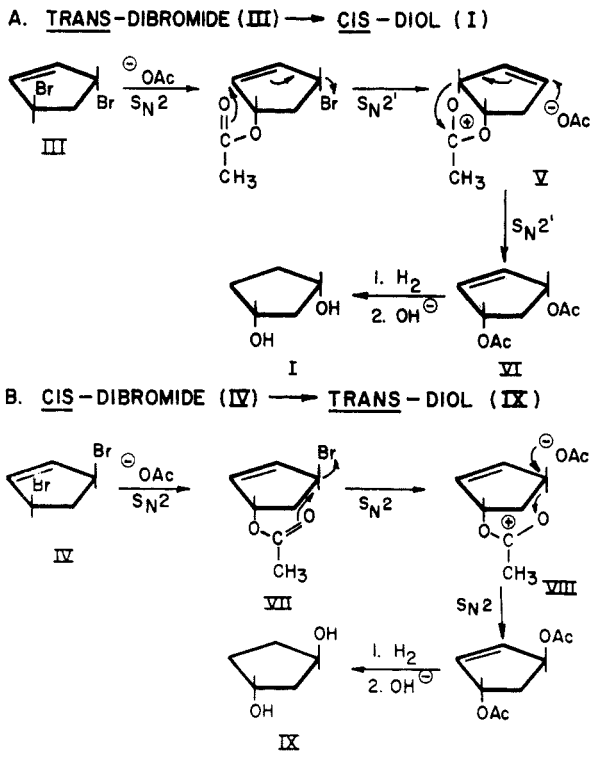


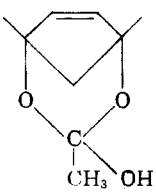
Figure 1

cyclopentanediol (I) and *cis*-3,5-dibromocyclopentene(IV) yields *trans*-1,3-cyclopentanediol (IX). A reasonable scheme by which these conversions could occur is shown in Fig. 1.

In the case of the *trans*-dibromide (III) the formation of V and VI by an internal S_N2' displacement leading to the observed final product (I) appears likely in view of the favorable *cis* relationship between the entering acetoxy group and the leaving halide ion.[8] However, for the *cis*-dibromide (IV) the orientation in (VII) is *trans*, making the acetoxonium ion (VIII) preferred.[9]

(8) G. Stork and W. N. White, *J. Am. Chem. Soc.*, **75**, 4119 (1953), have demonstrated the *cis* relationship of entering and departing groups in the S_N2' reaction in cyclic allylic systems.

(9) F. V. Brutcher, Jr., and F. J. Vara, *J. Am. Chem. Soc.*, **78**, 5695 (1956), reported the reaction of cyclopentadiene with lead tetraacetate in "wet" acetic acid followed by hydrogenation and saponification to give a 93:7 mixture of *cis*-1,2-cyclopentanediol and *cis*-1,3-cyclopentanediol (previously assigned the *trans*-structure on the basis of the argument presented in ref. (7) in a 75–80% yield. In this conversion the formation of the *cis*-1,3-glycol may arise from the interaction of the intermediate cation (VIII) (see Fig. 1) with water to give



which subsequently would yield the observed product.

EXPERIMENTAL[10]

cis-1,3-Cyclopentanediol. Diborane,[2] 0.36 mole, was passed into a solution of 50 ml. (39.6 g., 0.6 mole) of cyclopentadiene in 100 ml. of dry ether and 150 ml. of dry pentane. The addition required 2.5 hr. during which time a copious white precipitate of the organoborane separated. The solvent was removed under reduced pressure and the solid product treated with a solution of 16.0 g. (0.4 mole) of sodium hydroxide in 250 ml. of ethanol. The slurry was oxidized[2] with 150 ml. of 30% aqueous hydrogen peroxide. Most of the ethanol was removed under reduced pressure, the remaining solution was continuously extracted with ether for 48 hr., and the ether solution was dried over anhydrous magnesium sulfate. Distillation gave 25.0 g. (41%) of *cis*-1,3-cyclopentanediol, b.p. 86–87° at 0.5 mm., n_D^{25} 1.4832, which gave a negative periodic acid test for vicinal glycol.[11] A high resolution infrared spectrum (lithium fluoride prism) exhibited strong absorption at 3620 cm.$^{-1}$ and 3450 cm.$^{-1}$, due to free and bonded hydroxyl bands. The ratio of the two intensities of the two bands was independent of concentration.[4]

Anal. Calcd. for $C_5H_{10}O_2$ (102.13): C, 58.8; H, 9.9. Found: C, 58.4, 58.6; H, 9.8, 9.9.

Bis-p-nitrobenzoate, m.p. 186–187° (ethyl acetate).

Anal. Calcd. for $C_{19}H_{16}O_8N_2$ (400.34): C, 57.0; H, 4.0; N, 7.0. Found: C, 56.7, 56.4; H, 4.1, 4.0; N, 6.8, 6.8.

Bisphenylurethan, m.p. 172–173° (toluene).

Anal. Calcd. for $C_{19}H_{20}O_4N_2$ (340.37): C, 67.1; H, 5.9; N, 8.2. Found: C, 67.4, 67.0; H, 6.3, 6.0; N, 8.5, 8.4.

cis-Cyclopentyl-1,3-p-nitrobenzylidene acetal. To a solution of 1.51 g. (0.01 mole) of *p*-nitrobenzaldehyde in 50 ml. of dry xylene was added 1.00 g. (0.01 mole) of *cis*-1,3-cyclopentanediol and a catalytic amount of *p*-toluenesulfonic acid. The solution was distilled until the volume was reduced to 20 ml. and the remaining solvent removed *in vacuo*. The residue was dissolved in 75 ml. of ether and the ether solution passed through a 15 × 300 mm. column of alumina; elution was accomplished with 250 ml. of ether. Evaporation of the solvent gave 2.0 g. (80%) of white, crystalline acetal, m.p. 139.5–140.5° (hexane).

Anal. Calcd. for $C_{12}H_{13}NO_4$ (235.23): C, 61.2; H, 5.7; N, 6.0. Found: C, 61.3, 61.0; H, 6.1, 6.0; N, 6.0, 5.9.

Acknowledgment. The author is indebted to Prof. J. D. Roberts, California Institute of Technology, for his interest and helpful discussions in connection with this work.

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(10) Melting points are corrected and boiling points are uncorrected.

(11) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th Edition, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 129.

Formation of Cyclopropane Derivatives from 4-Bromocrotonic Esters[1]

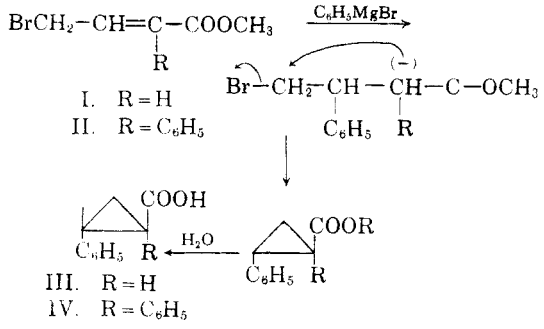
Ronald S. Ratney[2] and James English, Jr.

Received May 17, 1960

During the course of another investigation, we were led to examine the reaction of methyl 4-bromocrotonate with phenylmagnesium bromide by

inverse addition. It was hoped that a coupling could be effected with the formation of 4-phenylcrotonic ester. However, the only acidic product isolated from the hydrolyzed reaction mixture (in 13% yield) was found to be *trans*-2-phenylcyclopropane carboxylic acid (III). Its identity was proved from its analysis and properties[3] and by comparison with an authentic sample.[4]

The mechanism of the formation of this product probably involves the initial 1,4-addition of phenylmagnesium bromide to the methyl 4-bromocrotonate (I) followed by intramolecular displacement of the bromide:



The carboxyl group might reasonably be expected to take up the less hindered *trans* position as observed.

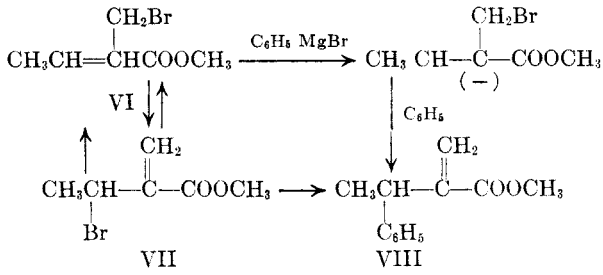
Methyl, isopropyl, cyclohexyl, and α-naphthyl Grignard reagents were treated with methyl 4-bromocrotonate and the results with all four were disappointing. In all cases, the yields of acidic products were very small and proved to be complex mixtures.

The substitution of isopropyl 4-bromocrotonate for the methyl ester in the reaction with the phenyl Grignard reagent gave the same acid III with no improvement in the yield.

When methyl 4-bromo-2-phenylcrotonate (II) was treated with phenylmagnesium bromide by inverse addition, a crystalline carboxylic acid (IV) was obtained in 0.6% yield. Its analysis corresponded to $C_{16}H_{14}O_2$. The melting point was different from those recorded for the known olefinic isomers; it did not decolorize potassium permanganate in acetone and the ultraviolet spectrum showed only a peak at 208 mμ and a shoulder at 220 mμ with no higher peaks which might be indicative of a phenyl group conjugated with a double bond. The substance is believed to be *cis*- or *trans*-1,2-diphenylcyclopropanecarboxylic acid (IV).

The preparation of methyl 4-bromotiglate has been described by Inhoffen, Bork, and Schweiter.[5] This preparation was repeated and the product treated with phenylmagnesium bromide as before. There was isolated a crystalline acid, m.p. 103–104°, showing an ultraviolet spectrum (λ_{max} 215 mμ) of an α,β-unsaturated acid. The phenyl group is apparently not conjugated with either the double bond or the carboxyl group since there is no absorption in the 250–270 mμ range (as in benzoic acid, styrene, and cinnamic acid). Hydrogenation gave a dihydro acid m.p. 132.5–134° believed to be the known 2-methyl-3-phenyl-butyric acid (m.p. 132°).[6]

On this evidence the acid m.p. 103–104° is assigned structure VIII.



This result may be rationalized by the assumption that the 4-bromotiglic ester of Inhoffen contains some 2-bromomethylcrotonic ester (VI) or its allylic isomer (VII), and the reaction is then either a displacement or an addition followed by elimination as shown.

EXPERIMENTAL[7]

trans-2-Phenylcyclopropanecarboxylic acid. A solution of 0.1 mole of phenylmagnesium bromide in about 100 ml. of ether was added to a stirred solution of methyl 4-bromocrotonate (17.9 g., 0.1 mole) in 100 ml. of ether. After the addition was complete, water was added to the solution and the mixture was acidified. The aqueous layer was extracted twice with ether and the combined ether layers were dried over magnesium sulfate. Evaporation of the ether gave 16.5 g. of yellow oil which was distilled at 4 mm. to give 4.1 g., b.p. 61.5–98° and 5.5 g., b.p. 99–106°. The infrared spectrum of the first fraction showed it to be unchanged methyl 4-bromocrotonate. The higher boiling fraction was saponified by refluxing with aqueous alcoholic sodium hydroxide. Biphenyl and other neutral materials were extracted with ether and then the basic solution was acidified. The acidic materials were isolated by ether extraction to give 2.7 g. of crude product. This was recrystallized from water to give 2.4 g. (13% yield) of *trans*-2-phenylcyclopropane carboxylic acid, m.p. 94–95.5°. It was sublimed in vacuum to give the analytical sample, m.p. 97–98.5° (undepressed on mixing with authentic material).[4] The ultraviolet spectrum showed a peak at 220 mμ (ε 10,060) and a shoulder at 204 mμ (ε 9078).

(1) Taken from a thesis submitted by Ronald S. Ratney to the Faculty of the Graduate School of Yale University in Candidacy for the Degree of Doctor of Philosophy. This work was supported by a grant from the American Cancer Society.

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(3) Alfred Burger and William L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).

(4) Kindly supplied by Professor Alfred Burger, University of Virginia.

(5) H. H. Inhoffen, S. Bork, and V. Schweiter, *Ann.*, **580**, 16 (1953).

(6) P. A. Plattner, A. Furst, and K. Jirasek, *Helv. Chim. Acta.*, **30**, 1327 (1947).

(7) All melting points are uncorrected. Microanalyses were done by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

The infrared spectrum was identical with that of the authentic sample.[4]

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.44, 74.35; H, 6.28, 6.37.

trans-2-Phenylcyclopropane carboxhydrazide. A 127-mg. sample of acid was esterified with diazomethane and the ester evaporatively distilled. This ester was treated with hydrazine hydrate to give 2-phenylcyclopropane carboxhydrazide which was recrystallized twice from water; m.p. 124–126.5° (lit.[3] m.p. 127.5–129.5°).

Methyl 2-phenylcrotonate. 2-Phenylcrotononitrile[8] (2 g.) was heated with 30 g. of "100% phosphoric acid" (70 g. of 85% phosphoric acid and 30 g. of phosphorus pentoxide) at 140° for 3.5 hr. The mixture was poured onto ice and the product extracted with ether. The ether solution was extracted with 3*N* sodium hydroxide. Evaporation of the ether gave 0.7 g. of precipitated 2-phenylcrotonic acid. Filtration gave 1.0 g. (44% yield) of crystalline acid, m.p. 132–137° (lit.[8] m.p. 136–137°). The acid was esterified by refluxing for 22.5 hr. with methanol, sulfuric acid, and chloroform under a Soxhlet extractor to give a 37% yield of methyl 2-phenylcrotonate.

Methyl 4-bromo-2-phenylcrotonate. A mixture of methyl 2-phenylcrotonate (12.8 g.), *N*-bromosuccinimide (13 g.), benzoyl peroxide (0.033 g.) and carbon tetrachloride (25 ml.) was refluxed for 9.7 hr. The mixture was cooled and the succinimide was filtered and washed with more carbon tetrachloride. The combined filtrates were evaporated to dryness. Residual succinimide was extracted with water. The remaining oil was taken up in ether and dried over magnesium sulfate. Evaporation of the ether gave 14 g. of red oil which was evaporatively distilled to give 12.2 g. or orange oil. When this was fractionated, 3.7 g. of methyl 4-bromo-2-phenylcrotonate was obtained, b.p. 135–138°/3 mm., n_D^{25} 1.5668.

1,2-Diphenylcyclopropane carboxylic acid. A solution of 0.0145 mole of phenylmagnesium bromide in ether was added dropwise to a stirred solution of methyl 4-bromo-2-phenylcrotonate (3.7 g., 0.0145 mole). The solution became cloudy. After the mixture had stood overnight, water was added and the mixture was acidified with dilute hydrochloric acid. Working up in the same manner as 2-phenylcyclopropane carboxylic acid gave a brown gum which could not be crystallized from water. This gum was taken up in ether and isolated as a cloudy orange glass (2.8 g.) by evaporating the ether. When a small quantity of this glass was taken up in alcohol and allowed to evaporate, seeds were formed which were used in the crystallization of the rest of the material. About 20 mg. (0.6% yield) of 1,2-diphenylcyclopropane carboxylic acid was obtained after two recrystallizations from alcohol: m.p. 223–224°. The ultraviolet spectrum showed a peak at 208 mμ (ε 17,600) and a shoulder at 220 mμ (ε 13,500). There was no absorption at higher wave lengths. The acid did not decolorize permanganate.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.45; H, 6.02.

Bromination of methyl tiglate with N-bromosuccinimide.[5] Methyl tiglate (13.1 g.) was brominated by refluxing for 2.5 hr. with 17 ml. of carbon tetrachloride and *N*-bromosuccinimide (22.7 g.) under strong incandescent illumination. The mixture was then cooled to −18° for 3 hr. and filtered. More succinimide precipitated from the dark filtrate on standing. The solution was evaporated and the product distilled to give 13.4 g. (60% yield) of yellow liquid boiling at 86–90°/8 mm. This was presumed to be methyl 4-bromotiglate.

Formation of 2-methylene-3-phenylbutyric acid from "methyl 4-bromotiglate" and phenylmagnesium bromide. To a stirred solution of "methyl 4-bromotiglate" (6.0 g., 0.031 mole) in 100 ml. of ether was added 0.031 mole of phenylmagnesium bromide in ether. Immediately after the addition was complete, the mixture was poured into water. The ether was separated and the aqueous phase was extracted with more ether. The combined ether layers were washed with saturated sodium bicarbonate, with water and then dried over magnesium sulfate. The solvent was removed and the residue was distilled at 2 mm. to give 4.4 g., b.p. 48–90°. This distillate was redistilled through a small Vigreux column to give 1.8 g., b.p. 58–64°/2 mm. and 1.3 g., b.p. 64–80°/2 mm. Each fraction was saponified by refluxing for an hour with 40 ml. of 1.5*N* sodium hydroxide in 50% ethanol. The acidic materials from the low boiling fraction (863 mg.) were evaporatively distilled. A gas liquid chromatogram of this distillate showed five peaks. The largest was collected and examined in the infrared. It showed no phenyl absorption. Apparently it was not formed by phenyl addition to the starting material and was not further investigated. The acidic products from the higher boiling fraction consisted of 204 mg. of a solid acid and 398 mg. of a liquid. After sublimation, the solid acid melted at 103–104°. Ultraviolet spectrum: λ_{max} 215 mμ, ε 5720. Infrared spectrum: peaks at 5.86 (s), 6.10 (m), 6.20 (w), 6.67 (m), 6.85 (m) and a phenyl peak at 14.5 μ.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.85; H, 6.92.

2-Methyl-3-phenylbutyric acid. An 11.440-mg. sample of the above acid was hydrogenated in 95% ethanol over platinum oxide. Hydrogen (1.04 moles) per mole of acid was absorbed. 2-Methyl-3-phenylbutyric acid was isolated from a larger run. It was sublimed and recrystallized three times from 50% ethanol and once from hexane to give crystals, m.p. 132.5–134° (hot stage) (lit.,[6] m.p. 132).

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Decarbonylation of Aromatic Aldehydes

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The decarbonylation of benzaldehyde, furfural, citral, *d*-citronellal,[1] and myrtenal[2] by heating the aldehydes over a palladium catalyst has been reported. It was desired to determine the scope of this decarbonylation reaction.

The various aromatic aldehydes listed in Table I were heated at the given temperatures with 5% palladium on carbon powder in an initial carbon dioxide atmosphere. Carbon monoxide was evolved and was collected over water. In most cases, the decarbonylation was essentially quantitative as judged from the volume of carbon monoxide collected. Reaction times varied from one quarter to two hours. A sample of gas from the decarbonylation of 2,2′-biphenyldicarboxaldehyde was qualitatively analyzed by gas phase chromatography. Carbon monoxide, but no hydrogen, was identified. The decarbonylation products were recovered from the reaction mixtures by distillation or, when the product was a solid, by dissolving the reaction mixture in an appropriate solvent, removing the