

dioxide was evolved. The mixture was slowly heated to 180°. The resulting clear melt was dissolved in 35 ml. of boiling absolute ethanol and cooled. The fine needles of the alcoholate were recrystallized again and dried to constant weight at 105°. The white salt was soluble in benzene and tetralin.

*Anal.* Calcd. for  $C_{14}H_{22}O_4Pb$ : Pb, 45.09. Found. Pb, 44.61, 44.77.

Attempts to prepare lead 2-ethylhexanoate by the same method gave a liquid salt of only 97% purity.

*Manganous 3-cyclohexanepropionate.* A mixture of 8.13 g. (0.052 mole) of 3-cyclohexanepropionic acid and 2.88 g. (0.025 mole) of manganous carbonate was heated for 12 hr. on a steam bath, then the temperature of the melt was raised to 175°. Most of the excess acid was removed by distillation at 40 mm. The residue was dissolved in boiling benzene and filtered from unreacted manganous carbonate (0.4 g.). After clarification with infusorial earth the solution was poured into three times its volume of ethyl acetate. The precipitated pink salt, now insoluble in organic solvents, was dried at 40°.

*Anal.* Calcd. for  $C_{15}H_{20}O_4Mn$ : Mn, 15.05. Found. Mn, 15.39, 14.45.

Manganous cyclohexanecarboxylate could not be obtained in pure condition by use of this method with manganous acetate.

*Cobaltous 2-ethylhexanoate.*<sup>12,13</sup> To a mixture of 8.65 g. (0.06 mole) of 2-ethylhexanoic acid, 10.3 g. of petroleum ether b.p. 90–100° and 2.4 g. of distilled water heated to 75° was added slowly with stirring 7.1 ml. of 8.4*N* sodium hydroxide, followed by a filtered solution of 9 g. (0.0032 mole) of cobalt sulfate,  $CoSO_4 \cdot 7H_2O$ , dissolved in 10.3 ml.

of water at 75°. After 1 hr. at 75°, the two layers were separated. The top heptane layer was washed twice with water, the solvent distilled off, the residue treated with heptane to dissolve the organic salt. After filtration, with use of filter-aid, and removal of solvent, the product was a dark purple plastic material.

*Anal.* Calcd. for  $C_{16}H_{26}O_4Co$ : Co, 17.10. Found. Co, 17.44, 17.44.

*Kinetic studies.* The all-glass apparatus was arranged for passage of nitrogen through the reaction mixture, which served to stir it, as well as through the introducing funnel. Care was taken to bring reactants to the temperature of the bath before mixing. The zero peroxide value was determined immediately before contact with the salt. Analyses for peroxide were done by the method of Wagner, Smith, and Peters.<sup>14</sup>

*Free radical nature of the decompositions.* Proof of the presence of free radicals was that in a mixture of  $2.35 \times 10^{-4}$  mole of tetralin hydroperoxide,  $3 \times 10^{-7}$  mole of cobaltous 2-ethylhexanoate and  $1.8 \times 10^{-3}$  mole of styrene, 9% of the styrene was polymerized<sup>15</sup> after 22 hr. at 25.5° to a polymer of limiting viscosity number 71 (in benzene), whereas a control did not polymerize.

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NEWARK, DEL.

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(15) Done by Dorothy A. Delker.

(12) L. Roon and W. Gotham (to Nuodex Products Co.), U. S. Patent **2,113,496**, Apr. 5, 1938.

(13) Preparative details kindly furnished by Dr. J. T. Kingsbury, Harshaw Chemical Co.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY

## Influence of Alkoxides and the Dimetalation of Some Alkylaryl Hydrocarbons<sup>1</sup>

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Cumene, *t*-butylbenzene, *n*-butylbenzene, toluene, and *p*-cymene were dimetalated by amylsodium in the presence and absence of various sodium alkoxides or sodium oxide. The percentage of disubstitution was higher with *n*-butylbenzene and toluene where both nuclear and lateral metalation occurred, than in cumene and *t*-butylbenzene where nuclear metalation only took place. Sodium 2-methyl-2-heptoxide accelerated metalation and favored dimetalation. A cyclic hexoxide repressed dimetalation. *p*-Cymene was dimetalated at a lateral and either of the two nuclear positions available in spite of some hindrance at the latter places. The compositions of the reacting mixtures changed slowly during storage, even over a year.

The high percentage of 1,4-polymerization of butadiene induced by the Alfin catalyst<sup>2,3</sup> has demonstrated the unusual and powerful influence of certain associated salts upon organosodium reagents. An effect has been realized also in common alkylation,<sup>4</sup> ether cleavage,<sup>5</sup> and metalations.<sup>6,7</sup>

For this class of reagent, therefore, the use of associated salts to modify or alter reactions is as important as are changes in concentration, temperature, and solvent to more common chemical reagents. The present study of dimetalation and of the effect of alkoxides extends our information of this type of control and of the factors favorable to dimetalation.

(1) This work was performed as part of a research project sponsored by the National Science Foundation.

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(3) A. A. Morton, *Advances in Catalysis IX*, Academic Press, Inc., New York, 1957, p. 743.

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The alkali metal reagent used in most of these experiments was amylsodium. To it was added either (a) an alcohol, water, or glycol to form the associated salt *in situ* or (b) commercial sodium oxide. An alkylaryl hydrocarbon was added next. In a few cases the reaction was completed at 60° for 3 hr. Most of the time, however, the temperature was that attained by the friction of high-speed stirring for 3 hr. and, thereafter, by storage for many months. Aliquots were removed occasionally, carbonated, and analyzed for acids—dicarboxylic, aromatic monocarboxylic, and caproic. The proportions of these always changed and, after many months, reached near constant values in spite of the insolubility, or extremely low solubility, of the reagents.

Two other metalating agents were used but without success in dimetalation. Potassium and sodium oxide<sup>8</sup> metalated the alpha carbon atom of cumene but failed to dimetalate that hydrocarbon by attacking also the nucleus. The result is understandable in view of the preference of the potassium ion for the side chain.<sup>9</sup> Phenylsodium failed to metalate itself in a disproportionation process which would have given a disodium product. Previously<sup>10</sup> a similar effort with *m-t*-butylphenylsodium failed.

The hydrocarbons tested were cumene, *t*-butylbenzene, *n*-butylbenzene toluene, and *p*-cymene. The first pair (a, Fig. 1) was dimetalated at the 3,5-positions. On long standing the amounts of these nuclear dimetalated products decreased,

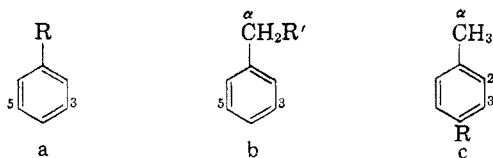
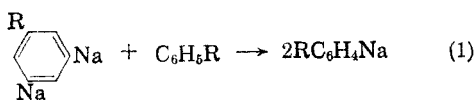


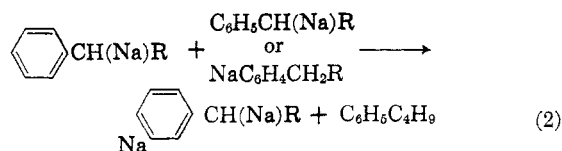
Fig. 1. Positions of dimetalation in different hydrocarbons. A signifies isopropyl or *t*-butyl. A signifies H or *n*-C<sub>3</sub>H<sub>7</sub>.

when sodium 2-methyl-2-heptoxide was present, in favor of the monometalated compound as per Equation 1. The second pair (b, Fig. 1) was



dimetalated at the  $\alpha,3$ -positions except that two aliquots from *n*-butylbenzene gave minute amounts of a dicarboxylic acid assumed to be the 3,5-product. The yields of dimetalated product were higher than with the first pair. On long standing the yield of  $\alpha,3$ -product from *n*-butylbenzene increased

as per Equation 2. With toluene also the yield of dimetalated product increased during storage, but



where R = *n*-C<sub>3</sub>H<sub>7</sub>

part, or all, of that change could be attributed to metalation by amylsodium.

*p*-Cymene (c, Fig. 1) was dimetalated at a lateral (methyl) and nuclear (2- or 3-) position. Nuclear metalation was unexpected because no position is available except ortho to a sodiomethyl (NaCH<sub>2</sub><sup>-</sup>) or to an isopropyl group, and in separate compounds (benzylsodium<sup>11,12</sup> and cumene) these ortho positions have been relatively inactive. The combined effect of these two groups in *p*-isopropylbenzylsodium did not prevent dimetalation when no other position on the nucleus was available.

The alkoxide influence upon metalation of the first three hydrocarbons (the only ones tested comparatively) was striking. In the tests at 60° upon cumene, sodium 2-methyl-2-heptoxide caused the highest yield. Sodium pinacolate, sodium 1-methylcyclohexoxide, and sodium hydroxide caused progressively less dimetalation just as they had done<sup>6</sup> in the case of *t*-butylbenzene. Data for both hydrocarbons are shown in Table I.

TABLE I  
COMPARISON OF OXIDE INFLUENCE IN THE DIMETALATION OF CUMENE AND *t*-BUTYLBENZENE AT 60°

Sodium Salt of <sup>a</sup>	Cumene		<i>t</i> -Butylbenzene	
	Total <sup>b</sup> Acid, %	Di <sup>c</sup> Acid, %	Total <sup>b</sup> Acid, %	Di <sup>c</sup> Acid, %
Hep.	61	46	67	37
Pinacol	68 <sup>d</sup>	40	75 <sup>d</sup>	34
Cy.	63	39	51	29
Water	46	29	41	14

<sup>a</sup> The abbreviations refer to 2-methyl-2-heptanol and 1-methylcyclohexanol. <sup>b</sup> Total acid means the sum of the carboxyl groups in the diacid and all monocarboxylic acids. <sup>c</sup> This value represents the percentage of the total carboxyl groups present in the diacid. <sup>d</sup> This value is high because pinacol does not react completely with amylsodium, that is to say all of the hydroxyl hydrogens do not react.

The influence of alkoxides in reactions carried out at a lower temperature (that attained by the friction of stirring) and, thereafter, during months of storage is shown in Table II. The two controls at the top and bottom of the table did not vary greatly, certainly no more than might be expected from the

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TABLE II

CONSUMPTION OF AMYLSODIUM AND PERCENTAGE OF DICARBOXYLIC ACID ATTAINED DURING DAYS OF STORAGE WHEN METALATING SOME ALKYLARYL HYDROCARBONS IN THE PRESENCE OF DIFFERENT OXIDES

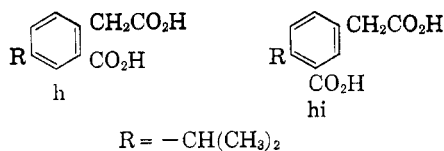
Oxide <sup>a</sup>	Days storage (S), Amylsodium (A), total carboxyl (T), Dicarboxylic acid (D) <sup>b</sup> with		
	Cumene	<i>t</i> -Butylbenzene	<i>n</i> -Butylbenzene
None	S- A- T- D	S- A- T- D	S- A- T- D
	0-58-80- 4	0-61-43- 3	0-50-77- 0
	20-25-71-20	13-43-75-10	97- 1-67-57
	50- 4-64-35	34- 4-73-22	191- 3-65-55
	104- 1-62-44	64-10-70-27	260- 3-68-67
Na <sub>2</sub> O	272- 1-62-44	204- 3-67-27	
	422- 0-56-43	382- 1-66-29	
	0-74-74- 4	0-86-79- 0	0-81-78- 0
	28-44-73-14	97-14-59-21	119- 2-67-44
	101- 2-61-38	119- 9-62-23	226- 2-62-62
Hep.	189- 1-58-50		
	283- 2-56-49		
	0- 1-45-24	0- 2-64-53	0- 0-54-57
	35- 1-64-30	14- 0-60-57	90- 0-53-58
	85- 0-50-12	78- 1-59-42	226- 1-53-82
Cy.	106- 0-52- 9	218- 0-58-47	
	366- 2-52- 9	313- 1-54-40	
	0-35-67- 5	0-28-69- 2	0-28-68- 4
	35- 9-61-10	30-22-68- 5	96-13-65-20
	79- 7-57-18	99- 8-67- 6	189- 4-62-14
None or Na <sub>2</sub> O as shown	261- 6-55-13	223-13-60- 9	263- 6-64-38
	398-10-54-19	385-14-60-12	
	Cumene (None) <sup>c</sup>		Toluene (Na <sub>2</sub> O) <sup>d</sup>
	S- A- T- D		S- A- T- D
	0-45-77- 7		0-69-81- 8
Na <sub>2</sub> O as shown	32-39-75-18		94- 4-70-53
	63- 8-69-36		
	138- 1-56-49		
	343- 1-47-50		

<sup>a</sup> Hep. refers to sodium 2-methyl-2-heptoxide; Cy. refers to sodium cyclohexoxide. <sup>b</sup> The four columns under each hydrocarbon represent in order (S) the days of storage before an aliquot was removed for analysis, (A) the percentage of amylosodium judged by recovery of caproic acid and referred to the moles of amyl chloride less the moles of whatever alcohol was added, (T) the total percentage of carboxyl group as determined by titration of an aliquot of a solution of all of the acids and referred to the same basis of amyl chloride minus alcohol if added and (D) the proportion of these carboxyl groups which were in the dicarboxylic acid isolated. These values were those observed and any discrepancies such as differences in the amounts of amylosodium after days of storage (for example no amylosodium after 85 and 106 days followed by 2% after 366 days in the heptoxide-cumene series) where amylosodium seemed to reappear, indicate only the limit of error in the measurements. <sup>c</sup> This none-cumene series is a second control test identical with the first one except that less cumene was used. The proportion of dicarboxylic acid is, on the average, a little higher than in the first control, as would be expected. <sup>d</sup> This test with toluene in the presence of sodium oxide parallels roughly the sodium oxide-*n*-butylbenzene series.

higher ratio (by twice) of amylosodium to cumene in the latter. Neither did the presence of sodium oxide alter the results significantly. 2-Methyl-2-heptoxide, however, caused the consumption of amylosodium by all three hydrocarbons to be virtu-

ally complete by the end of stirring (marked as zero time of storage in the table). Thereafter a small rise in the proportion of dicarboxylic acid took place at first with all three hydrocarbons followed by a decline with the first two. With *n*-butylbenzene, this proportion continued to increase substantially, possibly because nuclear and lateral metalations took place. Sodium cyclohexoxide acted differently. Amylosodium was still unconsumed even after a year. The proportion of dimetalation was low even in *n*-butylbenzene which had proven generally favorable to dimetalation. The evidence for specific influences by associated salts seems clear.

The tests on *p*-cymene were made in the presence of sodium oxide which had had no adverse influence in dimetalation and might have helped a little with cumene. A dicarboxylic acid had been obtained before<sup>11</sup> but no structure had been suggested. In the present case two diacids were obtained in about equal amounts. The assignment of structures was made on the basis that monometalation occurs at the methyl<sup>8,11</sup> rather than the isopropyl group. The second metalation had to occur on the nucleus because infrared absorptions were at 1712-1705 and 1692-1683 cm.<sup>-1</sup> characteristic for aliphatic and aromatic carboxyl. In accord with Sudborough's<sup>18</sup> findings (that aliphatic carboxyl esterifies faster than aromatic) partial esterifications yielded half esters, which absorbed in the infrared at 1740-1736 cm.<sup>-1</sup> (aliphatic carbomethoxy) and at 1690 cm.<sup>-1</sup> (aromatic carboxyl). Finally the diesters absorbed at 1741-1740 and 1726-1723 cm.<sup>-1</sup> characteristic for aliphatic and aromatic carbomethoxy, respectively. The only diacid which yielded a crystalline anhydride must be 4-isopropylhomophthalic (h). The other diacid must be 4-isopropylhomoisophthalic (hi).



The dimetalation of *p*-cymene demonstrates that amylosodium was powerful enough to overcome some resistance to a second metalation when no other alternative existed, but this result does not prove that the reagent is all-powerful and will metalate always at some position. In a previous paper<sup>10</sup> no second metalation occurred on *p*-*t*-butylphenylsodium. There a larger alkyl group and a sodium ion directly on the nucleus closed off the area on the nucleus where a second metalation might have taken place.

As a means of obtaining bifunctional systems (either disodium or dicarboxyl) which can be used subsequently in polymerization or other reactions, the dimetalation of alkylaryl hydrocarbons with

unbranched side chains seems preferred. A tertiary alkoxide hastens the process, and, according to the previous paper<sup>6</sup> (but not tested in the present work) a potassium alkoxide would further benefit dimetalation.

#### EXPERIMENTS

*Metalation at 60°.* Amylsodium was prepared at  $-10^{\circ}$  in heptane from one gram atom of sodium metal and 0.5 mole of amyl chloride in the manner regularly employed<sup>14</sup> in this laboratory. The alcohol (0.2 mole) was added dropwise at  $0^{\circ}$  over 15 min. but the mixture was stirred 30 min. more in order to ensure completion of the reaction. The hydrocarbon (0.15 mole) was added next and the temperature raised as rapidly as possible to  $60^{\circ}$ . Stirring was maintained at 5000 r.p.m. at  $60^{\circ}$  for 3 hours. Then the mixture was cooled to room temperature and the contents of the flask forced by nitrogen pressure onto solid carbon dioxide. The next day more carbon dioxide followed by water was added. The aqueous layer was separated and the hydrocarbon layer was extracted with alkali to recover all sodium carboxylates. The combined aqueous portions were extracted with ether, then the aqueous layer was acidified. The precipitate and water layer were extracted with ether and the ether solution was dried over Drierite. The dried ether solution was diluted to 500 ml. and a 5-ml. aliquot titrated to determine the total acid. The rest of the ether solution was evaporated to a small volume on a steam bath. Petroleum ether (200 ml.) was added and the mixture was allowed to stand overnight. The next day the precipitated crude dicarboxylic acid was recovered, dried, and weighed. This crude light tan colored product was recrystallized from water or ethanol-water mixture. The white crystalline 5-isopropylisophthalic acid melted at  $282-286^{\circ}$  (literature<sup>7,15</sup>  $285^{\circ}$ ). The infrared spectra showed a broad band at 1695 to  $1681\text{ cm.}^{-1}$  The dimethyl ester made from methanol with sulfuric acid melted at  $64-65^{\circ}$  and showed a single band at  $1724\text{ cm.}^{-1}$

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{16}\text{O}_4$ : C, 66.10; H, 6.78. Found: C, 66.18; H, 6.84.

The petroleum ether portion was evaporated to one-half its volume and cooled. *p*-Isopropylbenzoic acid (cuminic acid) separated. It melted at  $116-119^{\circ}$  (recorded<sup>11,16</sup>  $116-118^{\circ}$ ) and showed a band at  $1681\text{ cm.}^{-1}$  The amide melted at  $150-153^{\circ}$  (recorded<sup>16,17</sup>  $153^{\circ}$ ). The methyl ester distilled at  $82-83^{\circ}$  at 2 mm. (recorded<sup>18</sup>  $126^{\circ}$  at 14 mm.) and absorbed in the infrared at  $1725\text{ cm.}^{-1}$

The percentages of total carboxylic acid from the four experiments were 61 (300 meq. of carboxyl) in the presence of sodium 2-methyl-2-heptoxide, 68 with the sodium pinacolate, 63 with sodium 1-methylcyclohexoxide, and 46 with sodium hydroxide. These percentages were based on the amyl chloride originally used less the mole equivalent of hydroxyl added, and appropriate corrections were made for any aliquots removed for analysis. Actually these percentages are low because the conversion of amyl chloride to amylna-sodium is not 100% but nearer 85 or 90%. The corresponding proportions of carboxyl groups as dicarboxylic acid were 46, 40, 39, and 29%.

*Metalations during storage in the presence of sodium 2-methyl-2-heptoxide and sodium cyclohexoxide.* In all cases the

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(17) L. Gattermann and G. Schmidt, *Ann.*, **244**, 52 (1888).

(18) L. Bert, *Bull. soc. chim.*, **37**, 1404 (1925).

reagents were used in the amounts described below or in some proportion of those amounts. Amylsodium was prepared from 3 g.-atoms of sodium and 1.5 mole of amyl chloride in heptane as described before. The alcohol (0.6 mole) was added dropwise over 20-30 min. at  $0^{\circ}$ . One hour after the first of the alcohol had been added 0.45 mole of the hydrocarbon was added and the mixture was stirred for 3 hr. with no attempt to control the temperature. During that time the temperature usually rose to  $39$  or  $45^{\circ}$ . Next the mixture was forced by nitrogen pressure into a calibrated gallon jug which had been heated and swept out with a current of dry nitrogen. The jug was stoppered by a cork and sealed with a glyptal cement. At appropriate times aliquots were removed immediately after the jug had been vigorously shaken by hand. The usual procedure was to force the suspension upward by nitrogen pressure into a 100-ml. pipet which had a wide tip. Each aliquot was run onto solid carbon dioxide. Thereafter the separation of di and mono acids was the same as described in the previous section except that one-fifth of the volumes of solvents was used. In a few cases the crude diacid was gummy and was determined by titration rather than by weighing. In all cases, however, pure diacid was obtained eventually by crystallization. The mixture of mono acids which was recovered from the petroleum ether solution was fractionated to determine the amount of caproic acid. The mixture of meta and para monosubstituted benzoic acids was not separated but was examined by infrared spectra. No significant changes indicative of ortho or of lateral metalations were noted.

The constants of the acids separated after the metalation of cumene have been described in the previous section. In each case the identity of the acid obtained was assured by mixed melting point with an authentic sample or by infrared measurement.

From the metalation of *t*-butylbenzene crystals of 5-*i*-butylisophthalic acid, m.p.  $>300^{\circ}$ , were recovered. The dimethyl ester melted at  $97-98^{\circ}$  (recorded<sup>6</sup>  $99^{\circ}$ ).

From *n*-butylbenzene (0.124 mole) the dark green suspension yielded by carbonation *n*-butylbenzene- $\alpha$ , $\beta$ -dicarboxylic acid which melted at  $157-160^{\circ}$  after crystallization from hot water. The neutralization equivalent was 109 (calcd. 111). Infrared absorptions at 1705 and  $1685\text{ cm.}^{-1}$  were characteristic for aliphatic and aromatic carboxyl, respectively.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}_4$ : C, 64.86; H, 6.31. Found: C, 64.88; H, 6.47.

Only one diacid was present because fractional esterification of 0.233 g. with methanol and sulfuric acid for 3 hr. gave 43% of an oily half ester and 36% of diester. Each fraction when saponified yielded the original diacid as shown by unchanged melting points and mixed melting points.

A sample of this diacid was oxidized by potassium permanganate to isophthalic acid which sublimed around  $300^{\circ}$  and yielded a *p*-bromophenacyl ester which melted at  $187-190^{\circ}$  (recorded<sup>19</sup>  $186^{\circ}$ ). This isophthalic acid showed absorption at  $1703-1670\text{ cm.}^{-1}$  identical with that for an authentic sample.

*Metalation of the three hydrocarbons by amylna-sodium and the 3,5-dimetalation of n-butylbenzene.* These control reactions were carried out with the reagents in the proportions of (and usually with amounts equal to) 3 g.-atoms of sodium, 1.5 moles of amyl chloride, and 0.72 mole of hydrocarbon in heptane in a 3-liter creased flask. In the second control reaction with cumene (bottom of Table II) the amount of cumene was only 0.45 mole in order to double approximately the ratio of amylna-sodium to cumene.

All carboxylic acids derived by carbonation were the same as described in the previous section except that the first aliquot from the metalation of *n*-butylbenzene yielded a dicarboxylic acid in the petroleum ether soluble portion.

(19) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 3rd ed., John Wiley and Sons, Inc., New York, 1948.

This mixture was distilled to remove caproic acid and the dicarboxylic acid crystallized in the residue. These crystals, when reprecipitated from a mixture of petroleum ether and ethyl ether, yielded 0.06 g. of a dicarboxylic acid which melted at 226–229°, and depressed the melting point of the other diacid from this hydrocarbon. The neutralization equivalent was 114 (calcd. 111). The infrared spectrum showed absorption at 1698–1681  $\text{cm}^{-1}$  similar to that from 5-isopropylisophthalic acid derived by dimetalation of cumene. A few milligrams of this same acid were recovered from the third aliquot from dimetalation in the presence of cyclohexoxide.

*Metalation in the presence of sodium oxide.* The proportions of (and usually the amounts of) reagents were 3 g.-atoms of sodium, 1.5 mole of amyl chloride, 0.5 mole of sodium oxide, and 0.75 mole of the hydrocarbon. The sodium oxide (Du Pont) was added at 0° after preparation of amylsodium was completed. The hydrocarbon was added immediately after the oxide. All other operations including the separation of the carboxylic acids were the same as described in previous paragraphs.

*Cumene, potassium, and sodium oxide.* The reagents were used in the proportions of 8.5 g. (0.22 g.-atom) of potassium, 56 g. (0.9 mole) of sodium oxide, and 250 ml. of cumene. All operations were essentially the same as described in an earlier publication,<sup>8</sup> except that the reaction mixture, after the usual period of stirring at 90°, was stored in a bottle. The yield of  $\alpha$ -phenylisobutyric acid (m.p. 79–81°, recorded<sup>8,20</sup> 80–81°) after metalation with 3-hr. stirring was 7%. After 74 days storage at room temperature the yield was still 7%. No dicarboxylic acid was recovered.

From a second experiment at 90° for 14 hr. the yield from the first aliquot, taken immediately after transfer to the storage bottle, was 30% (7 meq. from a 100-ml. aliquot). After 44 and 268 days storage the amount from 100-ml. aliquots was 36% (9 meq.) within experimental error virtually unchanged. The infrared absorption of the acid in all cases was at 1691  $\text{cm}^{-1}$  typical for an aliphatic carboxyl. The methyl ester, made by esterification with methanol and sulfuric acid boiled at 81–86°/5 mm.; 220°/760 mm. (recorded<sup>21</sup> 225°/760 mm.). It absorbed strongly at 1738  $\text{cm}^{-1}$ , as expected for an aliphatic carbomethoxy group. No trace of nuclear metalation was observed.

*Metalation of toluene by amylsodium and sodium oxide.* The respective quantities of reagents were 1 g.-atom of sodium, 0.5 mole of amyl chloride, 0.167 mole of sodium oxide, and 0.25 mole of toluene, all in heptane as in the other experiments. At the end of the 3-hr. stirring period the reaction temperature was 37°. The dark green suspension was stored but only two aliquots were removed for analysis. From each homoisophthalic acid, which melted at 183–186° (recorded<sup>12</sup> 184–185°), was the sole dicarboxylic acid obtained.

*Attempted disproportionation of phenylsodium.* The quantities of reagents were 1 g.-atom of sodium, 0.5 mole of chlorobenzene, and 0.17 mole of sodium oxide per 500 ml. of heptane. The mixture was heated 5 hr. at 60°. Carbonation yielded 374 meq. (75%) of benzoic acid, m.p. 120–122°.

*Metalation of p-cymene.* The proportion of reagents was 1-g. atom of sodium, 0.5 mole amyl chloride, 0.167 mole of sodium oxide, and 0.25 mole (33.6 g.) of p-cymene. The medium was heptane. After 3 hr. stirring with p-cymene at 60° the light green reaction mixture was forced onto solid carbon dioxide. All of the carboxylic acids were dissolved in 500 ml. of ether as described for the metalation of cumene. Titration of a 5-ml. aliquot showed that the carboxyl groups were equivalent to 60.4% of the amyl chloride originally used. Evaporation of the remainder of the solution to about one-half its volume caused the precipitation of a dicarboxylic acid (later judged to be 4-isopropylhomophthalic acid) which was insoluble in petroleum ether and in hot water. The crystals were washed in ice cold ether and the washings

were added to the mother liquor which was again concentrated to obtain more of the same crystals. Repeated use of this technique yielded 9.4 g. of a dicarboxylic acid which accounted for 26% of the total carboxyl groups. This acid, after recrystallization from ether, melted at 190–193°. The neutralization equivalent was 112 (theory 110). The infrared spectra showed bands at 1712 and 1683  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}_4$ : C, 64.86; H, 6.31. Found: C, 65.06; H, 6.27.

A sample of this acid was allowed to stand for 16 hr. at room temperature in methanol with a little concentrated sulfuric acid. The mixture was poured into ice water and the ester extracted with ether, which in turn was extracted with sodium bicarbonate solution to remove the half ester. The aqueous solution was acidified and the half ester, after being recrystallized from methanol-water melted at 118–119°. The yield was 0.62 g. or 58%. Infrared absorptions at 1740  $\text{cm}^{-1}$  and 1690  $\text{cm}^{-1}$  indicated respectively an aliphatic ester and aromatic carboxyl.

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{16}\text{O}_4$ : C, 66.10; H, 6.78. Found: C, 65.91; H, 7.10.

The dimethyl ester boiled at 134–139°/2 mm.,  $n_D^{25}$  1.5249. The infrared absorptions at 1740  $\text{cm}^{-1}$  and 1723  $\text{cm}^{-1}$  agreed with reported<sup>22</sup> values for aliphatic and aromatic esters.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{18}\text{O}_4$ : C, 67.20; H, 7.20. Found: C, 67.33; H, 7.32.

A small sample of this diacid was heated in acetic anhydride until dissolved. Platelets of the anhydride separated from the cooled solution. The m.p. was 87–88°. Infrared bands at 1759  $\text{cm}^{-1}$  and 1803  $\text{cm}^{-1}$  coincided with those for known anhydrides.<sup>22</sup>

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{12}\text{O}_3$ : C, 70.52; H, 5.89. Found: C, 70.45; H, 5.99.

The separation of the isomeric acid, 4-isopropylhomoisophthalic acid, was achieved by evaporation of the mother liquor from the first separation. The thick brown oily residue was heated in a Claisen flask at 150–160°/2 mm. in order to remove a small amount of caproic acid. Crystallization proved difficult but the sticky brown amorphous mass was heated with 200 ml. of water until well dispersed. When this aqueous extract and suspension was cooled a brown oil separated. The supernatant aqueous layer, while still warm, was decanted from the oil and the latter was subjected to another treatment with hot water. Three extractions of the oil were made in this manner. The combined extracts were evaporated to 250 ml. and cooled. The tan colored precipitate was recrystallized from ethanol water. The crystals melted at 167–169° and depressed the melting point when mixed with the other isomer. The neutralization equivalent was 114 (calcd. 111). The infrared absorption bands were at 1705 and 1692  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}_4$ : C, 64.86; H, 6.31. Found: C, 65.28; H, 6.36.

The half ester made from 1.13 g. of the acid in 15 ml. of methanol with 0.7 ml. of concentrated sulfuric acid for 72 hr. (26% yield) melted at 86–87° and had a neutralization equivalent of 237 (calcd. 236). The infrared absorptions were at 1736 and 1690  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{16}\text{O}_4$ : C, 66.10; H, 6.78. Found: C, 66.21; H, 7.02.

The diester boiled at 131–132°/2 mm.,  $n_D^{25}$  1.5103. The infrared absorptions were at 1741 and 1726  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{18}\text{O}_4$ : C, 67.20; H, 7.20. Found: C, 68.25; H, 7.35.

Treatment of the diacid with hot acetic anhydride yielded crystals of the original acid in 90% yield instead of an anhydride.

*Fractional esterifications.* Many of the conclusions about the positions of carboxyl groups were made after observing the esterification under conditions favorable for making

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