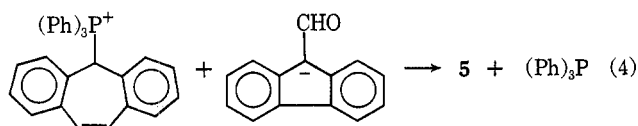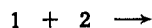The divergent reaction described by eq 2 is unprecedented. We suggest that alkylation took place at the α position of the aldehyde because of the unusual acidity of the α proton in 9-fluorenecarboxaldehyde and eq 4 offers a plausible mechanism for this reaction.

$$1 \ + \ 2 \ \longrightarrow \qquad \longrightarrow \ 5 \ + \ (Ph)_3P \quad (4)$$

If the proposed mechanism is correct, aldehydes and other carbonyl compounds containing α protons of comparable acidity might be expected to undergo this α alkylation reaction with phosphonium ylides.

Experimental Section[4]

Preparation of 7-(1,2,4,5-Dibenzocycloheptatrienyl)triphenylphosphonium Chloride (4).—7-Chloro-1,2,4,5-dibenzocycloheptatriene (680 mg, 3 mmol), prepared by the method of Berti,[5] was combined with triphenylphosphine (787 mg, 3 mmol) in 10 ml of dry benzene and the solution warmed at 50° for 12 hr. The mixture was cooled to room temperature and a white crystalline precipitate (1.138 g) was collected. This material showed the correct nmr spectrum.

Anal. Calcd for $C_{33}H_{26}ClP$: C, 81.07; H, 5.36. Found: C, 81.21; H, 5.24.

Reaction of 9-Fluoroenecarboxaldehyde (2) with 7-(1,2,4,5-Dibenzocycloheptatrienylidene)triphenylphosphorane (1). Formation of the Aldehyde 5.—The ylide 1 was generated *in situ* at 0° by treating 4 (8.8 g, 18 mmol) in 50 ml of dry ether with *n*-butyllithium (12 ml of a 1.5 mol hexane solution; Foote Chemical Co.) in a nitrogen atmosphere. The solution became brick red and was stirred for 40 min, after which time 9-fluorenecarboxaldehyde (3.5 g, 18 mmol), prepared by the method of Wislicenus and Waldmuller,[6] in 25 ml of dry ether was introduced by means of a hypodermic syringe. A copious white precipitate formed immediately and the mixture was refluxed for 17 hr. The mixture was cooled to room temperature and the crystalline precipitate filtered. Evaporation of the filtrate provided a slightly yellow semisolid which was treated with warm pentane and filtered. The cooled filtrate deposited 2 g of a white solid which was shown to be triphenylphosphine by comparison with an authentic sample. The crystalline precipitate which was filtered from the original reaction mixture was treated with 300 ml of chloroform and 300 ml of water. The chloroform layer was separated, dried (MgSO₄), and filtered. Evaporation of the filtrate gave a yellow oil which was shaken and refluxed with 50 ml of MeOH to give a crystalline colorless solid. The filtered dry solid (3.6 g) was homogeneous by tlc. The analytical sample was prepared by successive recrystallization from CCl₄, C₆H₆-EtOH, and C₆H₆, to give colorless prisms, mp 183–186°. The product gave a positive test with Tollens reagent. The ir spectrum (KBr), in addition to a strong carbonyl band at 1709 cm⁻¹, contained weak, sharp bands at 2817 and 2703 cm⁻¹, characteristic of aldehydes.[7] The nmr spectrum (CDCl₃) exhibited signals at τ 0.63 (s, 1, CHO), 2.5–3.2 (m, 14, Ar H), 3.43 (s, 2, ethylene), 3.78 (d, 2, J = 7 Hz, Ar H; the number 1 and 10 protons of the dibenzotropylidene group are shifted upfield by shielding from the fluorenyl group), and 5.23 (s, 1, methine proton of the tropylidene ring).

Anal. Calcd for $C_{29}H_{20}O$: C, 90.60; H, 5.24. Found: C, 90.63; H, 5.26.

Decarbonylation of the Aldehyde 5 to Give 7-(9′-Fluorenyl)-1,2,4,5-dibenzocycloheptatriene (6).—To a refluxing solution of 5 (192 mg, 0.5 mmol in 50 ml of absolute EtOH) was added 0.5 g of KOH pellets. A white precipitate formed immediately and the mixture was refluxed for 1 hr. The precipitate was filtered, washed with MeOH, and dried to give 174 mg of colorless solid, mp 293–294°. The melting point was unchanged on recrystallization from benzene: uv max (methylcyclohexane) 245 mμ (ϵ 19800), 269 (22500), 270 (18600), 290 (15030), and 302 (16100); ir max (Nujol) 12.31, 12.91, 13.10, 13.17, 13.33, 13,39, and 13.69 μ; mass spectrum[8] m/e 356 (1, parent ion, $C_{28}H_{20}$), 191 (100, dibenzotropylidenyl ion, $C_{15}H_{11}$), and 165 (79, fluorenyl ion, $C_{13}H_9$).

Anal. Calcd for $C_{28}H_{20}$: C, 94.36; H, 5.64. Found: C, 94.59; H, 5.51.

Dehydrogenation of 6 to the Tetrabenzosesquifulvalene 7.—The hydrocarbon 6 (86 mg, 0.24 mmol) was combined with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, DDQ (114 mg, 0.5 mmol) in 5 ml of bromobenzene and the mixture refluxed for 12 hr. The hydroquinone separated on cooling and was filtered. The filtrate was washed with saturated bicarbonate, dried (MgSO₄), and filtered. Evaporation of the filtrate gave a pale yellow powder (83 mg), mp 298–300° (lit.³ mp 303°). The melting point was unchanged on recrystallization from benzene. The uv spectrum contained a complex series of bands and was identical with that reported previously for this compound.³


The Friedel–Crafts Reaction with 2,3-Dibromo-3-phenylpropionic Acid

Roderick A. Barnes* and Adelina Costa Neto[1]

Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

The reaction of 2,3-dibromo-3-phenylpropionic acid (I) with benzene in the presence of aluminum bromide is a normal Friedel–Crafts synthesis, producing 2,3,3-triphenylpropionic acid (II).[2] However, Earl and
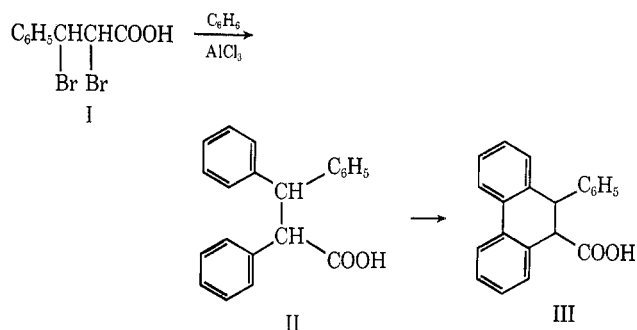
Wilson³ have reported that when aluminum chloride was used in this reaction another substance, which they believed to be a phenanthrene derivative III, was

---

(4) Melting points are uncorrected. Nmr spectra were recorded on a Varian Associates A-60 spectrometer, ir spectra on a Perkin-Elmer Model 137 spectrometer, and uv spectra on a Cary Model 11 spectrometer. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., and Schwarzkopf Laboratories, Woodside, N. Y.

(5) G. Berti, *Gazz. Chim. Ital.*, **87**, 293 (1957); *Chem. Abstr.*, **52**, 11803 (1958).

(6) W. Wislicenus and M. Waldmuller, *Chem. Ber.*, **42**, 786 (1909).

(7) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 48.

* To whom correspondence should be addressed.

(1) Abstracted from a thesis presented by A. Costa Neto to the Instituto de Química, Universidade Federal do Rio de Janeiro, for the M.S. degree, 1965.

(2) C. C. Price, *Org. Syn.*, **33**, 98 (1953).

(3) J. C. Earl and C. H. Wilson, *J. Proc. Roy. Soc., N. S. W.*, **66**, 178 (1932); *Chem. Abstr.*, **26**, 2976 (1932).

formed. While reactions similar to the transformation of II to III do take place in the presence of aluminum chloride, the conditions are usually much more drastic[4] than refluxing of a benzene solution.

In an attempt to verify this cyclization we have restudied the reaction of the dibromide I with benzene in the presence of aluminum chloride. In our hands this reaction, when allowed to proceed for 4 hr as recommended by Earl and Wilson, yielded the normal product, triphenylpropionic acid (II). However, with shorter reaction times, another product could be isolated which had the melting point reported for the supposed cyclized product III. This product was found to be an acid which contained bromine. Dehydrobromination of the methyl ester of this acid and subsequent saponification yielded β-phenylcinnamic acid (V).

Thus the Friedel–Crafts reaction was incomplete and only one bromine atom had reacted to yield an acid of structure IV. In accord with this idea, it was observed that further reaction of IV with benzene and aluminum chloride yielded triphenylpropionic acid (II).
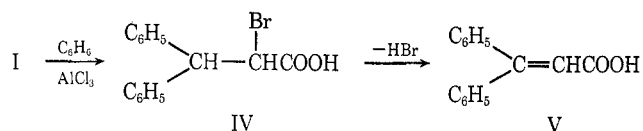
The formation of IV as the first step, is reasonable mechanistically since the complex (VII) for its formation would be of lower energy than for the alternate acid. Complex VI has a positive center adjacent to the carboxyl group while in VII the necessary positive center is adjacent to a phenyl group.
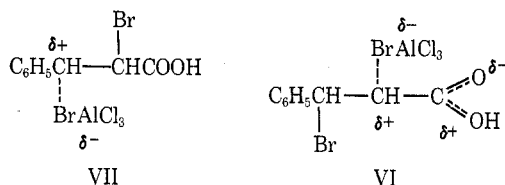
The nuclear magnetic resonance spectrum[5] was also in agreement with structure IV for the bromo acid. The two aliphatic hydrogens appear as an AB pattern typical of two hydrogens strongly coupled and with fairly similar chemical shifts (4.28 and 4.69 ppm). An unusual aspect was that the aromatic hydrogens appeared as two peaks having chemical shifts of 7.01 and 7.09 ppm. A phenyl group linked to carbon does not normally show much difference in the chemical shift of the ortho, meta, and para hydrogens and so appears as a single peak or complex of very closely spaced peaks. We suggest that in acid IV there is sufficient restriction of rotation that the two phenyl groups exist in different environments. Thus VIII is probably the favored

VIII
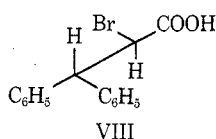
(4) For example, 1-benzoylnaphthalene can be cyclized to 1,9-benzanthrone by heating with anhydrous aluminum chloride at 150° for 2.5 hr: see L. Scholl and C. Seer, Justus Liebigs Ann. Chem., 394, 111 (1912).

(5) The authors wish to thank Dr. Ronald R. Sauers, School of Chemistry, Rutgers the State University, New Brunswick, N. J., for determining this spectrum.

conformation with one phenyl group closer to the bromine atom and the other nearer to the carboxyl group. The coupling of the two aliphatic hydrogens ($J = 12$ cps) is approximately what would be expected if they are trans as in VIII. A part of the evidence for structure III advanced by Earl and Wilson was a decarboxylation to yield a product which they believed to be 9-phenyl-9,10-dihydrophenanthrene (IX) and which had mp 121.5°. Later, in connection with other work, Bergmann and Bergmann[6] reduced 9-phenylphenanthrene to obtain an authentic sample of IX which was found to melt at 84°. We repeated the decarboxylation reaction using triphenylpropionic acid (II) and obtained a crystalline product, mp 124°, which proved to be stilbene (X). Thus, one phenyl group was lost in the decarboxylation perhaps by a process somewhat as
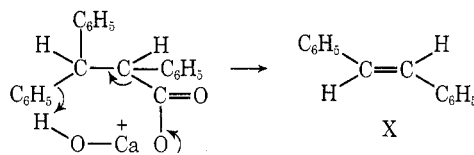
shown. From this result and our difficulties in separating acids II and IV by crystallization, we suspect that some of the data reported by Earl and Wilson for their abnormal product were actually obtained with a sample which was partly if not largely acid II. Further experiments on the Friedel–Crafts reaction with α,β-dihalo acids are in progress.

Experimental Section

2,3-Dibromo-3-phenylpropionic Acid (I).—Cinnamic acid (5 g) was treated with bromine in chloroform solution according to the procedure of Michael.[7] There was obtained 8.1 g (78%) of product which melted at 187–195°. Recrystallization from chloroform raised the melting point to 196–198°.

Friedel–Crafts Reactions. A.—Aluminum chloride (9.5 g) was added to a well-stirred solution of acid I (14 g) in dry benzene (113 ml). The mixture was heated in a water bath with continued stirring for 4 hr. The cooled reaction mixture was treated with dilute hydrochloric acid. A major part of the product, triphenylpropionic acid (II), separated at the interface of the two liquid layers. The benzene layer was washed with sodium hydroxide solution (10%) and acidification of the aqueous extract liberated the rest of product II. There was obtained 10.6 g (76%) of II which melted at 216–217° after recrystallization from benzene.

B.—The reaction was carried out exactly as in part A except that the reflux time was reduced to 20–25 min. No crystalline triphenylpropionic acid separated at the interface when the reaction mixture was treated with dilute hydrochloric acid. The alkaline extraction and subsequent acidification yielded a mixture of acids (12–15 g). When this mixture of acids was boiled with ethanol–water (1:9) most of the triphenylpropionic acid (ca. 7 g) was left undissolved. Upon cooling of the alcoholic solution, there was obtained a precipitate of impure acid IV (5–6.5 g) with a melting point in the range of 120–130°.

C.—When acid II (30 g) was boiled with aluminum chloride (16 g) in benzene (200 ml) for 5 hr, it was recovered unchanged.

D.—Impure acid IV (2.5 g), mp 146–148°, was treated with aluminum chloride (2.5 g) and benzene (50 ml). After the solution had refluxed for 4 hr, it was processed as in part A. The crude acid product was recrystallized to yield 1.5 g of triphenylpropionic acid, mp 210–215°, and a smaller amount of material of lower melting point, undoubtedly a mixture of II and IV.

Purification and Properties of Acid IV.—Crude acid IV was recrystallized several times from dilute alcohol whereupon the melting point was raised to 146–148°.

(6) E. Bergmann and F. Bergmann, J. Amer. Chem. Soc., 59, 1443 (1937).

(7) A. A. Michael, J. Prakt. Chem., 52, 292 (1907).

Anal. Calcd for $C_{15}H_{13}O_2Br$: C, 59.03; H, 4.29. Found: C, 62.11, 62.24; H, 4.59, 4.59.

These figures are in agreement with those for a mixture of acid IV (96%) and acid II (4%). Further recrystallization from ligroin (bp 80–100°) raised the melting point to 155–156°. However this sample is still not pure since the melting point for pure acid IV prepared in another manner[8] is reported to be 164°.

Thin layer chromatography using silica gel and butanol saturated with aqueous ammonia (C_4H_9OH–concentrated ammonia–H_2O 8:15:5) readily separated acid II (R_f 0.96) and acid IV (R_f 0.58). Crude acid IV directly from the Friedel–Crafts reaction, part B, had an additional spot (R_f 0.45) which was found to be the starting acid I.

Methylation of acid IV (1.34 g, mp 146–148°) with an ether solution of diazomethane furnished the methyl ester. Evaporation of the ether left a residue which was recrystallized first from petroleum ether and then from isopropyl alcohol, mp 99–101°.

Anal. Calcd for $C_{16}H_{15}O_2Br$: C, 60.20; H, 4.74. Found: C, 60.13; H, 4.80.

3-Phenylcinnamic Acid (V).—The methyl ester of acid IV (0.37 g) and a solution of potassium hydroxide in anhydrous methanol (4 ml, 50%) were refluxed for 3 hr in a water bath. The reaction mixture was cooled, diluted with distilled water, and acidified to yield white needles, mp 140–156°. Recrystallization raised the melting point to 157–158°. The melting point of a mixture of this sample with an authentic sample[9] was also 157–158°. Also the infrared spectra of the two samples were identical.

Decarboxylation of 2,3,3-Triphenylpropionic Acid.—Acid II (1 g) was mixed with finely powdered soda lime (4 g) and about 1 g of copper powder[10] and heated with a free flame in a small distilling flask. The heating was continued was until no more material distilled. The crystalline part of the distillate was filtered to remove the major part of the accompanying oil and recrystallized from methanol, mp 123–124°. This substance was identified as stilbene by its characteristic nmr spectrum[11] and by observing the melting point of a mixture with authentic *trans*-stilbene.

Registry No.—I, 6286-30-2; IV, 19811-27-9; IV methyl ester, 24689-50-7.

(8) E. P. Kohler and G. L. Heritage, *Amer. Chem. J.*, **33**, 34 (1900).

(9) Prepared by the Reformatsky reaction of benzophenone with ethyl bromoacetate, followed by saponification and dehydration.

(10) The copper was used to more nearly duplicate the conditions used by Earl and Wilson who carried out the decarboxylation in a copper flask.

(11) Determined using the Varian A-60A spectrometer. See spectrum no. 306, Varian catalog of nmr spectra.

Stereochemistry of Dicoordinated Oxygen.
## II. Reinvestigation of the Purported 1,8-Monooxynaphthalene

A. J. GORDON

*Department of Chemistry, The Catholic University of America, Washington, D. C. 20017*

In connection with studies of unusual ether structures,[1] an old report of the preparation of a "*peri*-monoxynaphthalene" (1) was of great interest.[2] It was claimed that heterogeneous oxidation of α-naphthol with aqueous $FeCl_3$, or dehydration at 300° in a CO_2 atmosphere of 1,8-dihydroxynaphthalene gave good yields of 1, whose structure was assigned from combustion analysis, cryoscopic molecular weight, and chemical

(1) Paper I: A. J. Gordon and J. P. Gallagher, *Tetrahedron Lett.*, 2541 (1970).

(2) E. Ayers, British Patent 394,511 (June 29, 1933).

behavior.[2] Such a claim might ordinarily be discarded out-of-hand;[3] however, the recent isolation of a stable *peri* sulfone 2,[4] the evidence for 1,8-naphthyne,[4,5] and the existence of other highly strained aromatic systems, particularly benzocyclopropene,[6] warranted a reexamination of this highly unusual system.
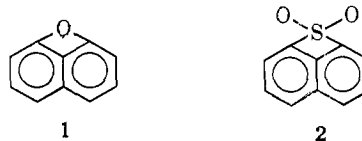
Following the published procedures in detail[2] and with some modifications, no trace of a substance corresponding to 1 or to the properties given for 1 could be detected. Rather, the only nonresinous, isolable products were starting material (α-naphthol) and 4,4'-dihydroxy-1,1'-dinaphthyl (3a)[7,8] purified as its diacetate 3b. Although 3a has the same melting point (300–
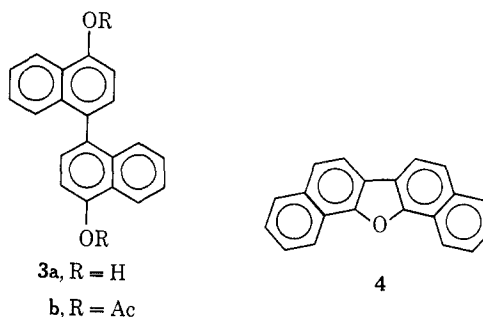
302°) assigned to 1,[2] it is difficult to reconcile the cited properties[2] with those of a naphthol. There is some evidence[8] that with hot acid (HI) or at very high temperature (>300°) 3a undergoes a rearrangement and dehydration to dinaphthofuran (4) (mp 183°). Neither of these conditions is applicable to the $FeCl_3$ reactions (see Experimental Section) and no product resembling 4 was detected. It is concluded that the reported synthesis of 1 is erroneous, and that $FeCl_3$ oxidation does occur to form the expected coupling product.[7,8]

Experimental Section[9]

Oxidation of α-Naphthol.—In a typical experiment, a 750-ml aqueous mixture of α-naphthol [Eastman, distilled, mp 95.5–96.0° (lit.[10] mp 94°)] (30 g, 0.21 mol) and $FeCl_3$ (100 g, 0.6 mol) was refluxed for 60 min, giving a heterogeneous, purplish mixture. Filtration gave 5.5 g of dark blue powder and 27.4

(3) Particularly in view of the reported melting point (>300°); this work has been cited with criticism more recently [V. Balasubramaniyan, *Chem. Rev.*, **66**, 593 (1966)].

(4) R. W. Hoffmann and W. Sieber, *Justus Liebigs Ann. Chem.*, **703**, 96 (1967); *Angew. Chem.*, **77**, 810 (1965).

(5) C. Rees and R. Storr, *J. Chem. Soc. C*, 760, 765 (1969); R. W. Hoffmann, G. Guhn, M. Preiss, and B. Dittrich, *ibid.*, 769 (1969).

(6) For example, in *o-di-tert*-butylbenzene the high strain is relieved by bending of the bonds to the alkyl groups out of the aromatic plane [E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Amer. Chem. Soc.*, **89**, 5389 (1967)]; a classic example is the 2,2-paracyclophanes [for recent studies on spectroscopic properties, see O. Weigang, Jr., and M. Nugent, *ibid.*, **91**, 4555, 4556 (1969)]. Benzocyclopropene: *e.g.*, R. Anet and F. A. L. Anet, *ibid.*, **86**, 525 (1964).

(7) Originally prepared by a similar oxidation of α-naphthol: R. Willstätter and L. Schuler, *Chem. Ber.*, **61**, 362 (1928).

(8) G. Clemo, J. Cockburn, and R. Spence, *J. Chem. Soc.*, 1265 (1931).

(9) All melting points are uncorrected. Ir spectra were recorded on a Beckman IR-8; mass spectra were determined on Varian-Mat CH-5. Combustion analyses were obtained from MHW Laboratories, Garden City, Mich.

(10) E. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1965.