The original ether layer also contained a large amount of insoluble material melting between 160–200° which resisted purification.

Cleavage of *o*-Hydroxybenzeneboronic Acid Anhydride.—Eight grams (0.067 mole) of *o*-hydroxybenzeneboronic acid anhydride in 250 ml. of ether was treated with 0.134 mole of *n*-butyllithium[7] in 97 ml. of ether at room temperature. This addition required 10 minutes. Color Test II[18] was negative immediately upon completion of the addition so another 0.67 mole of *n*-butyllithium in 49 ml. of ether was added. Color Test II[18] was also negative after this addition. Stirring was continued for 20 minutes at room temperature after which the reaction was carbonated in the usual way. The mass was hydrolyzed by the addition of 100 ml. (0.29 mole) of 10% hydrochloric acid and then the ether layer was extracted four times with 25-ml. portions (0.1 mole) of 8% sodium bicarbonate and four times with 25-ml. portions (0.131 mole) of 5% sodium hydroxide. Acidification of the sodium bicarbonate extract with 10% hydrochloric acid gave 1.65 g. (18%) of material melting at 151–155° which was identified as salicylic acid (159°) by the infrared spectrum.

Acidification of the sodium hydroxide extract gave 1.3 g. of material melting over the range of 155–165°. This decomposed before positive identification could be made. No 1-butaneboronic acid was isolated.

***o*-Hydroxybenzeneboronic Acid Anhydride and Bromine.**—To a solution of 0.48 g. (0.004 mole) of *o*-hydroxybenzeneboronic acid anhydride in 10 ml. of acetic acid, prepared by warming the mixture, was added slowly 3 ml. of bromine in 10 ml. of water containing potassium bromide. The mixture was stirred for a period of 15 minutes and was then diluted to 120 ml. by the addition of water. This caused the precipitation of a solid contaminated with the red color of bromine. This color was destroyed by the addition of a sodium bisulfite solution. The cream-colored product was recovered by filtration, washed with 2% hydriodic acid and then with water, and dried to yield 1.1 g. (85%) of 2,4,6-tribromophenol identified by the method of mixed melting point. The infrared spectra of this product and authentic 2,4,6-tribromophenol were identical.

***o*-Hydroxybenzeneboronic Acid Anhydride and Hydrogen Peroxide.**—To a solution of 0.48 g. (0.004 mole) of *o*-hydroxybenzeneboronic acid anhydride in 10 ml. of acetic acid and 5 ml. of water was added 10 ml. of 30% hydrogen peroxide. After allowing the solution to stand for 5 minutes the mixture was diluted with 70 ml. of water. A small amount of shiny white product was deposited upon cooling. A mixed melting point determination showed it to be catechol.

***o*-Hydroxybenzeneboronic Acid Anhydride and Acetyl Chloride.**—To a stirred solution of 2.4 g. (0.02 mole) of *o*-hydroxybenzeneboronic acid anhydride in 25 ml. of pyridine was added 5 ml. of acetyl chloride dropwise. The mixture was allowed to stand for 20 minutes and was then treated with 100 ml. of water. A reddish-brown oil separated and hardened somewhat upon standing. The crude product was recovered by filtration and dissolved in a mixture of hot acetone and benzene, treated with Norit A for a few minutes, filtered and allowed to cool. The cream-colored solid which separated melted over the range of 165–170° and was identified as metaboric acid, HBO_2, by determination of its neutralization equivalent and comparison of its infrared spectrum with that of an authentic specimen. The presence of phenol was indicated by odor.

Other attempts of acetylation of the anhydride using acetyl chloride or acetic anhydride with and without a sulfuric acid catalyst were unsuccessful.

Acknowledgment.—We are indebted to Mr. E. Miller Layton, Jr., of the Ames Laboratory of the Institute for Atomic Research for the infrared spectra. We also wish to acknowledge the support of the Division of Biology and Medicine of the United States Atomic Energy Commission whose financial assistance has made this work possible. The results of the biological testing of compounds in the boronic acid series will be reported by Dr. Otho D. Easterday of the Brookhaven National Laboratory.

AMES, IOWA

[CONTRIBUTION FROM THE STAMFORD LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Organoboron Compounds. I. A New Synthesis of B-Trialkyl and Triaryl-N-triphenylborazoles[1]

BY STEPHEN J. GROSZOS AND STANLEY F. STAFIEJ

RECEIVED OCTOBER 23, 1957

A new method for the preparation of B-trialkyl- and triaryl-N-triphenylborazoles is described. B-Trichloro-N-triphenylborazole has been found to react smoothly at room temperature with the appropriate Grignard or lithium reagents to give the desired products in yields of 65–84%. All the compounds prepared are colorless crystalline solids which are easily purified by recrystallization and are stable to moisture.

Substituted borazoles comprise one of the more stable classes of organoboron compounds. The relatively few known substituted borazoles and the limitations of the synthetic methods employed for their preparation[2-6] prompted us to investigate alternate routes to this class of compounds. The availability of a variety of substituted borazoles is of particular interest in studying effects of substituents on the properties of the borazole ring.

Many of the preparative methods for substituted borazoles have relied largely on vacuum line techniques where products were obtained in only small quantities. Recently, however, Ruigh and his associates[7-10] have found that sizable quantities of several B-substituted borazoles can be prepared by the reaction of a substituted boron dichloride and ammonia.[11]

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(1) A preliminary account of this work was presented at the 131st National Meeting of the American Chemical Society, Miami, Fla., April, 1957.

(2) H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1 (1942).

(3) E. Wiberg, *Naturwiss.*, **35**, 182, 212 (1948).

(4) F. G. A. Stone, *Quart. Revs.*, **9**, 174 (1955).

(5) E. M. Smolin and L. Rapoport, "1,3,5-Triazines and Derivatives," Chapter entitled, "*s*-Triazaborane and Derivatives," Interscience Publishers, Inc., New York, N. Y., to be published.

(6) G. E. Coates, "Organo-metallic Compounds," Methuen and Co., Ltd., London, 1956.

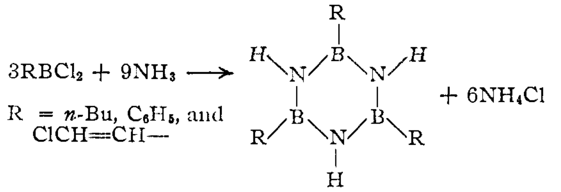
(7) W. L. Ruigh and C. E. Erickson, WADC Technical Report 55-26, "Research on Boron Polymers," Part I, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, March, 1955.

(8) W. L. Ruigh, C. E. Erickson, F. C. Gunderloy and M. Sedlak, *ibid.*, Part II, May, 1955.

(9) W. L. Ruigh, F. C. Gunderloy, M. Sedlak and P. A. Van Der Meulen, *ibid.*, Part III, May, 1956.

(10) W. L. Ruigh, A. D. Olin, M. G. Steinberg and P. A. Van Der Meulen, *ibid.*, Part IV, September, 1956.

(11) The reaction of $BuBCl_2$ and NH_3 was first studied by R. B. Booth and C. A. Kraus, THIS JOURNAL, **74**, 1415 (1952). Ruigh has proposed the borazole structure for the product of this reaction.



The one common feature shared by the various routes of preparative value so far reported is that substituents are built into the ring by a suitable choice of starting material. An alternate path was sought, whereby a variety of groups might be introduced onto an already formed borazole ring. Replacement of chlorine in various B,B′,B″-trichloroborazoles *via* organometallic reagents appeared to offer a possible approach toward this objective. B,B′,B″-Trichloro-N,N′,N″-triphenylborazole (I) was initially selected to explore this route and the results obtained using this intermediate form the subject of this communication.

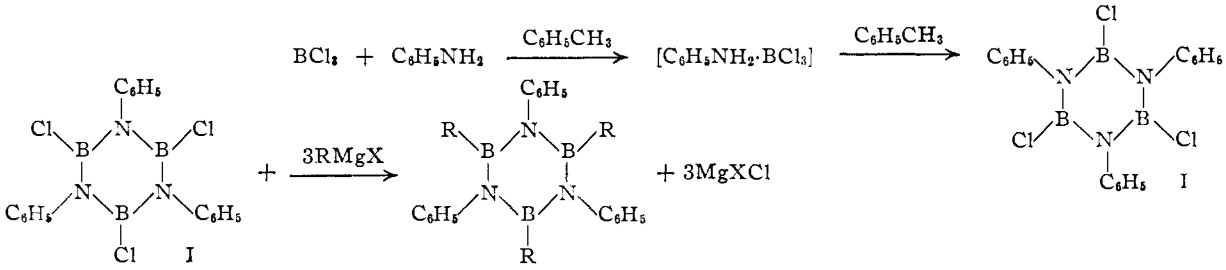
Compound I was prepared by a modification of the procedure of Jones and Kinney.[12] Refluxing the addition compound obtained from boron trichloride and aniline in toluene solution until HCl evolution ceased, followed by concentration and cooling of the solution, led to a 73% yield of I as a nicely crystalline, but water-sensitive compound. Gel formation sometimes encountered by the previous workers during recrystallization of this compound could be overcome by avoiding the use of filter paper during recrystallization of the crude product. Substituting glass wool or sintered glass consistently gave pure, nicely crystalline material.

high state of purity is then isolated in the usual manner.

When these reaction conditions were employed with isobutylmagnesium bromide, B-triisobutyl-N-triphenylborazole was obtained only in low yields. Examination of Stuart–Briegleb models indicted that the preparation of this compound might be difficult due to steric interference of the substituents. However, when the reaction was run at steam-bath temperature for 17 hours in di-*n*-butyl ether, a reasonable yield (67%) of the B-triisobutyl compound was obtained. Under the same conditions, however, the B-triisopropyl compound, for which the steric factor is of even greater consequence, could be isolated in only 20% yield.

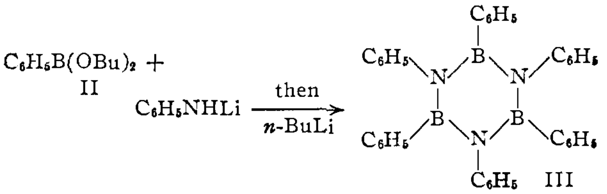
Hexaphenylborazole (III) because of its limited solubility in ether, separates from solution together with the inorganic salts during the course of the reaction. It is isolated in 65% yield by a continuous extraction of the latter with chloroform. Decomposition of the reaction mixture with 5% HCl, whereby the magnesium salts are brought into solution leaving the hexaphenylborazole insoluble in the two liquid phases, results in a lower yield (29%).

Compound III was also prepared for direct comparison by Kuivala's method.[14,15] In this procedure, di-*n*-butyl phenylboronate (II) is treated with an equimolar quantity of lithium anilide and the intermediate treated with a molar equivalent of *n*-butyllithium. The compounds prepared by these two routes proved identical by comparison of infrared and ultraviolet spectra.



In the present investigation, it has been found that addition of *n*-alkyl Grignard reagents to I leads to a very smooth, slightly exothermic reaction at room temperature whereby the corresponding B-trisubstituted-N-triphenylborazoles[13] can be isolated in yields of 70–84%. The conditions found to give maximum yields are as follows: An ether solution of a Grignard reagent is added dropwise to a suspension of I in ether and the reaction mixture refluxed for 2–3 hours. The cooled mixture is then titrated with a saturated aqueous solution of ammonium chloride to the point at which the magnesium salts separate from a clear, colorless ether layer. The ether solution, after being filtered through anhydrous Na_2SO_4, is concentrated and methanol slowly added to the boiling solution until the product begins to crystallize. The product in a

The substituted borazoles prepared in this investigation are listed in Table I. They are all colorless, crystalline solids which can be handled and stored without any special precautions. All appear to be stable with the exception of the allyl and phenyl compounds which become slightly colored after standing for several months.



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[12] R. Jones and C. Kinney, THIS JOURNAL, 61, 1378 (1939); see also C. Kinney and M. Kolbezen, *ibid.*, 64, 1584 (1942).

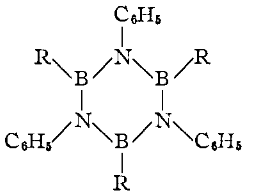
[13] This shortened nomenclature will be used since borazoles ported here are all symmetrically substituted.

[14] H. G. Kuivala, Ph.D. Dissertation, Harvard University, 1948. Kuivala also prepared hexaphenylborazole by treating phenylboron dibromide with aniline and correctly assigned the borazole structure to this compound.

[15] No reaction could be effected between I and phenylmercuric chloride under a variety of conditions. H. R. Snyder and C. Weaver, THIS JOURNAL, 70, 232 (1948), were unsuccessful in effecting reaction between aryl mercury compounds and tri-*n*-butyl borate.

TABLE I

COMPOUNDS PREPARED BY THE COUPLING REACTION



R	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Boron, % Calcd.	Boron, % Found
CH_3	267–269	77	71.88	71.79	6.89	6.89	11.97	12.20	9.25	9.03
C_2H_5	169–171	68	73.35	73.10	7.70	7.74	10.69	10.84	8.26	8.26
n-C_3H_7	169–171	84	74.54	74.25	8.34	8.17	9.66	10.09	7.46	7.19
i-C_3H_7	197–198	20	74.54	74.83	8.34	8.46	9.66	10.08	7.46	7.19
n-C_4H_9	129–132	70	75.51	75.39	8.87	8.67	8.81	8.78	6.80	6.43
i-C_4H_9	185–187	67	75.51	75.21	8.87	8.86	8.81	8.78	6.80	7.13
C_6H_5	413–415	65	80.50	80.43	5.63	5.58	7.83	7.75	6.04	6.33
$CH_2{=}CHCH_2$	98–99	78	75.59	75.11	7.05	7.15	9.79	9.87	..	..

B-Trimethyl-N-triphenylborazole displays remarkable stability to boiling water. Refluxing a suspension of this compound in water (solubility, 1 mg./100 ml. at 25°) for one hour led to no appreciable decomposition (97% recovery) while the position isomer, B-triphenyl-N-trimethylborazole under the same conditions (solubility, 2 mg./100 ml. at 25°) decomposed to the extent of 94% as indicated by ultraviolet analysis.[16]

The present investigation demonstrates the feasibility of preparing a variety of substituted borazoles by the coupling reaction, the limitation being the availability of the intermediate chloroborazoles. Extension of this reaction to the preparation of other substituted borazoles and the study of various structural relationships in this class of compounds is currently under investigation in this laboratory.

Acknowledgments.—The authors are indebted to Dr. J. A. Kuck and members of his group, in particular to Mrs. E. C. Grim, for the microanalyses and to Dr. J. E. Lancaster, Dr. R. C. Hirt and Mr. R. G. Schmitt for helpful discussions concerning the infrared and ultraviolet spectra. The authors also wish to thank Dr. W. M. Thomas for his continued interest and for many helpful discussions during the course of this work.

Experimental

Melting points were taken on a Fisher–Johns block and are uncorrected. Boron was determined by oxidation in a Parr bomb, and titration of the boric acid so obtained with standard alkali in the presence of mannitol. The details of this procedure will be published elsewhere.

1. **B-Trichloro-N-triphenylborazole (I).**—This procedure is a modification of that reported by Jones and Kinney.[12] In a 500-ml. three-necked flask, equipped with stirrer, Dry Ice condenser and a Claisen head provided with a nitrogen inlet and a Drierite filled drying tube, was placed 200 ml. of dry toluene (freshly distilled from calcium hydride) and the flask was cooled in an ice-bath. Boron trichloride (50 g., 0.43 mole) was distilled into the flask through the Dry Ice condenser causing a purple-brown color to develop in the toluene solution. After replacing the drying tube with an addition funnel and fitting the exit end of the condenser with a drying tube, a solution of 30.4 g. (0.33 mole) of aniline (freshly distilled from zinc dust) in 100 ml. of dry toluene was added dropwise with stirring over a period of 1 hour. An immediate precipitate of $C_6H_5NH_2{:}BCl_3$ separated from the purple solution. After the Dry Ice condenser was replaced with a water-cooled one, the reaction mixture was refluxed until evolution of HCl and excess BCl_3 had ceased (about 12 hours). During this period the color of the solution had changed from purple to a light brown. Solvent was then distilled off until the product began to separate from solution. After being cooled to room temperature, the nicely crystalline, almost colorless product was collected by rapid filtration. B-Trichloro-N-triphenylborazole was obtained in 73% yield (32.6 g.). Recrystallization from dry benzene (filtered through glass wool) gave colorless crystals, m.p. 270–272°. Since the compound is quite susceptible to hydrolysis it must be stored in a desiccator over a suitable drying agent or under dry benzene or toluene.

2. **B-Tri-*n*-alkyl-N-triphenylborazoles.**—The following procedure is typical for the preparation of the simple B-*n*-alkylborazoles. *n*-Butylmagnesium bromide, prepared in the usual manner from 3.54 g. (0.146 g. atom) of magnesium turnings and 20.1 g. (0.146 mole) of *n*-butyl bromide, was added dropwise over a period of 45 min. to a suspension of 14.1 g. (0.0342 mole) of I in 150 ml. of anhydrous ether. After addition was complete, the mixture was refluxed for 2 hours.[17] With intermittent external cooling (ice-bath) a saturated aqueous NH_4Cl solution was added dropwise to the rapidly stirred reaction mixture.[18] Initially, the mixture turned cloudy, then milky. Gradually, on further addition of the NH_4Cl solution, the salts slowly separated from solution and, finally, at the end-point coagulated and settled rapidly from a clear, nearly colorless ether solution. After being decanted and filtered through anhydrous Na_2SO_4, the ether solution was concentrated to a volume of *ca.* 75 ml. Methanol was added gradually to the boiling ether solution until the crystalline product began to separate. On cooling, there was obtained 11.3 g. of product, m.p. 126–128°, and a second crop, 0.38 g. of the same m.p. The yield of B-tri-*n*-butyl-N-triphenylborazole was 70%. Recrystallization from the same solvent pair raised the m.p. to 129–132°.

The B-trimethyl-, ethyl-, propyl- and allylborazoles were also prepared by this procedure in yields given in Table I.

3. **B-Triisopropyl- and B-Triisobutyl-N-triphenylborazoles.**—For the preparation of these compounds, the above procedure was modified as follows: A diethyl ether solution of the Grignard reagent, prepared from magnesium (3.5 g., 0.14 g. atom) and isobutyl bromide (19.8 g., 0.14 mole) was added to a suspension of I (10.0 g., 0.02 mole) in di-*n*-butyl ether (100 ml.). After addition was complete, diethyl ether was removed *in vacuo* and was replaced with an equal volume of di-*n*-butyl ether (100 ml.). The reaction mixture was heated on a steam-bath for 17 hours and the di-*n*-butyl ether removed by distillation *in vacuo*. After diethyl ether was added to the solid residue, the stirred mixture was titrated with saturated aqueous NH_4Cl solution and the reaction product isolated in the manner described above. In this way a 7.73 g. yield, m.p. 176–178°, was obtained. Two recrystallizations from ether–methanol

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(16) Experimental work by Miss J. A. Hall of this Laboratory.

(17) In general, the mixture separates into a dark, almost black, lower layer and a nearly colorless upper layer.

(18) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Edition, Heath and Co., Boston, Mass., 1955, p. 270.

gave the analytical sample, m.p. 185–187°. Using these conditions, B-triisopropyl-N-triphenylborazole was obtained in 20% yield.

4. **Hexaphenylborazole. a. From Phenylmagnesium Bromide.**—Phenylmagnesium bromide prepared from magnesium (2.36 g., 0.097 g. atom) and bromobenzene (15.2 g., 0.097 mole) in 100 ml. of ether was added to a suspension of I (10 g., 0.024 mole) in ether (100 ml.) as described in 1. At the end of a 2-hour reflux period, the reaction mixture contained solid material. A filter stick was used to remove the supernatant solution and the solid residue, after being washed with several fresh portions of ether, was dried, ground in a mortar and continuously extracted with $CHCl_3$ for a period of 4 hours. After being decolorized with charcoal, the solution was concentrated and the crystalline hexaphenylborazole was collected in three crops; weight 8.5 g., yield 65%. The analytical sample was obtained by two further recrystallizations from chloroform, m.p. 413–415°.

The following alternate procedure for isolating hexaphenylborazole gave lower yields: The reaction mixture was cautiously decomposed with 5% HCl solution. The solid material which was insoluble in both the organic and aqueous layers was collected and recrystallized from chloroform to give a 29% yield of hexaphenylborazole.

b. From Phenyllithium.—To a 500-ml. flask containing a solution of phenyllithium, prepared from 1.46 g. (0.21 g. atom) of lithium shot in 25 ml. of dry benzene and 15.7 g. (0.1 mole) of bromobenzene in 50 ml. of dry ether, was added with stirring a suspension of I (10.3 g., 0.025 mole) in 100 ml. of dry benzene and 200 ml. of dry ether over a period of 45 minutes. A very gentle exothermic reaction ensued causing the separation of a finely-divided solid from a peach-colored solution. The quantity of solid increased with further addition of I. After being refluxed overnight, the reaction mixture was cooled and filtered. During this operation the solid assumed a purple color and the filtrate became blood red. Working up this filtrate in the usual manner furnished a viscous, red residue which was not further investigated. The solid was washed with hot water to remove LiCl and the water-insoluble solid, after air-drying, was recrystallized from $CHCl_3$ to give 2.45 g. (18%) of hexaphenylborazole. Two further recrystallizations from $CHCl_3$ furnished the analytical sample, m.p. 413–415°.

C. Kuivala's Method.[14]—To 187 ml. of a solution of *n*-butyllithium (0.3 molar) in ligroin (b.p. 60–90°) was added with stirring a solution of aniline (4.72 g., 0.054 mole) in 50 ml. of ligroin followed by the dropwise addition of a solution of di-*n*-butyl phenylboronate[19] (0.054 mole) in 50 ml. of ligroin. No temperature change was observed. After another 187 ml. of a solution of *n*-butyllithium (0.3 molar) in ligroin was added, the reaction mixture was stirred at room temperature overnight, followed by a 24-hour reflux. The cooled reaction mixture was filtered and the filtrate refluxed for 24 hours longer without depositing additional solid material. The precipitate was digested with water and the water-insoluble material was collected, dried and recrystallized from $CHCl_3$ to give 0.517 g. (5.3%) of hexaphenylborazole. The infrared and ultraviolet spectra of this material were identical with those of the hexaphenylborazole prepared above.

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(19) K. Torsell, *Acta Chem. Scand.*, **8**, 1779 (1954).

STAMFORD, CONN.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Friedel–Crafts Condensation of *trans*-2-Hydroxycyclohexaneacetic Acid Lactone with Aromatic Hydrocarbons. I. Benzene and Naphthalene

BY DONALD D. PHILLIPS AND D. N. CHATTERJEE[1]

RECEIVED OCTOBER 21, 1957

The lactone I in the title has been condensed with benzene to give an 87% yield of an isomeric acid mixture from which *trans*-4-phenylcyclohexaneacetic acid (II, R = C_6H_5) and a solid mixture of II (R = C_6H_5), 3-phenylcyclohexaneacetic acid (III, R = C_6H_5) and *trans*-2-phenylcyclohexaneacetic acid (IV, R = C_6H_5) have been isolated. The latter has been cyclized and reduced to the octahydrophenanthrol (VII). A similar condensation between lactone I and naphthalene afforded a 45% yield of the corresponding β-naphthylcyclohexaneacetic acids (II, III and IV, R = β-$C_{10}H_7$). The latter (IV) has been cyclized, reduced and dehydrogenated to yield chrysene. A possible mechanism for this abnormal Friedel–Crafts reaction is discussed.

The lactone of *trans*-2-hydroxycyclohexaneacetic acid (I), conveniently prepared[2] from the commercially available cyclohexene oxide, seemed to be particularly suitable[3] as a starting material for the synthesis of polynuclear aromatic hydrocarbons. With this view in mind, we have studied the Friedel–Crafts condensation of this lactone with several hydrocarbons and, in every instance, we have found the reaction to take an unexpected course.

From the aluminum chloride-catalyzed reaction between lactone I and benzene there was isolated an 87% yield of isomeric phenylcyclohexaneacetic acids. By fractional crystallization, this mixture has afforded approximately 15% of pure *trans*-4-phenylcyclohexaneacetic acid (II, R = C_6H_5) and 85% of a mixture of acids, m.p. 70–71°. Although the exact composition of this latter mixture has not been determined, we have been able to show that it contains a small amount of II, R = C_6H_5, about 15% of the *trans-ortho* isomer IV (R = C_6H_5) and a *major* amount of the *meta* isomer III (R = C_6H_5), of unknown stereochemistry.

The structure of the *para* condensation product II (R = C_6H_5) was established both by a comparison with authentic material[4] as well as by dehydrogenation to *p*-phenylphenylacetic acid (V, R = C_6H_5) which was independently synthesized. Although it was not possible to obtain a pure specimen of the *o*-acid IV (R = C_6H_5), its relative concentration in the mixture was established by cyclization to the known octahydrophenanthrone (VIII). The determination of the relative amount of the *meta* isomer (III, R = C_6H_5) in the 70–71° acid mixture was more difficult although its presence in substantial concentrations was clearly indicated by dehydrogenation and oxidation where-

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(1) Fulbright Scholar, 1956–1958; permanent address, Krishnagar College, West Bengal, India.

(2) M. S. Newman and C. A. VanderWerf, THIS JOURNAL, **67**, 235 (1945).

(3) A preliminary report of the use of this lactone in the synthesis of chrysene has been published recently; D. D. Phillips, *Chemistry & Industry*, 54 (1956).

(4) L. F. Fieser, *et al.*, THIS JOURNAL, **70**, 3190 (1948). We are grateful to Dr. H. E. Zaugg of Abbott Laboratories for a sample of this acid.