shechter, *J. Am. Chem. Soc.*, **75**, 1382 (1953).

(5) J. D. Roberts and V. C. Chambers, *J. Am. Chem Soc.*, **73**, 3176 (1951).

(6) H. Hart and D. P. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959).

(7) F. Fichter and H. Reeb, *Helv. Chim. Acta*, **6**, 450 (1923). However, note that this reaction is suspect as a free radical process, see E. J. Corey and co-workers, *J. Am. Chem. Soc.*, **82**, 2645 (1960).

(8) J. N. Pitts, Jr., and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954).

(9) (a) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); (b) G. S. Hammond and R. W. Todd, *J. Am. Chem. Soc.*, **76**, 4081 (1954); (c) J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.*, **79**, 825 (1957).

propanecarboxaldehyde showed it to be methane containing only traces of carbon monoxide. The evolved gas with the other aldehydes proved to be carbon monoxide containing some methane.

The given extents of decarbonylation represent essentially complete reaction. Two- to threefold longer reaction times gave almost the same yields of decarbonylation products.

No cyclopropane or propylene could be detected from the attempted decarbonylation of cyclopropanecarboxaldehyde. The principal product was cyclopropanecarboxylic acid (about 50% yield). The methylcyclopropane was produced in yield of 30–40% in the decarbonylation of 1-methylcyclopropanecarboxaldehyde and appeared to be completely homogeneous as judged by vapor-phase chromatography. About 12–15% of 1-methylcyclopropanecarboxylic acid was formed. Phenylcyclopropane and 1-phenylcyclopropanecarboxylic acid were isolated from the decarbonylation of 1-phenylcyclopropanecarboxaldehyde in 55% and 9% yield, respectively. No α- or β-methylstyrene or allylbenzene was found in the reaction mixture.

One of the key reactions in the free radical chain reaction mechanism for decarbonylation of aldehydes is: $RCO\cdot \rightarrow R\cdot + CO$.[10] That cyclopropanecarboxaldehyde does not undergo decarbonylation to a measurable extent is apparently due to failure of the cyclopropanecarbonyl radical to lose carbon monoxide. Instead, an alternate reaction leading ultimately to cyclopropanecarboxylic acid occurs. Benzaldehyde behaves similarly in that the intermediate benzoyl radicals react exclusively by paths other than decarbonylation.[11] That the cyclopropanecarbonyl radical does not lose carbon monoxide easily is reasonable in view of the unusual strength of bonds to cyclopropane rings.[9]

The greater ease of decarbonylation of 1-methyl- and 1-phenyl-substituted cyclopropanecarboxaldehydes in the order $C_6H_5— > CH_3—$ reflects the expected enhanced stability of 1-methyl- and 1-phenylcyclopropyl radicals as compared with unsubstituted cyclopropyl radicals.

The lack of ring opening of cyclopropyl and substituted cyclopropyl radicals might appear surprising since ring opening would appear to be energetically favored by at least 30 kcal./mole, as estimated by the relief of steric strain on isomerization and the formation of an allyl radical with a resonance energy of approximately 25 kcal./mole. The barrier to isomerization thus must be quite large. There appears to be no such barrier for the cyclopropyl cation, which isomerizes to the allyl cation at low temperatures.[12]

EXPERIMENTAL[13]

Cyclopropanecarboxaldehyde was prepared in 45% yield by lithium aluminum hydride reduction of cyclopropyl cyanide by the method of Smith and Rogier[14]; b.p. 95–98°, n_D^{25} 1.4264 (reported[14] b.p. 97–101°). The product was at least 98% pure according to vapor-phase chromatography.

The 2,4-dinitrophenylhydrazone recrystallized from ethanol–ethyl acetate had m.p. 182.6–183.7° (lit.[14,15,16] m.p. 185.5–186.5°; 182–185°; 185.0–186.5°).

1-Phenylcyclopropanecarboxaldehyde was prepared by reduction of 1-phenylcyclopropanecarbonitrile[17] by the procedure for the preparation of cyclopropanecarboxaldehyde.[14] A filtered solution of 4.2 g. (0.11 mole) of lithium aluminum hydride in 250 ml. of dry ether was added dropwise over 1 hr. to a well stirred solution of 57.2 g. (0.4 mole) of 1-phenylcyclopropanecarbonitrile in 130 ml. of dry ether cooled in a Dry Ice–acetone bath. The mixture was then stirred for 8 hr. as the temperature of the bath was gradually raised to 5°. The mixture was cautiously hydrolyzed with 10% sulfuric acid. The layers were separated, and the aqueous acidic layer was extracted with ether. The ethereal solution was dried over magnesium sulfate. The ether was removed by distillation through a 30-cm. Vigreux column, and the residue was distilled through a 30-cm. wire-spiral packed column. The yield of 1-phenylcyclopropanecarboxaldehyde was 33.4 g. (57%), b.p. 65–71° (1 mm.), n_D^{25} 1.5400–1.5404. The infrared spectrum showed C—H bands at 2650 cm.$^{-1}$, 2740 cm.$^{-1}$, and 2800 cm.$^{-1}$ (aldehyde); 1707 cm.$^{-1}$ (carbonyl); 1600 cm.$^{-1}$, 1500 cm.$^{-1}$, and 690 cm.$^{-1}$ (phenyl); and 1025 cm.$^{-1}$ (cyclopropane).[18] The infrared spectra of some of the fractions had a band at 2250 cm.$^{-1}$ due to some unreacted 1-phenylcyclopropanecarbonitrile.

An analytical sample of 1-phenylcyclopropanecarboxaldehyde was prepared by dissolution in ethanol, followed by addition of saturated sodium bisulfite solution. Filtration (to remove inorganic salts, not the bisulfite addition product), then extraction of the filtrate with ether and decomposition of the bisulfite complex in the aqueous phase with base, followed by ether extraction and distillation, afforded aldehyde of b.p. 43.0–45.5° (0.5 mm.), n_D^{25} 1.5402.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.12; H, 7.11.

The *2,4-dinitrophenylhydrazone* had m.p. 190.4–191.8° after three recrystallizations from ethanol–ethyl acetate.

Anal. Calcd. for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.32. Found: C, 59.10; H, 4.45.

Considerable quantities of a high-boiling neutral compound were isolated in some of the preparations of aldehyde. In one run, a fraction, 9.6 g., b.p. 160–164° (1 mm.), was redistilled to give 6.3 g. of material having b.p. 164–166°

---

(10) C. Walling, *Free Radicals in Solution*, John Wiley & Sons, Inc., New York, 1957, p. 279.

(11) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

(12) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

(13) All melting points and boiling points are uncorrected. Elementary analyses were performed by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif., and by Midwest Microlab, Inc., Indianapolis, Ind. Most of the infrared absorption spectra were determined using a Perkin-Elmer Model 21 double-beam recording infrared spectrophotometer. Vapor chromatograms were obtained with a Perkin-Elmer vapor fractometer, Model 154-C. The NMR spectra were obtained at 60 Mc. with the Varian Associates high resolution spectrometer (V-4300B) with 12-inch magnet and equipped with a flux stabilizer.

(14) L. I. Smith and E. R. Rogier, *J. Am. Chem. Soc.*, **73**, 4047 (1951).

(15) R. Van Volkenburgh, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 3595 (1949).

(16) J. D. Roberts, *J. Am. Chem. Soc.*, **73**, 2959 (1951).

(17) F. H. Case, *J. Am. Chem. Soc.*, **56**, 715 (1934); E. C. Knowles and J. B. Cloke, *J. Am. Chem. Soc.*, **54**, 2028 (1932).

(18) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, John Wiley & Sons, Inc., New York, 2nd ed., 1958, pp. 29–30.

(0.5 mm.), n^{25}_{D} 1.5685. This formed a 2,4-dinitrophenylhydrazone of m.p. 189.0–190.6° after recrystallization from ethanol–ethyl acetate, which, on admixture with authentic 1-phenylcyclopropanecarboxaldehyde 2,4-dinitrophenylhydrazone, did not depress its melting point. The neutral compound showed no carbonyl band in the infrared but had a band of medium intensity at 1655 cm.$^{-1}$ that can be assigned to C=N. The NMR spectrum supports an imine structure: There was a one-proton resonance at slightly lower field than the phenyl resonance; a two-proton resonance in the region characteristic of methylene protons attached to nitrogen and four-proton resonances superimposed on a characteristically complex cyclopropane doublet. The compound was therefore assumed to be the *Schiff's base of 1-phenylcyclopropanecarboxaldehyde and (1-phenylcyclopropyl)carbinylamine.* The analytical sample had b.p. 125–130° (0.4 mm.), n^{25}_{D} 1.5682.

Anal. Calcd. for $C_{20}H_{21}N$: C, 87.23; H, 7.69. Found: C, 87.08; H, 7.81.

There was also obtained some *(1-phenylcyclopropyl)carbinylamine* when the acidic aqueous solution obtained from the reduction of 1-phenylcyclopropanecarbonitrile was made basic with sodium hydroxide solution. Ether extraction and distillation gave, in several fractions, 5.8 g. (9%) of (1-phenylcyclopropyl)carbinylamine, identified by its infrared spectrum, and having b.p. 103–108.5° (18.5 mm.), n^{25}_{D} 1.5385–1.5392.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.900. Found: C, 81.46; H, 8.90.

1-Methylcyclopropanecarboxaldehyde was prepared by reduction of 1-methylcyclopropanecarbonitrile[19] with lithium aluminum hydride by the procedure described for 1-phenylcyclopropanecarboxaldehyde. In a typical run, 20 g. (0.25 mole) of 1-methylcyclopropanecarbonitrile and a solution prepared from 2.8 g. (0.074 mole) of lithium aluminum hydride afforded 15.9 g. (76.8%) of 1-methylcyclopropanecarboxaldehyde, b.p. 90–108°, n^{25}_{D} 1.4245–1.4251. The main fraction had b.p. 106–108°, n^{25}_{D} 1.4251, and was indicated to be at least 98% pure by vapor-phase chromatography. The infrared spectrum of the aldehyde showed bands at 1710 cm.$^{-1}$ (carbonyl); 2700 cm.$^{-1}$ and 2800 cm.$^{-1}$ (aldehyde C=H), and 1020 cm.$^{-1}$ (cyclopropane).[18] The analytical sample, b.p. 103–104°, n^{25}_{D} 1.4259, was distilled through a 30-cm. wire-spiral packed column under nitrogen and sealed under nitrogen.

Anal. Calcd. for C_5H_8O: C, 71.39; H, 9.59. Found: C, 71.00, 70.91; H, 9.51, 9.40.

The *2,4-dinitrophenylhydrazone* had m.p. 222.1–222.8° after recrystallization from ethanol–ethyl acetate.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58. Found: C, 49.90; H, 4.80.

Attempted decarbonylation of cyclopropanecarboxaldehyde. The following run is typical: A solution of 4.1 g. (0.059 mole) of cyclopropanecarboxaldehyde in 37 ml. of redistilled diphenyl ether was prepared in a small three-necked flask equipped with a magnetic stirrer, a dropping funnel, a reflux condenser, and a nitrogen inlet. The condenser was connected in series to an air-cooled trap, a small Dry Ice-cooled trap, another air-cooled trap, and gas burette. The system was flushed with nitrogen for 5–10 min.; the reaction flask was then immersed in a magnetically stirred oil bath, maintained at 135–140°. After 1–2 min., the nitrogen flow was stopped and the contents of the flask allowed to come to equilibrium at the reaction temperature (about 10 min.). A total of 4.3 g. (0.029 mole) of redistilled di-*t*-butyl peroxide was added through the dropping funnel. The peroxide was added intermittently whenever the gas evolution appeared to subside. The total reaction time was 5 hr.

The evolved gas (190 ml.) was shown to be principally methane by comparison of its infrared spectrum with authentic material.[20] Only a trace of carbon monoxide was present, as shown by the low intensity of the peaks at 2110 and 2170 cm.$^{-1}$[21] No cyclopropane or volatile hydrocarbon other than methane was detected. Distillation of the residue in the reaction flask gave acetone, *t*-butyl alcohol and some recovered cyclopropanecarboxaldehyde and small amounts of other unidentified components. Higher boiling fractions were judged by vapor phase chromatography to consist of cyclopropanecarboxaldehyde, cyclopropanecarboxylic acid, and diphenyl ether, in addition to other minor components. The main product was cyclopropanecarboxylic acid (about 50% yield).

Decarbonylation of 1-methylcyclopropanecarboxaldehyde. The apparatus and procedure were as described above in the case of cyclopropanecarboxaldehyde. In a typical run, 3.8 g. of aldehyde, 3.3 g. of di-*t*-butyl peroxide in 40 ml. of diphenyl ether at 135–145°, gave, over 11 hr., 59% of the theoretical amount of carbon monoxide (contaminated with some methane). The contents of the Dry Ice-cooled trap were analyzed by vapor-phase chromatography, using diisodecyl phthalate or tetraisobutylene on fire brick and infrared spectroscopy.

The yield of methylcyclopropane (99.8% pure by vapor-phase chromatography, identified by comparison of its spectrum with authentic material from 1,3-dibromobutane with zinc dust) was 30–40%. The residue in the reaction flask when fractionally distilled gave acetone, *t*-butyl alcohol, 10–15% of recovered 1-methylcyclopropanecarboxaldehyde and 12–15% of 1-methylcyclopropanecarboxylic acid, identified by comparison of its infrared spectrum with that of authentic material as prepared by Cox and co-workers.[22]

The decarbonylation of 1-phenylcyclopropanecarboxaldehyde was carried out at 135–145° with 2.47 g. (0.017 mole) of freshly distilled aldehyde and with 1.5 g. (0.010 mole) of di-*t*-butyl peroxide in the absence of solvent. The procedure was as described above for cyclopropanecarboxaldehyde except no traps were used ahead of the gas burette. Gas evolution was rapid, and 420 ml. (96.5%) was collected over 1.5 hr. Distillation of the liquid products through a short column gave Fraction 1, b.p. 30–81° (35 mm.), 0.21 g.; Fraction 2, b.p. 80–83° (35 mm.), 0.71 g., n^{25}_{D} 1.5292; Fraction 3, b.p. 80–67° (40–14 mm.), 0.51 g.; and Fraction 4, b.p. 117–150° (1.5 mm.), 0.25 g. Fraction 2 consisted of 96% of phenylcyclopropane according to vapor-phase chromatography analysis. The identity of this substance, which was also present in Fraction 1 (10%) and Fraction 3 (90%), was confirmed by comparison of its infrared and NMR spectra with an authentic sample. The total yield of phenylcyclopropane was estimated to be 55%. No allylbenzene or propenylbenzene could be detected.

Fraction 4 solidified after distillation and the solid after recrystallization from hexane had m.p. 83–85°. The infrared spectrum was identical with that of authentic 1-phenylcyclopropanecarboxylic acid (lit.[17] m.p. 86–87°) prepared by the hydrolysis of 1-phenylcyclopropanecarbonitrile. The yield of acid was about 9%.

PASADENA, CALIF.

---

[19] D. Gotkis and J. B. Cloke, *J. Am. Chem. Soc.*, **56**, 2710 (1934).

[20] "Documentation of Molecular Spectroscopy," Butterworths Scientific Publications, London, 1958, Infrared Spectrum No. 1644.

[21] J. D. Roberts, D. R. Smith, and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 618 (1951).

[22] E. F. Cox, M. S. Silver, M. C. Caserio, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961).