phthalate column) to give 99% IV containing 0.4% III and 0.6% of an unknown low boiling material which was easily removed by fractionation at reduced pressure through a semi-micro Vigreux column. Infrared, carbon-hydrogen and n.m.r. analyses were obtained on the material thus obtained.

Anal. Calcd. for $C_5H_8Cl_2$: C, 43.19; H, 5.80. Found: C, 43.39; H, 5.86.

Preparation of Trichloroacetyl Peroxide.—Trichloroacetyl peroxide was prepared in low yield by the method of Zimmerman[22] and used without recrystallization.

Liquid-phase Chlorination of Spiropentane. Reaction E, No Initiator.—To a small ampule with a constriction at the top to facilitate sealing was added 0.41 g. (0.00603 mole) of spiropentane of 99.4% purity. The resulting liquid was cooled to Dry Ice temperature, and 29.6 ml. (0.0014 mole) of gaseous chlorine was then slowly added by means of a gas buret through a capillary tube extending below the surface of the liquid. The addition of chlorine was made in total darkness. After addition was complete, the ampule was quickly sealed with an oxygen torch and allowed to stand at room temperature in total darkness for 24 hr. At the end of this time, the ampule was broken and the reaction mixture poured into a saturated solution of sodium bisulfite at 0°. After remaining in contact with the bisulfite solution for 10 min. to destroy all unreacted chlorine, the mixture was removed from the dark and the organic layer separated, dried and distilled. The mixture was analyzed by vapor chromatography at 156° (didecyl phthalate column), employing Eastman's correction for molecular weights.[20] The molecular weights of unknown compounds, which were present in small amounts in all three liquid phase reactions, were estimated by their retention times with relation to known compounds. Major products were identified by comparison of retention times with those of known samples of I, II and III. An infrared spectrum of the reaction mixture was identical with that of a known sample of spiropentane except for a weak absorption at 1265 cm.$^{-1}$ which may be attributed to the presence of III.

Reaction F, Initiation by Peroxide.—The same apparatus and procedure was used as was discussed for the uninitated case. The spiropentane used was of 97.5% purity and amounted to 0.88 g. (0.0129 mole). The impurities were all present in less than 0.4%, except 1,1-dimethylcyclopropane which was present in a concentration of 1.2% (determined by vapor chromatography).[1] After the ampule containing spiropentane had been cooled to Dry Ice temperature, approximately 10 mg. of trichloroacetyl peroxide was added. The peroxide could not be weighed due to its rapid, and sometimes violent decomposition at or near room temperature. Chlorine (62 ml., 0.0025 mole) was then added, as before, in total darkness. After sealing, the ampule was completely submerged in a beaker of water at room temperature and allowed to stand in total darkness for 4 hr. Any excess chlorine was again decomposed with bisulfite and the organic layer separated, dried and distilled. The reaction mixture was analyzed by vapor chromatography in a manner identical to that described for the reaction E, retention times being compared with those of known samples of I, II, III, IV and V. After removal of excess spiropentane, a crude distillation of the reaction mixture yielded three fractions. The infrared spectrum of fraction 1 clearly showed the presence of II. Similarly, infrared analysis of fraction 2 indicated a mixture of III and IV. Compound V was further identified by comparison of the vapor chromatographic retention time of this component in fraction 3 with a known sample at 190° (silicone oil column).

Reaction G, Initiation by Light.—The same apparatus and general procedure was used as was employed in the two previous liquid phase chlorinations. Chlorine (57.7 ml., 0.0023 mole) was added to 0.795 g. (0.0117 mole) of spiropentane of the same purity as that used for the peroxide-initiated reaction. The addition of chlorine and the sealing of the ampule were, as before, carried out in darkness. After submerging the sealed ampule in a beaker of water at room temperature, the contents of the beaker were irradiated with a 275 w. sunlamp for 1.5 hr. starting at a distance of 12 ft. and moving to 6 ft. at the end of 45 min. Since no noticeable reaction occurred with the lamp at these distances, the reaction mixture was irradiated at 3 ft. for a total of 3.5 hr. After 1 hr. at this distance, the reaction mixture was almost colorless. At the end of the 5 hr. reaction time, the colorless reaction mixture was treated with bisulfite, separated, dried and distilled as before. Analysis and identification of products by comparison of vapor chromatographic retention times with authentic samples at 156° was carried out as in the two previous reactions. Since the concentration of spiropentyl chloride was too low to permit isolation by distillation, the presence of II was further proved by comparison of its rentention time with that of a known sample at 132° (didecyl phthalate column). Infrared analysis of the above reaction mixture, after removal of excess spiropentane, clearly showed the presence of III and suggested the presence of IV. Final identification of V in the above concentrated reaction mixture was accomplished by comparison of its retention time with that of an authentic sample at 190° (silicone oil column).

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra were measured in carbon tetrachloride solution with a Varian high resolution spectrometer (model V-4300B with super stabilizer) using methylene chloride as an external standard. The 40 mc. spectra were measured in carbon tetrachloride solutions at the following concentrations for the various substances: I, 296 mg./ml.; II, 370 mg./ml; III, 284 mg./ml.; IV, 260 mg./ml.; V, 212 mg./ml.; and VI, 260 mg./ml. The signal of the methylene chloride external standard was assumed to be at −0.65 p.p.m. from water. The 60 mc. spectrum of III was measured on the neat liquid, but the chemical shifts assigned in the discussion are those measured on the above 40 mc. spectrum in carbon tetrachloride. Where peaks were obscured by overlap at the lower frequency, it was assumed that relative shifts were the same in the two cases.

URBANA, ILL.

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[22] C. Zimmerman, U. S. Patent 2,580,373 (1951); *C. A.*, **46**, P 6668a (1952).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of the Hunsdiecker Reaction on a Cyclopropane Ring[1]

BY DOUGLAS E. APPLEQUIST AND ALAN H. PETERSON

RECEIVED SEPTEMBER 21, 1959

The brominative decarboxylation (Hunsdiecker reaction) of silver 2-methylcyclopropanecarboxylate in carbon tetrachloride at room temperature has been found to give the same mixture of *cis*- and *trans*-2-methylcyclopropyl bromides from either the *cis* or *trans* silver salt. It is concluded that the cyclopropyl free radical is either planar about the 1-position or inverts its configuration very rapidly, and is thus qualitatively like an unstrained alkyl free radical.

Although extensive physical[2] and chemical[3] data have revealed that ordinary free alkyl radicals are either planar in configuration about the trivalent carbon or subject to rapid inversion if they are non-planar, very little attention has been given to the effect of hybridization changes on the stereo-

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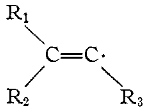
[1] Taken from the Ph.D. thesis of Alan H. Peterson, University of Illinois, 1960.

[2] (a) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956); (b) M. Karplus, *J. Chem. Phys.*, **30**, 15 (1959).

[3] (a) E. L. Eliel in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 140; (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 502.

chemistry of free radicals. Thus it is not yet known whether an alkenyl radical (I) is capable of maintaining its geometric configuration, nor do there



I

appear to be strong theoretical grounds for predicting whether or not it should be so capable.

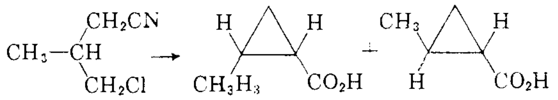
The question of the stereochemical behavior of the alkenyl radical is of particular importance in view of the now well known configurational stability of alkenyllithiums as compared with alkyllithiums,[4] a fact which is most easily interpreted in terms of a higher energy barrier to inversion of the alkenyl anion (where the unshared pair must change from an sp^2 orbital to a p orbital in the linear transition state) than for the alkyl anion (where the unshared pair climbs only from sp^3 to p in the trigonal transition state). Even assuming the correctness of this interpretation, it is not clear how it might be extrapolated to predict the behavior of I with certainty.

Skell and Allen[5] have found that hydrogen bromide adds stereospecifically *trans* to 1-propyne at −78 to −60° under illumination to give *cis*-1-bromo-1-propene. This result could be due to finite configurational stability of the intermediate alkenyl radical, or it could arise from a chain-carrying step in which a bromine atom reacts with an acetylene–hydrogen bromide complex. It was unfortunately not possible to repeat the experiment in the gas phase. Nesmeyanov and Borisov[6] have found that metal–metal replacements on vinylmetals brought about with mercury, tin–sodium alloy or stannous chloride proceed stereospecifically, and have classified these reactions as being "undoubtedly" homolytic. However, there appears to be no reason to believe that free alkenyl radicals are intermediates.

Hunsdiecker reactions of the stereoisomeric α-phenylcinnamates[7a] and cinnamates[7b] have been studied, but the experiments have not been such as to permit a conclusion about the stereochemistry of any intermediate radicals.

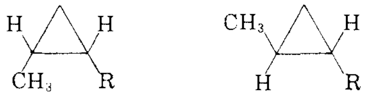
The approach of the present work was to employ the cyclopropane ring as a source of radicals with modified hybridization. There is voluminous evidence, summarized in part by Walsh,[8] that the C–H bonds in cyclopropane resemble sp^2 bonds in almost all respects more than they resemble sp^3 bonds. Furthermore, the Hunsdiecker reaction is known to occur satisfactorily with silver cyclopropanecarboxylate.[9] The Hunsdiecker reaction is one of the most reliable sources of free alkyl radicals, with a minimum of stereospecificity due to geminate recombination being observed.[10] Thus the reactions of optically active silver α-ethylcaproate,[11] α-methylbutyrate[12] or α-ethylvalerate[12] gave completely racemic bromides, and *cis*- and *trans*-4-*t*-butylcyclohexanecarboxylate gave essentially the same mixture of *cis*- and *trans*-4-*t*-butylcyclohexyl bromides.[13]

The acids chosen for investigation here were the *cis*- and *trans*-2-methylcyclopropanecarboxylic acids (IIa and IIIa). A mixture of IIa and IIIa was prepared by cyclization of β-methyl-γ-chlorobutyronitrile (IV) with powdered potassium hydroxide, followed by basic hydrolysis. Efforts to separate the acids by fractional distillation or gas chromatography met with no success, as did similar efforts



IV IIa IIIa

on the mixture of methyl esters. The acids were conveniently separated by means of their amides, IIb and IIIb. When the chloronitrile IV was cyclized under certain relatively mild conditions,



IIb, R = $CONH_2$
IIc, R = COCl
IId, R = CO_2Ag
IIe, R = Br

IIIb, R = $CONH_2$
IIIc, R = COCl
IIId, R = CO_2Ag
IIIe, R = Br

the amide of the minor isomer remained partially unhydrolyzed and was isolated in 13% yield. This amide was assigned the *cis* structure IIb on the grounds that it was the minor isomer and that it hydrolyzed more slowly than the other, presumably due to a steric effect of the *cis*-methyl group. The *trans*-amide IIIb was obtained by recrystallization of the ammonolysis product of the acid chloride prepared from the mixed acids IIa and IIIa. The acid chloride, prepared from the mixed acids and thionyl chloride in refluxing benzene, was apparently almost entirely (at least 95%) *trans* (IIIc), since hydrolysis of the chloride gave IIIa which contained no IIa detectable in the infrared spectrum. A similar phenomenon has been observed in the 2-phenylcyclopropanecarboxylic acid series.[14]

The *cis*- and *trans*-acids IIa and IIIa were obtained stereospecifically from the amides by hydrolysis with nitrous acid. The acids had distinctly different infrared spectra. The *cis* and *trans* silver salts IId and IIId were prepared from the acids in the usual way and again had distinctly different infrared spectra.

Hunsdiecker reactions were run in pentane or carbon tetrachloride by addition of the silver salts to bromine solutions, followed by brief refluxing to make certain that no acyl hypobromite remained

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[4] (a) D. Y. Curtin and J. W. Crump, THIS JOURNAL, **80**, 1922 (1958); (b) R. L. Letsinger, *ibid.*, **72**, 4842 (1950).

[5] P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958).

[6] A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

[7] (a) E. L. Sukman, Doctoral Dissertation, Rutgers University, 1958; *Dissertation Abstr.*, **19**, 1211 (1958); (b) J. D. Berman and C. C. Price, *J. Org. Chem.*, **23**, 102 (1958).

[8] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[9] J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 3176 (1951).

[10] C. V. Wilson in R. Adams, "Organic Reactions," Vol. 9, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 332.

[11] R. T. Arnold and P. Morgan, THIS JOURNAL, **70**, 4248 (1948).

[12] C. E. Berr, Ph.D. Thesis, University of California, Los Angeles, 1952; S. Winstein, *Bull. soc. chim. France*, [5] **18**, 70C (1951).

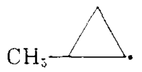
[13] E. L. Eliel and R. V. Acharya, *J. Org. Chem.*, **24**, 151 (1959).

[14] A. Burger and W. L. Yost, THIS JOURNAL, **70**, 2198 (1948).

unreacted. The reactions appeared to be fast and exothermic. The yields were approximately 50% in either solvent. The *cis* silver salt IId reacted with bromine in carbon tetrachloride to give the two bromides IIe and IIIe as a mixture with the composition 35.3 ± 0.8% IIe and 64.7 ± 0.8% IIIe, as determined by gas chromatography. The *trans* silver salt IIId gave 34.0 ± 0.8% IIe and 66.0 ± 0.8% IIIe, the same mixture within estimated experimental error. The configurations of the bromides were assigned entirely on the assumption that the predominant isomer should be *trans*.[15] The bromides IIe and IIIe were separated by gas chromatography of 0.1-ml. samples, and were characterized by their analyses, infrared spectra (which showed no unsaturation), and n.m.r. spectra. In the n.m.r., both isomers showed a low-field multiplet (2.05 to 2.36 p.p.m. from water in IIIe and 1.5 to 1.97 p.p.m. in IIe) due to the hydrogen α to bromine, a strong, sharp methyl signal (near 3.5 p.p.m.) and very high signals (near and above 4.0 p.p.m.) characteristic of cyclopropane methylenes.[16]

A control demonstrated that IIIe was not isomerized to a mixture of IIe and IIIe during a reaction of silver acetate with bromine in carbon tetrachloride under the same conditions as used in the above Hunsdiecker reactions.

It is concluded that the 2-methylcyclopropyl radical (V) is either planar about the 1-position,



V

or inverts its configuration very rapidly. The lifetime of V in the presence of bromine and unreacted acyl hypobromite must be exceedingly short,[17] so the energy barrier to inversion of configuration, if any, must be exceedingly small. If an alkyl radical is normally pyramidal and inverts through a planar transition state, then it would be expected that V would have a *larger* barrier at the planar configuration due to the extra I-strain in the rehybridized state.[18] The absence of an appreciable barrier in V is therefore confirmatory evidence that alkyl radicals are planar or very nearly so in their minimum-energy configurations. The problem of the stereochemistry of the alkenyl radical I is not settled by the present results, but one may at least say that it would be surprising if radical I can maintain its bent configuration for an appreciable time (relative to its lifetime).

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. We wish also to express our gratitude to the Research Corporation, which provided partial support in the early stages of the work; to Mr. J. Nemeth, Miss C. Higham, Mrs. M. Stingl, Mrs. F. Ju and Miss J. Liu for the microanalyses; to Mr. P. McMahon, Mr. J. Brader, Mr. B. Cloonan, and Mrs. J. Verkade for the infrared spectra; and to Mr. B. Shoulders for the n.m.r. spectra.

Experimental[19]

1-Bromo-3-chloro-2-methylpropane.—The method was suggested by Burgin, Hearne and Rust.[20] To 197.4 g. (2.18 moles) of redistilled methallyl chloride and 2.3 g. of benzoyl peroxide in a flask illuminated by a 200-watt tungsten lamp at a distance of 8 cm. was rapidly added anhydrous hydrogen bromide through a gas dispersion tube. The mixture was stirred and cooled in an ice-bath during the addition. After 1.5 hr., the reaction vessel had increased in weight by the theoretical amount, and the addition was stopped. The solution was stirred and irradiated for another hour, and was then washed successively with 100-ml. portions of water, sodium bicarbonate solution, and water. The mixture was then dried over magnesium sulfate and distilled through a 127-cm. spiral-wire (tantalum) column. The yield was 303.5 g. (81%), b.p. 79–80° (60 mm.), n^{25}_{D} 1.4794 (lit.[20] b.p. 49° (15 mm.), n^{20}_{D} 1.4816).

β-Methyl-γ-chlorobutyronitrile (IV).—The procedure was adapted from that of Allen.[21] 1-Bromo-3-chloro-2-methylpropane (171.5 g., 1 mole) was added rapidly to a refluxing solution of 82 g. (1.2 moles) of potassium cyanide in 100 ml. of water and 350 ml. of 95% ethanol, and the mixture was heated under reflux for 1.5 hr. The product was isolated by the literature method,[21] and was purified by fractional distillation to give 45.5 g. (66% yield, 39% conversion), b.p. 83.0–85.5° (15 mm.), n^{25}_{D} 1.4416 (lit.[22] b.p. 82–83° (16 mm.), n^{20}_{D} 1.44255), along with 71.4 g. of recovered dihalide. Somewhat higher conversions were obtained by doubling the reflux time.

2-Methylcyclopropanecarboxylic Acid (IIa and IIIa). Procedure I.—The literature procedure for cyclopropanecarboxylic acid[23] was adapted. A mixture of 128 g. of powdered potassium hydroxide (ground finely in a dry atmosphere) and 71.6 g. (0.61 mole) of β-methyl-γ-chlorobutyronitrile was stirred and heated on a steam-bath for 1.5 hr. The mixture was then diluted with 170 ml. of water, added in five portions over a 40-min. period, and heated for an additional 1.5 hr. The resulting solution was cooled in an ice-bath and acidified with concentrated sulfuric acid, which caused a second liquid phase to separate. The latter was taken up in ether and combined with an ether extract of the aqueous layer. The combined ether solution was dried over magnesium sulfate and fractionally distilled to give 39.8 g. (65%) of 2-methylcyclopropanecarboxylic acid, b.p. 97.5–99.0° (16 mm.), n^{25}_{D} 1.4372 (lit.[24] b.p. 190–191°). No separation of *cis* and *trans* isomers was obtained by distillation through a 127-cm. column packed with a tantalum spiral wire; nor was any separation observed by gas chromatography on columns of didecyl phthalate (139°), silicone oil (156°) or polyethylene glycol (180°).

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[15] The configurational assignments of the acids and bromides must both be considered tentative. Since the Hunsdiecker reactions were non-stereospecific, the conclusions of this research depend on no way upon the correctness of the assignments. Further confirmation of the assignments has been obtained by 100% stereospecific conversion of IIe to IIa, and of IIIe to IIIa, by halogen–metal interchange with isopropyllithium in 6% ether–94% pentane at 0°, followed by carbonation. These experiments will be reported in detail in the near future.

[16] D. E. Applequist and D. E. McGreer, THIS JOURNAL, **82**, 1965 (1960).

[17] Reference 3b, p. 370.

[18] Reference 3a, p. 121.

[19] Melting points are uncorrected. Infrared spectra were measured with a Perkin–Elmer model 21B spectrophotometer with sodium chloride optics. Gas chromatography was done with a Perkin–Elmer model 154B Vapor Fractometer, using helium as the carrier gas. The n.m.r. spectra were measured with a Varian high resolution spectrometer (model V-4300B with super stabilizer) using methylene chloride as an external standard. A frequency of 40 megacycles was used and shifts were recorded in parts per million (p.p.m.) from water, assuming methylene chloride to be −0.65 p.p.m. from water.

[20] J. Burgin, G. Hearne and F. Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

[21] C. F. H. Allen, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 156.

[22] J. B. Cloke, E. Stehr, T. R. Steadman and L. C. Westcott, THIS JOURNAL, **67**, 1587 (1945).

[23] C. M. McCloskey and G. H. Coleman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 221.

[24] R. Marburg, *Ann.*, **294**, 111 (1897).

Procedure II. *cis*-2-Methylcyclopropanecarboxamide (IIb).—Procedure I was modified primarily by the use of potassium hydroxide that had been coarsely ground in a humid atmosphere. A mixture of 130 g. of potassium hydroxide and 70.0 g. (0.60 mole) of β-methyl-γ-chlorobutyronitrile was stirred and heated (steam-bath) for 4 hr. A total of 230 ml. of water was added to the heated mixture in small quantities over 2 hr., and the mixture was then heated for an additional 40 min. Isolation as in procedure I gave 33.9 g. (57%) of 2-methylcyclopropanecarboxylic acid, b.p. 93–101° (14 mm.), $n^{25}\text{D}$ 1.4377.

The distillation residue (10.4 g.) was recrystallized from methylene chloride–pentane to give 7.4 g. (13%) of colorless crystals of the *cis*-amide, m.p. 128.0–128.5°. The melting point was not changed by further recrystallization. The infrared spectrum of the amide showed carbonyl absorption at 1667 cm.$^{-1}$, amide II band at 1588 cm.$^{-1}$, and other strong bands at 1442, 1421, 1065, 882 and 857 cm.$^{-1}$.

Anal. Calcd. for C_5H_9ON: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.37; H, 9.41; N, 14.32.

2-Methylcyclopropanecarbonyl Chloride (IIIc).—The procedure was adapted from one by Burger and Yost.[14] A mixture of 6.41 g. (0.0641 mole) of 2-methylcyclopropanecarboxylic acid (shown by subsequent infrared analysis to be approximately 15% *cis*), 20 ml. of benzene and 9.0 g. (0.0756 mole) of thionyl chloride was heated under reflux for 6 hr. Distillation through a Holzman semi-micro column[25] gave 6.57 g. of acid chloride, b.p. 134–135° or 62–63° (58 mm.) (lit.[26] b.p. 39.5° (15 mm.)).

***trans*-2-Methylcyclopropanecarboxamide (IIIb).**—Into 18 ml. of cold concentrated aqueous ammonia was poured 6.57 g. (0.055 mole) of 2-methylcyclopropanecarbonyl chloride. The solution was evaporated to dryness, and the colorless solid residue was extracted with four 20-ml. portions of boiling methylene chloride. The methylene chloride extracts were combined and evaporated to dryness to leave a colorless solid, which was recrystallized four times from methylene chloride–pentane to give 2.31 g. (42%) of pure *trans*-amide, m.p. 111.3–112.0°.

Anal. Calcd. for C_5H_9ON: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.71; H, 8.93; N, 14.18.

A mixed melting point with the *cis* isomer (m.p. 128.0–128.5°) gave m.p. 97.0–98.6°. The infrared spectrum of the *trans*-amide showed a carbonyl absorption at 1660 cm.$^{-1}$, amide II band at 1592 cm.$^{-1}$, and other strong bands at 1452, 1426, 1388, 1357, 1097, 1073, 947 and 867 cm.$^{-1}$.

***cis*-2-Methylcyclopropanecarboxylic Acid (IIa).**—To a cold, swirled solution of 2.03 g. (0.0205 mole) of *cis*-2-methylcyclopropanecarboxamide (m.p. 128.0–128.5°) in 5.5 ml. of concentrated sulfuric acid was added slowly a solution of 6.9 g. (0.10 mole) of sodium nitrite in 28 ml. of water. The resulting blue solution was allowed to warm to room temperature and then heated, carefully at first, on a steam-bath for 15 minutes. The reaction mixture was cooled and the floating layer of *cis*-acid was diluted with 15 ml. of ether and separated. The aqueous layer was extracted four times with 15-ml. portions of ether. The combined ether solution was dried over magnesium sulfate and distilled (Holzman column) to give 1.68 g. (82%) of *cis*-2-methylcyclopropanecarboxylic acid, b.p. 91.0–91.5° (14 mm.), $n^{25}\text{D}$ 1.4389. The infrared spectrum (carbon disulfide) showed carbonyl absorption at 1685 cm.$^{-1}$ and a broad OH and C–H band with maxima at 2940, 2690 and 2565 cm.$^{-1}$. Other prominent absorptions occurred at 1426, 1393, 1346, 1294, 1225, 1174, 1115, 1100, 1068 and 887 cm.$^{-1}$.

Anal. Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 59.62; H, 8.29.

***trans*-2-Methylcyclopropanecarboxylic Acid (IIIa). A. From the Amide.**—The same procedure as used above for the *cis* isomer was employed. From 1.91 g. (0.0193 mole) of *trans*-2-methylcyclopropanecarboxamide, 5.0 ml. of concentrated sulfuric acid and 6.5 g. (0.094 mole) of sodium nitrite in 25 ml. of water was obtained 1.79 g. (93%) of *trans*-2-methylcyclopropanecarboxylic acid, b.p. 96.0–97.0° (16 mm.), $n^{25}\text{D}$ 1.4348. The infrared spectrum (carbon disulfide) showed carbonyl absorption at 1685 cm.$^{-1}$, a broad band with maxima at 2920 and 2640 cm.$^{-1}$, and prominent bands at 1425, 1373, 1320, 1228, 1205, 1073, 1040, 1012 and 866 cm.$^{-1}$.

Anal. Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 60.11; H, 7.84.

B. From the Acid Chloride.—Into 10 ml. of ice-water was poured 3.78 g. (0.032 mole) of 2-methylcyclopropanecarbonyl chloride prepared from the isomeric mixture of acids as described above. The mixture was allowed to stand at room temperature for 4 hr., after which 10 ml. of ether was added. The two-phase liquid was allowed to stand for 20 hr., and then the layers were separated and the aqueous layer extracted three times with ether. The combined ether solution was dried over magnesium sulfate and distilled (Holzman column) to give 2.84 g. (89%) of *trans*-2-methylcyclopropanecarboxylic acid, b.p. 90–91° (11 mm.), $n^{25}\text{D}$ 1.4369. The infrared spectrum (smear) was identical to that of the *trans*-acid as prepared by method A.

Quantitative Infrared Analysis of Mixtures of *cis*- and *trans*-2-Methylcyclopropanecarboxylic Acids.—The base line method of Heigl[27] was employed. The peaks used were the 1174 cm.$^{-1}$ band for the *cis* isomer and the 1320 cm.$^{-1}$ band for the *trans* isomer. The base line was drawn between the minima at 1575 and 1135 cm.$^{-1}$. All spectra were determined on 10% solutions in carbon disulfide, and obedience to the Beer–Lambert law was assumed. The acid from procedure I was found to be about 10% *cis* and 90% *trans*, and that from procedure II was about 17% *cis* and 83% *trans*.

Silver 2-Methylcyclopropanecarboxylate.—A suspension of 20.39 g. (0.239 mole) of 2-methylcyclopropanecarboxylic acid (mixture of *cis* and *trans* isomers) in 250 ml. of water was neutralized (litmus) with 30% ammonium hydroxide. A solution of 34.70 g. (0.239 mole) of silver nitrate in 100 ml. of water was added dropwise to the stirred solution of ammonium salt. An additional 100 ml. of water was added, and the white precipitate was filtered, washed with water, and dried in a desiccator over calcium chloride. Finally, it was ground to a fine powder and dried over phosphorus pentoxide at 65° and 1 mm. for 48 hr., to leave 38.2 g. (90%) of colorless silver salt. The salt may be recrystallized from water, but no advantage for the subsequent reaction was found in so doing.

Silver *trans*-2-Methylcyclopropanecarboxylate (IIId).—The same procedure was used as for the mixture of *cis* and *trans* isomers. From 1.59 g. (0.0159 mole) of *trans*-acid (prepared by method A) was obtained 1.43 g. (44%) of silver salt. The infrared spectrum (Nujol) showed absorptions at 2920, 1504, 1433, 1382, 1359, 1278, 1080, 956 and 875 cm.$^{-1}$.

Silver *cis*-2-Methylcyclopropanecarboxylate (IId).—The same procedure was used as for the mixture of *cis* and *trans* isomers. From 1.00 g. (0.010 mole) of *cis*-acid was obtained 1.62 g. (78%) of silver salt. The infrared spectrum (Nujol) showed absorptions at 2915, 1500, 1436, 1312, 1174, 1117, 1093, 1070, 1039, 897, 865, 827 and 733 cm.$^{-1}$.

2-Methylcyclopropyl Bromide (IIe and IIIe).—Pentane solvent was shaken with sulfuric acid, washed with water, and distilled from sodium. Bromine was dried over phosphorus pentoxide. To a solution of 17.6 g. (0.11 mole) of bromine in 175 ml. of pentane was added 22.81 g. (0.11 mole) of silver 2-methylcyclopropanecarboxylate (mixed *cis* and *trans*) over a period of 1 hr., with careful exclusion of water. The exothermic reaction caused the solvent to reflux. The solution was colorless at the end of the addition, but was heated under reflux for an additional 30 min. The mixture was filtered, washed with sodium bicarbonate and then with water, and dried over magnesium sulfate. Distillation (Holzman column) gave 7.28 g. (49%) of mixed *cis*- and *trans*-bromides, b.p. 88–106°.

Separation of the isomers was achieved by gas chromatography on a didecyl phthalate column at 54° (86 ml. of helium per min. through a 200-cm. column, 5 mm. in diameter) of 0.1-ml. samples of the mixed dibromides. The retention times for *cis*- and *trans*-bromides were 24.2 and 18.3 min., respectively. Fractions were collected in Dry-Ice cooled traps.

The infrared spectrum (carbon tetrachloride) of the *trans*-bromide showed prominent absorptions at 2950, 1455, 1439, 1360, 1233, 1206, 1060 and 882 cm.$^{-1}$. The spectrum of the *cis* isomer showed bands at 2955, 1459, 1438, 1388, 1260, 1164, 1032 and 913 cm.$^{-1}$.

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(25) C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

(26) H. Wohlgemuth, *Ann. chim. (Paris)*, [9] **3**, 141 (1915).

(27) J. J. Heigl, M. F. Bell and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

The n.m.r. spectrum of the *trans* isomer (72 mg. per 0.25 ml. of carbon tetrachloride) showed the hydrogen alpha to bromine at 2.05 to 2.36 p.p.m. from water, the methyl at 3.56 p.p.m., and the remaining ring protons at 3.78 to 4.10 p.p.m. The n.m.r. spectrum of the *cis* isomer (33 mg. per 0.2 ml. of carbon tetrachloride) contained the same signals at 1.5 to 1.97 p.p.m., 3.5 p.p.m., and 3.62 to 4.39 p.p.m., respectively.

Anal. Calcd. for C_4H_7Br: C, 35.59; H, 5.22; Br, 59.20. Found for *trans* isomer: C, 35.45; H, 5.42. Found for *cis* isomer: C, 35.84; H, 5.50; Br, 58.74.

Hunsdiecker Reaction of Silver *trans*-2-Methylcyclopropanecarboxylate.—To a stirred solution of 1.105 g. (0.0069 mole) of bromine in 30 ml. of anhydrous carbon tetrachloride was added 1.43 g. (0.0069 mole) of silver *trans*-2-methylcyclopropanecarboxylate over a period of 30 min. The mixture was then stirred for an additional 2.5 hr., heated under reflux for 1 hr., and allowed to stand overnight. The silver bromide (1.29 g., 100%) was filtered out, and the filtrate was washed with 10% sodium bisulfite to remove unreacted bromine and with 10% sodium bicarbonate. The carbon tetrachloride solution was then dried over magnesium sulfate and distilled without fractionation. Analysis of the distillate by gas chromatography on didecyl phthalate at 53° (helium flow 92 ml./min.) and measurement of the relative areas of the *cis* (21.4 min.) and *trans* (15.9 min.) peaks showed the product to be 66.0 ± 0.8% *trans*- and 34.0 ± 0.8% *cis*-2-methylcyclopropyl bromide. The total yield was estimated to be 53%. The thermal conductivities of the two isomers were assumed to be equal.

As a control, a reaction of 0.200 g. (0.0012 mole) of silver acetate with 0.08 ml. of bromine in carbon tetrachloride which contained 0.0591 g. of *trans*-2-methylcyclopropyl bromide was run under the same conditions as described above. The silver bromide obtained amounted to 0.229 g. (102%), and the same analysis as used above revealed only *trans*-2-methylcyclopropyl bromide, with none of the *cis* isomer, in the product mixture.

Hunsdiecker Reaction of Silver *cis*-2-Methylcyclopropanecarboxylate.—The same procedure was used as with the *trans* isomer. From 1.62 g. (0.00782 mole) of silver *cis*-2-methylcyclopropanecarboxylate and 1.25 g. (0.00782 mole) of bromine in 25 ml. of carbon tetrachloride was obtained an estimated (from gas chromatography) 50% yield of 2-methylcyclopropyl bromide. The product consisted of 64.7 ± 0.8% *trans*- and 35.3 ± 0.8% *cis*-2-methylcyclopropyl bromide.

URBANA, ILL.

[CONTRIBUTION FROM THE McPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY COLUMBUS, OHIO]

The Synthesis of 1′,9-Dimethyl-1,2-benzanthracene

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The synthesis of pure 1′,9-dimethyl-1,2-benzanthracene (VIII) by the steps outlined in the chart is described. It is shown that a previous preparation of VIII consisted of a mixture of VIII and 1′-methyl-1,2-benzanthracene in unknown proportions.

The synthesis of 1′,9-dimethyl-1,2-benzanthracene has been reported previously.[3] Because of the small amount of hydrocarbon actually obtained[3] and because of our general interest in syntheses of such intramolecularly overcrowded[4] molecules we continued our efforts in this field. In particular, we thought that if we could obtain larger amounts of VIII and resolve it we might obtain a hydrocarbon which would be lesss easily racemized than 4,5,8-trimethyl-1-phenanthrylacetic acid[5] and 4-(1-methylbenzo[c]phenanthryl)-acetic acid[6] because of the buttressing effect of the fused benzene ring on the methyl group in the 9-position of VIII.

It was also deemed important to prepare enough 1′,9-dimethyl-1,2-benzanthracene (VIII) to provide workers in the field of carcinogenesis with ample material for various tests.[7] In this paper we report the successful synthesis of over 20 grams of pure 1′,9-dimethyl-1,2-benzanthracene.

When we first obtained supposedly pure VIII we had at hand over one gram which after many recrystallizations yielded colorless crystals which melted sharply at 139.1–139.5°. Because this melting point was higher than that reported (formation of an opalescent melt at 123° with clearing at 131.5–132.0°)[3] we obtained a sample from Dr. Cason.[8] For comparison with our compound we used X-ray powder photographs of the hydrocarbon and of its 2,4,7-trinitrofluorenone (TNF) complex.[8,9] The powder photographs of the hydrocarbons as well as of the TNF complexes showed that the substances were essentially identical.[10] At this point we believed that we had prepared the desired hydrocarbon in somewhat purer form than obtained previously.[3] We attributed the greater purity to the fact that we had prepared a larger quantity and hence could purify the material to a greater degree.[11]

Shortly thereafter, Dr. William Bailey reported to us that the sample of 1′,9-dimethyl-1,2-benzanthracene (supposedly) which we had sent to him was not a dimethyl but a monomethyl derivative.[12] By mixed melting point and X-ray powder photographic[10] means we then determined that our supposed 1′,9-dimethyl-1,2-benzanthracene, m.p. 139.1–139.5°, was actually 1′-methyl-1,2-benzan-

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[1] National Science Foundation Predoctoral Fellow, 1956–1958.

[2] National Science Foundation Postdoctoral Fellow, 1959–1960.

[3] J. Cason and D. D. Phillips, *J. Org. Chem.*, **17**, 298 (1952).

[4] F. Bell and D. H. Waring, *J. Chem. Soc.*, 2689 (1949), introduced the term "intramolecular overcrowding."

[5] M. S. Newman and A. S. Hussey, THIS JOURNAL, **62**, 2295 (1940).

[6] M. S. Newman and W. B. Wheatley, *ibid.*, **70**, 1913 (1948).

[7] In this connection VIII has long been of interest because of its similarity to 3,4-benzpyrene, one of the most potent carcingenic hydrocarbons; see L. F. Fieser and A. M. Seligman, THIS JOURNAL, **60**, 170 (1938).

[8] We wish to thank Dr. Cason for sending us the material which he and Dr. Phillips obtained.

[9] M. Orchin, L. Reggel and O. Woolfolk, THIS JOURNAL, **69**, 1227 (1947).

[10] We thank Dr. P. Harris of our department for supervising this part of our work and for the conclusions as to identity.

[11] This work formed the major part of the Ph.D. thesis of W. Sagar, the Ohio State University, 1958.

[12] Dr. Bailey, Shell Development Corp., Houston, Texas, had asked for samples of each of the twelve monomethyl-1,2-benzanthracenes for mass spectrographic studies. We sent a sample of our dimethyl compound along with the rest. Dr. Bailey also kindly determined the molecular weight of other hydrocarbons cited herein.