

The Decarbonylation of Aliphatic and Bridgehead Aldehydes

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A series of aliphatic and bridgehead aldehydes were decarbonylated in carbon tetrachloride, which served as an inefficient trap for the intermediate acyl radicals. The products were determined quantitatively, and the trapping efficiencies deduced from the product ratios were found to correlate with the stabilities of the alkyl radicals generated from the aliphatic aldehydes. The assumption that the same correlation applies to the bridgehead aldehydes led to the conclusions that the 1-adamantyl and 1-bicyclo[2.2.2]octyl radicals are more stable than *t*-butyl, while 1-bicyclo[2.2.1]heptyl is less stable than *n*-propyl.

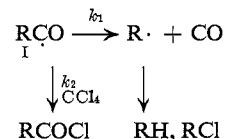
Introduction

One of the least ambiguous indications of the preferred geometries of simple alkyl cations has come from the experiments of Bartlett,¹ Doering,² Schleyer,³ and others⁴ on the solvolysis of bridgehead halides. The preferred planar geometry of the carbonium ion is a widely accepted conclusion from these experiments, which show that as the difficulty of achieving a planar configuration at the bridgehead increases, the solvolysis rate decreases, though the possibility of other complicating factors is also evident now.³

Until the present time, no comparable data have been collected on the generation of *free radicals* at bridgeheads to determine the effect of the same geometrical restrictions on these otherwise well-characterized intermediates, and the literature of organic chemistry in general provides only the most tenuous clues to the preferred geometry of the alkyl free radical.⁵ The usual observation is that the radical cannot maintain asymmetry at its trisubstituted carbon, and the conclusion which can be drawn is that the radical has either a planar configuration or a pyramidal one with rapid inversion. Direct physical measurements on the methyl radical have been more fruitful, especially the vacuum ultraviolet spectrum of the free radical, studied by Herzberg and Shoosmith.⁶ The deviation from planarity, if any, is less than 10°, according to these workers. Since the tetrahedral configuration would deviate 19.5°, the methyl radical may still be closer to tetrahedral than to planar. The possible relevance of the known carbon-13 hyperfine interaction constant to the ground-state geometry has been considered, but seems now to be in doubt.⁷ It might be supposed that all other alkyl

radicals would tend to be planar or near-planar also, but confirmation of this hypothesis and some measure of the effect of deviation from planarity on the energy of the radical are desirable research objectives.

The present work steps toward these objectives by a study of the ease of loss of carbon monoxide from bridgehead acyl radicals in ring systems having different degrees of restriction of bridgehead planarity. Ideally, the rate constants for loss of carbon monoxide from the acyl radical I would be desirable. Since such constants are not easily measured, the competition between loss of carbon monoxide (k_1) and the capture of acyl radical by carbon tetrachloride (k_2), a process whose rate is hopefully much less sensitive to the structure of I than is k_1 , was chosen as a means to obtain the relative values of k_1 .



Prior to the present study, it had been demonstrated that bridgehead free radicals can be generated in even the bicyclo[2.2.1]heptane system by decarbonylation of aldehydes,⁸ by the Hunsdiecker reaction,⁹ by the Kolbe oxidation,¹⁰ by the diacyl peroxide thermolysis,¹¹ and by the decomposition of a tertiary hypochlorite.¹² Qualitative indications of the instability of the 1-bicyclo[2.2.1]heptyl free radical can be inferred from the formation of some chlorides in the Hunsdiecker reaction in carbon tetrachloride,⁹ from the product ratio in the thermal decomposition of 1-norbornyldimethylcarbinyl hypochlorite,¹² and from the failure of chlorine atoms to abstract bridgehead hydrogens from norbornane.¹³ On the other hand, the bridgehead hydrogens of bicyclo[2.2.2]octane¹⁴ and adamantane¹⁵ show more typical tertiary behavior with respect to abstraction by free radicals.

Experimental¹⁶

Materials. *t*-Butyl peroxide, K and K 95–99% grade was distilled under nitrogen on a 5-ft., spiral-wire

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(6) (a) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956); (b) G. Herzberg, *Proc. Chem. Soc.*, 116 (1959); (c) G. Herzberg, *Proc. Roy. Soc. (London)*, **A262**, 291 (1961).

column and collected at 38.0° (55 mm.) (lit.¹⁷ b.p. 37° at 48 mm.). The product had n_D^{25} 1.3860 (lit.¹⁸ $n_D^{25.6}$ 1.3864). Carbon tetrachloride, Fisher reagent grade, was distilled from phosphorus pentoxide on a 5-ft., spiral-wire column and collected at 76.0° (747 mm.). The product had n_D^{25} 1.4568 (lit.^{19,20} n_D^{20} 1.46041 and 1.4610, respectively). *o*-Dichlorobenzene, Matheson Coleman and Bell reagent grade, was distilled on a 5-ft., spiral-wire column and collected at 95.4–96.2° (52–53 mm.). The product had n_D^{25} 1.5487 (lit.¹⁷ n_D^{20} 1.5506). Benzyl alcohol, Baker reagent grade, was distilled on a 5-ft., spiral-wire column and collected at 104° (5 mm.). *p*-Chlorotoluene, Eastman reagent grade, was distilled on a 5-ft., spiral-wire column and collected at 75° (26 mm.). *n*-Butyraldehyde, Eastman reagent grade, was distilled on a 1-ft., spiral-wire column and collected at 73.3–73.8°. *n*-Butyryl chloride, Eastman reagent grade, was distilled on a 6-in. Vigreux column and collected at 99.5°. Isobutyraldehyde, Matheson Coleman and Bell reagent grade, was distilled on a 1-ft., spiral-wire column and collected at 63.3°. Isobutyryl chloride, Matheson Coleman and Bell practical grade, was distilled on a 1-ft., spiral-wire column and collected at 91.0°. Trimethylacetaldehyde (pivaldehyde), K and K 95–99% grade, was distilled on a 1-ft., spiral-wire column and collected at 69–71°. Isopropyl chloride, Matheson Coleman and Bell reagent grade, was distilled on a 1-ft., spiral-wire column and collected at 34.0–34.1°. Pivaloyl chloride, Aldrich reagent grade, was distilled on a 1-ft., spiral-wire column and collected at 101.5–103.5°. *t*-Butyl chloride, Eastman reagent grade, was distilled on a 1-ft., spiral-wire column and collected at 49.5–50.0°. 2-Ethylhexanal, Matheson Coleman and Bell practical grade, was distilled on a 1-ft., spiral-wire column and collected at 160–161°. *n*-Heptanal, Matheson Coleman and Bell reagent grade, was distilled on a 1-ft., spiral-wire column, b.p. 150.6–151.6°. 1-Adamantanecarboxylic acid, m.p. 172–3.5°, was prepared by a literature method²¹ (lit.²¹ m.p. 181°). Bicyclo[2.2.2]octane-1-carboxylic acid, m.p. 138.5–140.8°, was prepared by essentially the procedure of Grob, Ohta, Renk, and Weiss²² (lit.²² m.p. 140.5–142°). 1-Norbornanecarboxylic acid, m.p. 108.5–111.5°, was prepared by the method of Boehme²³ (lit.²³ m.p. 111–112°).

Most of the hydrocarbon and alkyl chloride products from the decarbonylations were known compounds, prepared, when not commercially available, by the literature procedures. They include the following: bicyclo[2.2.2]octane, m.p. 164.3–167.6° (lit.²⁴ m.p. 168–171°), infrared spectrum identical with that of an

spectra were determined with Perkin-Elmer Models 21, 237, and 521 spectrophotometers. Nuclear magnetic resonance (n.m.r.) spectra were determined with a Varian 60-Mc. high-resolution spectrometer (Model A-60). Chemical shifts are expressed as τ , p.p.m., relative to tetramethylsilane (taken as $\tau = 10$). Microanalyses were performed at the University of Illinois microanalytical laboratory by Mr. Josef Nemeth and his associates. The n.m.r. spectra and some of the infrared spectra were determined by Mr. Dick Johnson and his associates.

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authentic sample²⁵; 1-chloronorbornane,²⁶ b.p. 76.7° (48.5 mm.) (lit.²⁶ b.p. 70–72° at 54 mm.), infrared spectrum identical with that of an authentic sample²⁷; and 1-chloroadamantane, m.p. 163–164° (lit.²⁸ m.p. 165°).

Benzyl Pivalate. To 10.1 g. (0.099 mole) of pivalic acid (Eastman reagent grade) was added 34 ml. (0.47 mole) of thionyl chloride over a period of 5 min. The solution was refluxed for 1.5 hr. and then allowed to cool to room temperature. Excess thionyl chloride was removed on a water aspirator. Benzyl alcohol (30 ml., 0.29 mole, Merck reagent grade) was added over a period of 20 min. and the resulting solution was refluxed for 10.5 hr. Distillation yielded a product, b.p. 60.5° (1.0 mm.).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.67; H, 8.34.

Benzyl α,α -Dimethylbutyrate. By the same method used for benzyl pivalate, except that both steps were carried out at room temperature, was prepared the ester with b.p. 135–137° (5 mm.).

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.70; H, 8.91.

α,α -Dimethylbutyraldehyde Semicarbazone. To 10 ml. of α,α -dimethylbutyric acid (Aldrich reagent grade) was added 12 ml. (0.16 mole) of thionyl chloride. The solution was allowed to stand at room temperature for 24.7 hr. Excess thionyl chloride was removed by distillation through a 6-in. Vigreux column. Three small portions of benzene were added to the pot during the distillation. Distillation of the residue yielded 6.5 g. (0.048 mole) of acid chloride, b.p. 123.5° (lit.²⁹ b.p. 132°). To 6.5 g. (0.048 mole) of α,α -dimethylbutyryl chloride and 30 ml. of diglyme (Ansul Chemical Co.) which had just been distilled under vacuum from lithium aluminum hydride (Metal Hydrides), a solution of 12.2 g. (0.048 mole) of lithium tri-*t*-butoxyaluminumhydride (Metal Hydrides) in 50 ml. of freshly dried diglyme was added dropwise over a period of 1.7 hr. while the reaction mixture was kept in a Dry Ice–isopropyl alcohol bath. The mixture was allowed to warm to room temperature for 1.7 hr. and then poured into crushed ice contained in a separatory funnel.³⁰ When the ice had melted, the solution was saturated with sodium chloride and shaken with 12 ml. of anhydrous ether. The thick mass which resulted was filtered with suction while the receiving flask was kept in a Dry Ice–isopropyl alcohol bath. The precipitate was washed well with ether and the aqueous phase was extracted with three 30-ml. portions of ether. The combined ether phases were dried with magnesium sulfate and distilled. A total of 5.8 g. was collected at 61.5–73°, and was shown by vapor phase chromatography to contain *t*-butyl alcohol and two other substances. The material was allowed to react with semicarbazide hydrochloride and sodium acetate in water to precipitate a total of 0.27 g. (4.1%) of semicarbazone, m.p. 153.0–153.3° (lit.³¹ m.p. 153–155°).

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Anal. Calcd. for $C_7H_{15}N_3O$: C, 53.48; H, 9.62; N, 26.73. Found: C, 53.28; H, 9.49; N, 26.30, 26.28 (semicarbazones often give low nitrogen analyses³²).

Carbon Tetrachloride Solution of α,α -Dimethylbutyraldehyde. The semicarbazone of α,α -dimethylbutyraldehyde (0.12 g., 0.00076 mole) and 15 ml. of 5 *N* hydrochloric acid were refluxed gently for 3.8 hr. The solution was cooled to room temperature and extracted with two 0.5-ml. portions of carbon tetrachloride. The combined pale yellow carbon tetrachloride extracts were allowed to stand over magnesium sulfate overnight at 6°. The infrared spectrum of the now colorless solution showed the presence of an aldehyde and an acid (characteristic absorption in the 3500–3000-cm.⁻¹ region and bands at 1680 and 1715 cm.⁻¹). The solution was washed with 2 ml. of 10% potassium hydroxide and 1 ml. of water and then dried with magnesium sulfate. Its infrared spectrum was consistent with the presence of aldehyde (1715 cm.⁻¹) plus some silicone grease (1000–1300 cm.⁻¹).

1-Adamantanecarbonyl Chloride. 1-Adamantanecarboxylic acid (1.5 g., 0.0084 mole) and 3 ml. (0.041 mole) of thionyl chloride were refluxed under nitrogen for 4 hr. in a 10-ml. flask equipped with reflux condenser and drying tube. The excess thionyl chloride was distilled off, the residue cooled to room temperature, and the last traces of thionyl chloride removed with a vacuum pump. The residue, m.p. 41–50.3°, was recrystallized from 1.8 ml. of sodium-dry pentane to yield 1.10 g. (67%) of product, m.p. 48.5–52.0°.

Anal. Calcd. for $C_{11}H_{15}ClO$: C, 66.49; H, 7.61. Found: C, 66.34; H, 7.66.

1-Carboethoxyadamantane. The acid chloride prepared as above from 1.5 g. (0.0083 mole) of 1-adamantanecarboxylic acid was dissolved in a 3.5% solution of ethanol in ether. The resulting brown suspension was filtered and distilled to yield ester, b.p. 89° (9.55 mm.) (lit.²⁸ b.p. 122–123° at 9 mm.). The n.m.r. spectrum showed only the expected ethyl multiplets at τ 6.0 and 8.8, and an unresolved multiplet at 7.9 to 8.4 for the adamantane hydrogens. The infrared spectrum showed a strong carbonyl band at 1730 cm.⁻¹ and no sign of other multiple bonds or OH functions. A v.p.c. analysis on silicone rubber revealed only trace impurities.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 73.01, 72.49; H, 9.53, 9.43.

1-Adamantanecarboxaldehyde. The acid chloride from 6.0 g. (0.033 mole) of 1-adamantanecarboxylic acid was reduced with the theoretical amount of lithium tri-*t*-butoxyaluminumhydride as described above for α,α -dimethylbutyraldehyde. The solution was poured onto 460 g. of crushed ice and, after the ice melted, was filtered with suction. The filtrate gave a very weak 2,4-dinitrophenylhydrazine test. The precipitate, after being washed with water, was triturated with four 100-ml. portions of ether. The combined ether phases were washed with 75 ml. of 10% sodium carbonate and 75 ml. of water and dried with magnesium sulfate. Evaporation of the ether yielded a yellow liquid which, after standing at 6° for 10.9 hr., yielded a wet solid. The

solid was slurried with 30 ml. of water and the mixture was filtered with suction to yield 1.28 g. (24%) of product, m.p. 189–198°. Three recrystallizations from acetonitrile raised the melting point to 195–197.3°, though the substance later showed erratic melting behavior for reasons not investigated. The infrared spectrum showed a strong peak at 1720 cm.⁻¹.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.40; H, 10.09.

A 2,4-dinitrophenylhydrazone, recrystallized twice from 95% ethanol-ethyl acetate and twice from acetonitrile, had m.p. 218.1° (lit.³³ m.p. 225°).

1-Norbornanecarboxaldehyde 2,4-Dinitrophenylhydrazone. The reaction mixture from reduction of 0.9 g. (0.0064 mole) of 1-norbornanecarboxylic acid by the method described above for α,α -dimethylbutyraldehyde was poured onto 230 ml. of a freshly prepared saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. The mixture was allowed to stand at room temperature for 24 hr. and filtered with suction, and the precipitate was washed with 2 *N* hydrochloric acid and water and dried in an oven at 92° to yield 0.735 g. (38%) of the 2,4-dinitrophenylhydrazone, m.p. 179–183.5°. Recrystallization from 61 ml. of acetonitrile yielded 0.413 g., m.p. 190.0–191.0°.

Anal. Calcd. for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30; N, 18.39. Found: C, 55.41; H, 5.31; N, 18.26.

Carbon Tetrachloride Solution of 1-Norbornanecarboxaldehyde. The 2,4-dinitrophenylhydrazone of 1-norbornanecarboxaldehyde (0.352 g., 0.00116 mole) was added to a 90 vol. % solution of levulinic acid (Eastman reagent grade) in water. The solution had previously been saturated with 6 ml. of carbon tetrachloride and washed with six 1-ml. portions of carbon tetrachloride. The mixture was heated at 100° under nitrogen for 10.3 hr., then allowed to cool to room temperature and extracted with ten 2-ml. portions of carbon tetrachloride. The combined carbon tetrachloride extracts were washed with two 15-ml. portions of 10% sodium carbonate and 15 ml. of water and dried with magnesium sulfate to yield a solution which was stirred at room temperature for 3.8 hr. and at about 70° for 2.8 hr. with some activated charcoal (Darco grade S-51). The mixture was filtered and the filtrate was evaporated down to a volume of about 1.5 ml. The resulting mixture was filtered at –13° to give 24 mg. of the 2,4-dinitrophenylhydrazone and a solution whose infrared spectrum showed a carbonyl band at 1715 cm.⁻¹, and whose n.m.r. spectrum was clear in the aromatic region but showed a formyl hydrogen at τ –0.05. This solution was used directly in the decarbonylations.

1-Carbomethoxynorbornane. To a mixture of 1.5 ml. of 40% potassium hydroxide and 5 ml. of ether which was swirled in an ice bath was slowly added 0.5 g. (0.005 mole) of *N*-nitroso-*N*-methylurea. The yellow ether phase was poured into a solution of 0.20 g. (0.0014 mole) of 1-norbornanecarboxylic acid in 5 ml. of ether until the solution remained yellow. Ether and excess diazomethane were evaporated off to yield an undetermined amount of product whose infrared spectrum showed a single carbonyl band at 1733 cm.⁻¹. This material was used for v.p.c. calibration without further characterization (see below).

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*1-Norbornanecarboxyl Chloride.*³⁴ 1-Norbornanecarboxylic acid (1.0 g., 0.0070 mole) and 2.5 ml. (0.034 mole) of thionyl chloride were refluxed under nitrogen for 2.2 hr. The solution was allowed to cool to room temperature and excess thionyl chloride was removed at 45° (150 mm.) to leave analytically pure acid chloride whose infrared spectrum showed a single carbonyl peak at 1780 cm.⁻¹.

Anal. Calcd. for C₈H₁₁ClO: C, 60.57; H, 6.99. Found: C, 60.23; H, 6.81.

1-Carbomethoxybicyclo[2.2.2]octane was prepared from 24 mg. of the acid in 79% yield by the method described above for 1-carbomethoxynorbornane. The infrared spectrum showed one carbonyl group, at about 1720 cm.⁻¹.

Bicyclo[2.2.2]octane-1-carboxaldehyde 2,4-dinitrophenylhydrazone, m.p. 222.2–222.7°, was prepared in 39% yield by essentially the method described above for the 2,4-dinitrophenylhydrazone of 1-norbornanecarboxaldehyde.

Anal. Calcd. for C₁₅H₁₆N₄O₄: C, 56.60; H, 5.70. Found: C, 56.47; H, 5.99.

Carbon Tetrachloride Solution of Bicyclo[2.2.2]octane-1-carboxaldehyde. The 2,4-dinitrophenylhydrazone of bicyclo[2.2.2]octane-1-carboxaldehyde (0.30 g., 0.00094 mole) was heated in a 50-ml. flask under nitrogen at 100° for 12.5 hr. with 31 ml. of a 90 vol. % solution of levulinic acid (Eastman reagent grade) in water. The levulinic acid solution had previously been saturated with 4.5 ml. of carbon tetrachloride and washed with five 1-ml. portions of carbon tetrachloride. The solution was allowed to cool to room temperature and extracted with eight 2-ml. portions of carbon tetrachloride. The combined carbon tetrachloride extracts were washed with two 10-ml. portions of 10% sodium carbonate and 12 ml. of water, dried with magnesium sulfate, and evaporated at about 35° (150 mm.) to a volume of about 1.5 ml. The mixture was filtered at –14° to yield a filtrate whose infrared spectrum showed a single carbonyl peak at 1715 cm.⁻¹, and whose n.m.r. spectrum showed no aromatic hydrogens and a formyl hydrogen singlet at τ 0.2. The solution was used directly in the decarbonylations (below).

*(1-Norbornyl)methanol.*²⁶ A mixture of 0.7 g. (0.02 mole) of lithium aluminum hydride and 15 ml. of ether was stirred until a fine suspension was obtained. A solution of 0.5 g. (0.0035 mole) of 1-norbornanecarboxylic acid in 15 ml. of ether was added dropwise over a period of 23 min. The mixture was stirred at room temperature for 3.5 hr. Water (4 ml.) was added and the mixture was poured into 20 ml. of 10% sulfuric acid. The phases were separated and the aqueous phase was extracted with two 5-ml. portions of ether. The combined ether phases were washed with 10 ml. of water, 10 ml. of 2 N sodium bicarbonate, and 10 ml. of water, and dried with magnesium sulfate. After evaporation of the ether, the pale yellow oily residue was sublimed at 80° (15 mm.) to yield 0.4 g. (90%) of product, m.p. 63.0–63.4° (lit.²⁶ m.p. 59.0–60.2°).

(34) This material has been prepared previously, but no analyses or spectra have been reported: D. B. Denney and R. R. DiLeone, *J. Am. Chem. Soc.*, 84, 4737 (1962); J. W. Wilt and C. A. Schneider, *Chem. Ind. (London)*, 865 (1963); W. R. Boehme, *J. Am. Chem. Soc.*, 81, 2762 (1959).

*1-Chlorobicyclo[2.2.2]octane.*³⁵ (1-Norbornyl)methanol (0.168 g., 0.00133 mole), 2 ml. of concentrated hydrochloric acid, and 1.3 g. of zinc chloride in a 10-ml. flask equipped with reflux condenser and magnetic stirrer were stirred at 83° for 4.6 hr. Vigorous gas evolution occurred immediately and the originally clear solution became turbid after 5 min. A white solid, which did not melt at bath temperature, began to sublime up to the top of the flask after 10 min. The mixture was allowed to cool and 2 ml. of water and 4 ml. of pentane were added. The aqueous phase was extracted with two 2-ml. portions of pentane. The combined pentane phases were washed with seven 2-ml. portions of water, five 2-ml. portions of concentrated sulfuric acid, 2 ml. of water, and 2 ml. of saturated sodium chloride solution, and dried with magnesium sulfate. After evaporation of the pentane, the white solid residue was sublimed at 80° and atmospheric pressure to yield 66 mg. (34%) of product, m.p. 99–100° (sealed capillary) (lit.³⁶ m.p. 100–101°), whose infrared spectrum was identical with that of an authentic sample.³⁷

Purity of Materials. Vapor phase chromatographic analysis of the compounds prepared and purchased has been mentioned only when there otherwise might have been some serious doubt regarding the purity of the material, e.g., when the elemental analysis did not check satisfactorily. However, all materials used as v.p.c. standards were at least 99% pure as judged by v.p.c. Starting materials were sufficiently pure, by the same criterion, that no impurity could have formed more than a 1% contaminant in any of the significant products.

Vapor Phase Chromatographic Analysis. The vapor phase chromatographic (v.p.c.) analyses were performed on an F and M Model 300 instrument with helium as the carrier gas. The separations were carried out by use of an 8-ft. column of silicone rubber on Chromosorb P. The operating parameters were as follows unless otherwise indicated: block temperature, 210°; injection port temperature, 175°. Peak area integrations were made by use of a disk chart integrator. Unless otherwise noted, each product was identified by comparison of retention time and infrared spectrum of collected material with those of an authentic sample. Relative response data and work-up procedure corrections were determined together by preparation of solutions of known composition and determination of the relative responses per mole. The relative amounts of the components approximated those occurring in the reaction mixtures.

General Procedure for Decarbonylation Experiments. Reactants were placed under a nitrogen atmosphere in a thick-walled Pyrex tube which was then sealed. The reactants occupied about half the volume of the tube. The tube was then placed in an oil bath at the desired temperature. The reaction time corresponded to at least 6 half-lives for *t*-butyl peroxide.³⁸ All experiments utilized Pyrex baths which contained approximately 8 gal. of oil (Cities Service, D. C. 915), a Lightnin

(35) According to a procedure used in the preparation of the corresponding bromide: W. P. Whelan, Jr., Ph.D. Thesis, Columbia University, 1952.

(36) A. A.-R. Sayigh, Ph.D. Thesis, Columbia University, 1952.

(37) Spectrum kindly supplied by Professor L. M. Stock, University of Chicago.

(38) (a) C. Walling and G. Metzger, *J. Am. Chem. Soc.*, 81, 5365 (1959); (b) L. Batt and S. W. Benson, *J. Chem. Phys.*, 36, 895 (1962).

Model L continuous-duty stirrer, a hydrogen-jacketed microthermoregulator, and a 500- to 750-w. continuous heat source which was connected to a Variac. Fine heating was controlled by means of a 100-w. light bulb attached through a zero-current relay to the thermoregulator. The entire bath assembly was packed in Vermiculite and had an aluminum foil covered lid to minimize radiation and convection heat losses near the surface of the oil. Temperatures were checked with calibrated thermometers. After the tube was removed from the bath and had cooled to room temperature, it was cooled to the freezing point of the contents (about -20°) and shaken well while still liquid in order to assure equilibration of the gases formed in the reaction with the solution at the lowest possible temperature. The tube was then frozen in liquid nitrogen, opened, and allowed to thaw, and the contents were transferred at the melting point to a second tube containing appropriate reagents (usually an internal standard for the v.p.c. analysis and an alcohol). This tube was sealed and allowed to stand at room temperature for at least 1 day, and the contents were analyzed by v.p.c. One day was an adequate length of time since samples allowed to stand longer yielded the same results in each system.

A typical run in the decarbonylation of isobutyraldehyde at 135° will be described in detail. All other decarbonylations were closely similar. Carbon tetrachloride (6.6218 g., 0.0431 mole), 0.1642 g. (0.002275 mole) of isobutyraldehyde, and 0.0934 g. (0.000639 mole) of *t*-butyl peroxide were reacted for 21.5 hr. The reaction mixture was then added to 1.3729 g. (0.01272 mole) of benzyl alcohol and 0.6226 g. (0.00492 mole) of *p*-chlorotoluene. A 50-ml. sample was analyzed under the following operating conditions [column temperature, carrier gas flowrate (ml./min.), and length of time (min.)]: room temperature, 19, 18; 35° , 38, 14; 50° , 38, 12; 75° , 38, 24; 95° , 38, 24; 100° , 38, 12; 135° , 38, 58; and 210° , 38, 44. The following major products were observed [retention time (min.) given]: isopropyl chloride (8), *t*-butyl chloride (11), chloroform (19), carbon tetrachloride (29), *p*-chlorotoluene (85), benzyl chloride (96), hexachloroethane (about 108), benzyl alcohol (about 120), benzyl isobutyrate (148), and benzyl ether (185).

Unreacted isobutyraldehyde, which has the same retention time as chloroform, was shown to be present by examination of the infrared and n.m.r. spectra of the collected chloroform peak. Propane, 1,2-dichloropropane, and 2,2-dichloropropane were shown to be absent by the absence of peaks at the retention times of authentic samples.

The measured amounts of materials in the reaction mixture were 1.032 mmoles of isopropyl chloride, 0.852 mmole of isobutyryl chloride, and 0.852 mmole of *t*-butyl chloride. These data, which correspond to $k_1/k_2 = 1.101$, averaged with those of ten similar runs, are included in Table I.³⁹ The activity of carbon tetrachloride was taken arbitrarily to be the mean of the

initial mole fraction (0.936 in the run above) and the final mole fraction (0.873 in the run above). The ratio of constants was then given by $k_1/k_2 = [\text{isopropyl chloride}]/[\text{isobutyryl chloride}]$. The mole fraction of carbon tetrachloride at the end of the reaction was obtained by subtraction of the mole fractions of all product

Table I. Decarbonylation Results

Aldehyde	Temp., $^{\circ}\text{C}$.	k_1/k_2	No. of runs
<i>n</i> -Butyraldehyde	135.0	0.137 ± 0.039^a	8
Isobutyraldehyde	135.0	1.14 ± 0.18^a	11
Pivaldehyde	135.0	12.3 ± 3.2^a	12
1-Adamantanecarboxaldehyde	95.3	23.9 ± 7.5^b	1
	121.0	28.5 ± 6.3^a	5
	135.0 ^c	30.5	
1-Norbornanecarboxaldehyde	135.0	0.0831 ± 0.0041^b	1
Bicyclo[2.2.2]octane-1-carboxaldehyde	135.0	15.2 ± 0.5^b	1

^a Average deviation from the average of all runs. ^b Standard deviation based upon repeated analysis of the product from a single run. ^c Extrapolated.

alkyl and acyl monochlorides from the mole fraction of carbon tetrachloride at the start of the reaction. It is possible that neglect of some products, e.g., hexachloroethane, which serve to dilute the carbon tetrachloride, could introduce an error into this estimate. However, the amount of hexachloroethane formed, estimated from its approximate v.p.c. peak area, is such that it could introduce about a 4% error in the difference between initial and final carbon tetrachloride mole fractions. Although the mole fraction of *t*-butyl chloride, formed in all reactions in which *t*-butyl peroxide was used as initiator, does not appear in the expression for k_1/k_2 , its value is necessary for the calculation of the mole fraction of carbon tetrachloride. In those cases (1-adamantanecarboxaldehyde, 1-norbornanecarboxaldehyde, and bicyclo[2.2.2]octane-1-carboxaldehyde) in which it was not possible to determine quantitatively the mole fraction of *t*-butyl chloride, *t*-butyl chloride was assumed to have been formed in 150% yield from the peroxide. In those cases (1-norbornanecarboxaldehyde and bicyclo[2.2.2]octane-1-carboxaldehyde) in which the absolute amount of each product was not determined, the mole fraction of carbon tetrachloride was taken as that formed in the 1-adamantanecarboxaldehyde runs. It should be emphasized that these approximations necessary to the calculation of the mole fraction of carbon tetrachloride can introduce only second-order errors in the relative rate constants.

To demonstrate that the products are stable to the reaction conditions, a solution of 5.8773 g. (0.0382 mole) of carbon tetrachloride, 0.2966 g. (0.00412 mole) of isobutyraldehyde, and 0.0868 g. (0.000595 mole) of *t*-butyl peroxide was reacted in the usual manner. The resulting solution was divided into two approximately equal portions. One portion was reacted with 1.1184 g. (0.01034 mole) of benzyl alcohol and 0.5669 g. (0.004475 mole) of *p*-chlorotoluene for 1 day. The analysis of this solution showed 1.703 mmoles of isopropyl chloride and 1.109 mmoles of isobutyryl chloride. The second portion was added to a solution containing 2.9638 g.

(39) A possible mode of formation of *t*-butyl chloride could involve a free-radical reduction of *t*-butyl alcohol to *t*-butyl radicals by isobutyraldehyde, the latter being oxidized to isobutyric acid. Since the resulting acid would have caused an erroneous analysis for isobutyryl chloride under the conditions used, controls were run to show that large increases in the amounts of peroxide initiator increased the *t*-butyl chloride without corresponding increases in benzyl isobutyrate.⁴⁰

(40) L. Kaplan, Ph.D. Thesis, University of Illinois, 1964.

(0.01924 mole) of carbon tetrachloride, 0.2369 g. (0.001849 mole) of 2-ethylhexanal, and 0.0735 g. (0.000503 mole) of *t*-butyl peroxide, and the resulting solution was allowed to react in the usual manner. The products were then allowed to react with 2.3720 g. (0.0219 mole) of benzyl alcohol and 0.5948 g. (0.00470 mole) of *p*-chlorotoluene for 2 days. The analysis of this solution showed 1.645 mmoles of isopropyl chloride and 1.107 mmoles of isobutyryl chloride.

The decarbonylation mixtures of the other aldehydes were processed in very much the same manner, using benzyl alcohol for *n*-butyraldehyde and pivaldehyde, methanol for the bicyclo[2.2.1]heptane- and bicyclo[2.2.2]octanecarboxaldehydes, and ethanol for the adamantanecarboxaldehyde. Product stability controls of the above-described type were run for the *n*-butyraldehyde products in the presence of decarbonylating *n*-heptanal, pivaldehyde products in the presence of decarbonylating α,α -dimethylbutyraldehyde, and adamantanecarboxaldehyde products in the presence of decarbonylating pivaldehyde. Details are recorded elsewhere.⁴⁰

Results

The values of k_1/k_2 derived from the decarbonylations are summarized in Table I. The sensitivity of the k_1/k_2 values to stability of the alkyl radicals generated by decarbonylation can be inferred by comparison of the data for the open-chain aldehydes in Table I with the known R-H dissociation energies. Recent literature values for the dissociation energy of propane to *n*-propyl and hydrogen atom, $D(n\text{-C}_3\text{H}_7\text{-H})$, are 97,⁴¹ 97.0,⁴² and 96.2 kcal.⁴³ Values for the isopropyl radical, $D((\text{CH}_3)_2\text{CH-H})$, are 94.5,⁴⁴ 93,⁴¹ and, perhaps best, 94.5 kcal.⁴⁵ Values for the *t*-butyl radical, $D((\text{CH}_3)_3\text{C-H})$, are 90.9⁴⁶ and 91.4 kcal.⁴⁴ If the variations in k_1/k_2 are due to changes in the activation energy part of k_1 , if differences in $D(\text{R-H})$ are proportional to differences in $D(\text{RCO})$, and if an Evans-Polanyi⁴⁷ relationship applies (*i.e.*, differences in activation energy are proportional to differences in bond dissociation energy), then we might expect a plot of $\log k_1/k_2$ vs. $D(\text{R-H})$ to be linear. Within the experimental errors indicated by the spread of values of $D(\text{R-H})$ cited above, such linearity is indeed observed. If one chooses 97, 94.5, and 91.2 kcal. as the best values of $D(\text{R-H})$ for *n*-propyl, isopropyl, and *t*-butyl, respectively, then the k_1/k_2 values given in Table I are fit best by the line $D(\text{R-H}) = -1.291 \ln(k_1/k_2) + 94.51$, the average deviation being 0.10 kcal. This line may be used to obtain extrapolated $D(\text{R-H})$ values for the bridgehead positions, and these are shown in Table II. In view of the various errors in the literature values of $D(\text{R-H})$ and in this work, no significance can be attached to the final digit in these extrapolated values, and they should be taken only as indicating that the 1-adamantyl radical is about 1 kcal. more stable than *t*-butyl, the 1-bicyclo[2.2.2]octyl radical is about like *t*-

(41) W. M. Jackson and J. R. McNesby, *J. Am. Chem. Soc.*, **83**, 4891 (1961).

(42) W. E. Falconer, B. S. Rabinovitch, and R. J. Cvetanović, *J. Chem. Phys.*, **39**, 40 (1963).

(43) G. L. Esteban, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3873 (1963).




(44) G. C. Fettes and A. F. Trotman-Dickenson, *ibid.*, 3037 (1961).

(45) P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964).

(46) H. Teranishi and S. W. Benson, *ibid.*, **85**, 2887 (1963).

(47) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938).

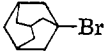
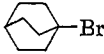
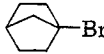
Table II. Extrapolated R-H Dissociation Energies, 25°

	k_1/k_2 (135°)	$D(\text{R-H})$, kcal./ mole
	0.0831	97.7
	15.2	91.0
	30.5	90.1

butyl (though the relative rates seem to show a real difference between these two), and the 1-norbornyl radical is about 1 kcal. less stable than *n*-propyl.

Discussion

Perhaps the most interesting aspect of the data presented above is the comparison of them with similar data for the corresponding carbonium ions, recently summarized by Schleyer.^{3,48} The approximate relative rates of solvolysis of the bromides at 25° in 80% ethanol are as shown below, the figure for 1-norbornyl being based upon an estimated ΔH^* (32 kcal.) and rate data from a much higher temperature (216°).

	$(\text{CH}_3)_3\text{CBr}$			
k_{rel}	1	10^{-3}	10^{-6}	10^{-14}
$\Delta\Delta H^*$	(0)	1.1	4.9	(10.5)

It is striking that all of the bridgehead cations are substantially destabilized with respect to *t*-butyl cation, whereas the two larger bridgehead radicals are more stable than or comparable with *t*-butyl radical. It is generally accepted that the bridgehead solvolyses are slow because of the strain introduced as the cationic carbon tries to approach its preferred planar geometry, and in fact it has been found³ that the standard Westheimer bending constant can be used for all disturbed angles to predict the rate depression of adamantyl almost exactly. If the free radical also has a preferred planar geometry, as the physical evidence reviewed earlier suggests, then it is clear that the force constants for bending away from the planar position must be much smaller than those pertaining to carbonium ions. In fact, we must account for some extra *stabilization* in at least the case of the adamantyl radical. The data obtained here provide no support for preferred planar geometry of alkyl free radicals, but they likewise do not suggest that the geometry is preferentially pyramidal. The possibility of a low bending force constant has also been suggested on the basis of theoretical studies.⁴⁹

Perhaps the extra stabilization of the adamantyl radical relative to *t*-butyl is just inductive, or perhaps there is special delocalization of the type which has been used to account for the unusual chemical shifts in the carbonium ion n.m.r. spectrum⁴⁸ and the fine structure in the e.s.r. spectrum of the adamantane radical anion.⁵⁰

(48) R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(49) (a) A. D. Walsh, *J. Chem. Soc.*, 2296 (1953); (b) J. W. Linnert and A. J. Poe, *Trans. Faraday Soc.*, **47**, 1033 (1951).

(50) K. W. Bowers, G. J. Nolfi, Jr., and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 3707 (1963).

If the out-of-plane bending force constant is indeed especially small in free radicals, as above suggested, then the effect does not seem to persist with larger distortions, as found in the 1-norbornyl radical. The latter is about 6.7 kcal. less stable than the 1-bicyclo[2.2.2]octyl radical (Table II), whereas in the carbonium ion series, an energy difference of just 5.6 kcal. (in $\Delta\Delta H^*$ of solvolysis) has been proposed³ and seems reasonable, although the data on the 1-norbornyl system here are too scanty to make much of the comparison. The present data are certainly enough, however, to make the point that whereas the data on the 1-bicyclo[2.2.2]octyl radical show no steric destabilization, the data on the 1-norbornyl radical show major destabilization.

A curious contrast with the results given by this work is presented by some recent findings of Baker, Holtz, and Stock,⁵¹ who reported that the 1-bicyclo[2.2.2]octyl radical, as generated by the Cristol-Firth modification of the Hunsdiecker reaction, abstracts chlorine from either carbon tetrachloride or bromotrichloromethane in competition with elemental bromine. Such behavior is unexpected for a radical as stable as *t*-butyl. No explanation will be offered here.

A possible source of difficulty in the interpretation of the decarbonylation results described above is that the rate constant k_2 may be neither invariant nor smoothly variant with k_1 . The result would be a failure of the linear correlation of $\ln(k_1/k_2)$ with $D(R-H)$, and the values of $D(R-H)$ in Table II would then be worthless.

(51) F. W. Baker, H. D. Holtz, and L. M. Stock, *J. Org. Chem.*, **28**, 514 (1963).

This possibility cannot be ruled out rigorously, but against it can be raised the following arguments. (1) If steric effects in any of the systems considered here are to affect k_2 materially, then the effect should be evident in the three aliphatic model compounds, which should therefore not give the linear correlation observed. (A steric effect would presumably lower k_2 for pivaloyl as much as it would for any of the bridgehead cases.) (2) A fairly good model reaction, $RCHO + CH_3 \rightarrow RCO + CH_4$, is known to go at almost exactly the same rate at 135° for acetaldehyde, propionaldehyde, *n*-butyraldehyde, isobutyraldehyde, pivaldehyde, and others.⁵² If either steric or electronic effects were going to cause variations in k_2 , then it might have been expected that the same effects would appear in the reaction of aldehydes with methyl. (3) The activation energies for abstraction of tertiary hydrogen by methyl from isobutane, 2,3-dimethylbutane, and 2,3,4-trimethylpentane are 7.6, 7.8, and 7.9 kcal., respectively,⁵³ indicating again a very small effect of β -substituents on an incipient free radical. (4) It is known that the acidities of acyl cations are rather insensitive to α -alkyl substituents,⁵⁴ so that even a polar contribution to the transition state for reaction of acyl radical with carbon tetrachloride cannot be expected to produce significant variation in k_2 .

(52) R. N. Birrell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 2059 (1960).

(53) (a) A. F. Trotman-Dickenson, J. R. Birchard, and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951); (b) H. O. Pritchard and G. O. Pritchard, *Can. J. Chem.*, **41**, 3042 (1963).

(54) N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964).

Heptaphenylcycloheptatrienyl Anion¹

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Reduction of heptaphenyltropylium bromide with potassium produces potassium heptaphenylcycloheptatrienide, an anion for which a possible triplet ground state is predicted. However, various magnetic studies show that the species is a singlet. The anion reacts with the original tropylium ion to produce heptaphenylcycloheptatrienyl radical, while reduction of the anion with potassium leads to fragmentation to stilbene and pentaphenylcyclopentadienyl anion.

Introduction

The possibility that certain derivatives of cyclic $4n$ π -electron systems could have triplet ground states is one of the most intriguing predictions made by simple m.o. theory.² This is based on the degeneracy of the highest occupied molecular orbitals, which are

(1) This work was supported in part by the National Science Foundation and the Sloan Foundation. For a preliminary communication of some of these results, see R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 1484 (1962).

(2) Cf. A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, especially Chapter 10.

half-filled, together with the usual³ electronic advantage of triplet states in such situations. A number of stable organic and inorganic triplets are known.⁴ However, the prediction² that the cyclobutadiene molecule, for instance, might be more stable with only one double bond and two unpaired electrons is relatively unusual; only in species such as O₂ and S₂ were cases known in which the structural principle⁵ of maximum bonding was violated, and special explanations⁶ had been offered here. Accordingly, it was of considerable interest to explore the possibility of triplet ground states for symmetrical $4n$ π -electron systems.

The first⁷ examples of such systems, heptaphenyl-

(3) C. Coulson, "Valence," 2nd Ed., Oxford University Press, London, 1961, p. 36.

(4) See for instance, E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 2304 (1964), and references therein.

(5) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 21.

(6) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 351 ff.

(7) Cyclooctatetraene would be such a system if it were planar.