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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[8] E. C. Knowles and J. B. Cloke, *J. Org. Chem.*, **54**, 2036 (1932).

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

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[1] H. E. Eschinazi, *Bull. soc. chim. France*, 967 (1952).

[2] H. E. Eschinazi and H. Pines, *J. Org. Chem.*, **24**, 1369 (1959).

TABLE I

Decarbonylation of Aromatic Aldehydes over Palladium Catalyst

Aldehyde	Reaction Temp.	Reaction Time, Hr.	Product	Yield, %	B.P. or M.P.	B.P. or M.P. (Lit.)
Benzaldehyde	179	1	Benzene	78	79–80	80.09[a]
p-Tolualdehyde	199	0.5	Toluene	88	110–111	110.8[a]
o-Methoxybenzaldehyde	243	1	Anisole	94	154–155	155[a]
m-Nitrobenzaldehyde	205	1.75	Nitrobenzene	86	210–211	210.9[a]
p-Nitrobenzaldehyde	205	0.5	Nitrobenzene	79	210–211	210.9[a]
Pyridine-2-aldehyde	180	1	Pyridine	68	114–115	115.3[a]
1-Naphthaldehyde	220	0.5	Naphthalene	80	M.P. 79–80	80.2[a]
2-Naphthaldehyde	250–255	0.5	No Reaction	—	—	—
9-Anthraldehyde	240–245	0.5	Anthracene	84	M.P. 213–214	213[a]
Methyl 2-formyl-2′-biphenylcarboxylate	240–250	0.5	2-Biphenylcarboxylic acid	20	108–109	109–110[b]
2-Formyl-2′-biphenylcarboxylic acid	240–250	0.5	No reaction	—	—	—
2,2′-Biphenyldicarboxaldehyde	240–245	0.5	Biphenyl	97	M.P. 68–70	69–71[a]
1-Formyl-9-fluorenone	240–250	0.25	9-Fluorenone	82	M.P. 82–83	84[a]
Phthalaldehydic acid	200	2	3,3′-Oxydiphthalide	61	M.P. 234–236	235–236[c]

[a] *Handbook of Chemistry and Physics*, Thirtieth Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1948. All melting points and boiling points (atmospheric pressure) are uncorrected. [b] G. W. Kenner, M. A. Murray, and C. M. B. Taylor, *Tetrahedron*, **1**, 265 (1957). Methyl 2-biphenylcarboxylate, the product, was hydrolyzed to the acid. The starting ester was recovered in 71% yield. [c] S. Hanai, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **17**, 1236 (1938).

catalyst by fitration, and recrystallizing the product.

The decarbonylation of aromatic aldehydes over palladium appeared to be fairly general. However, several exceptions were noted. 1-Naphthaldehyde readily lost carbon monoxide at 210° to form naphthalene, but not so the 2-isomer. Only a trace of gas was formed from the latter compound even at 250–255°. Methyl 2-formyl-2′-biphenylcarboxylate reacted slowly and the reaction was only 20–30% complete in one half hour. 2-Formyl-2′-biphenylcarboxylic acid was not decarbonylated at 240–245°. It may be that this aldehyde-acid forms 3-hydroxydiphenide at elevated temperatures. Phthalaldehydic acid, which is predominately in the cyclic form, 3-hydroxyphthalide, did not lose carbon monoxide but was dehydrated to 3,3′-oxyphthalide. This reaction also occurs above 170° in the absence of a catalyst.[3]

The study was extended to include a high-boiling (155°) aliphatic aldehyde, *n*-heptaldehyde. The rate of gas evolution was much slower than with aromatic aldehydes, requiring a reaction time of nine hours before gas evolution ceased. The gas stream not only contained carbon monoxide but also some hydrogen. Water was also a product of the reaction. A low-boiling fraction (67–69°) was a five-component mixture, probably containing isomeric hexenes, although only hexene-1 was identified by gas chromatography. The remainder of the product was unidentified liquid boiling above 220°. The heating of an aliphatic aldehyde over a palladium catalyst does not result in a single type of reaction but appears to involve dehydrogenation, isomerization, and polymerization as well as decarbonylation.

EXPERIMENTAL

The appropriate aldehyde (5 to 10 g.) and 1% of palladium on carbon powder catalyst (5% palladium, Baker and Company, Inc.) were placed in a pear-shaped flask (25 ml.). The flask was fitted with a micro Vigreux distillation column and a thermometer to measure pot temperatures. The system was evacuated and vented to a carbon dioxide atmosphere several times to displace oxygen. The flask was heated, and evolved gas was passed through a Dry Ice trap, a gas sampling bulb, and was then collected over water. The reaction temperatures of the lower-boiling aldehydes were at their reflux temperature. When the boiling point of the decarbonylation product was sufficiently lower than the reaction temperature, the product was continuously removed by distillation. The product was then redistilled. When the product was not recovered by distillation (anthracene, 2-biphenylcarboxylic acid, biphenyl, 9-fluorenone, and 3,3′-oxydiphthalide), the pot residue was dissolved in an appropriate solvent, and the catalyst removed by filtration. The product was then recrystallized from an appropriate solvent. The infrared spectra of all the compounds isolated compared favorably with those of authentic materials.

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(3) C. Graebe and F. Trümpy, *Ber.*, **31**, 371 (1898).