[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Hydrocarbo Acidity and Metalation[1]

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Received January 20, 1956

(1) Preparation of the sodium compound from reaction of either *meta*- or *para-tert*-butylchlorobenzene with sodium gives only the respective *m*- or *p-tert*-butylbenzoic acid as the end-product from carbonation.

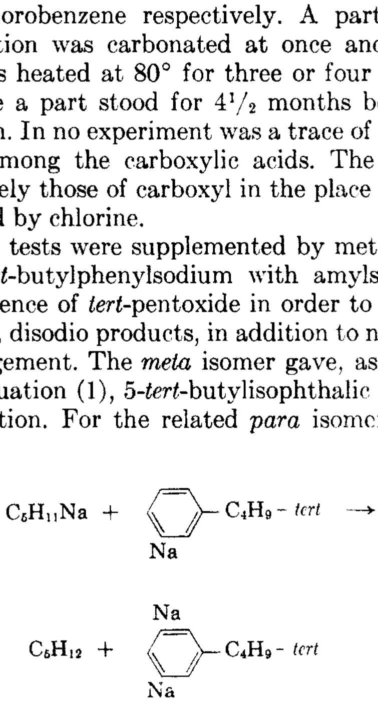
(2) *p-tert*-Butylphenylsodium is not metalated by amylsodium but its *meta* isomer is converted to *tert*-butyl-3,5-disodiobenzene isolated as the carbonation product 5-*tert*-butylisophthalic acid.

(3) No intramolecular change of sodium from the *para* to the *meta* position or the reverse occurs under the conditions previously used for metalation of *tert*-butylbenzene.

A rule which seems reasonable for metalation by hydrogen displacement is that the salt of the strongest acid should form. A previous paper[2] emphasized this principle, and a large number of processes have been interpreted on this basis. Among these are the reaction of butyllithium with bromodiphenylsulfones,[3,4] the generally decreasing ease of metalation of toluene, ethylbenzene, xylenes, and cumene by amylsodium,[5,6,7] ethylpotassium[8] or potassium-sodium oxide,[9] the decreasing reactivity of triphenylmethane, diphenylmethane, and toluene toward potassium or sodium,[10] the general variation in reactivity of numerous hydrocarbons with potassium-sodium oxide[9] and especially the preference of methyl over isopropyl in the displacement of hydrogen from *p*-cymene.[9] However the rule is not followed invariably. In reactions upon solid surfaces and by aggregates of ions, other factors probably steric, sometimes override the acidity influence. Already the metalations of cumene by amylsodium[5,6] and by potassium-sodium oxide[9] are known to take place at different positions which cannot have identical acidities. The metalation of fluorene by potassium hydroxide[11] appears out of the ordinary. The metalation of *tert*-butylbenzene[12] at the *para* and *meta* positions does not follow strictly the rule because the influence of the *tert*-butyl group would leave the *meta* hydrogen more acidic than the *para*. Alkoxides had a great[12] influence in that reaction. Generally they shifted metalation toward the *para* position, but always a mixture of *meta* and *para* acids, subsequent to carbonation, was obtained. These alkoxides might be supposed to induce fast metalation at opportune positions. Had time allowed, intramolecular changes might have corrected the supposed abnormality and increased the proportion at the *meta* position. The change seems simple. A hydrogen in the *tert*-butylphenyl anion would need to shift only to the adjacent carbon and the change would be favored by the respective acidities.

The present work shows, to the contrary, that intramolecular metalation does not occur under the conditions of these particular experiments. *Para*- and *meta-tert*-butylphenylsodium were prepared separately from sodium with *para*- and *meta-tert*-butylchlorobenzene respectively. A part of each preparation was carbonated at once and another part was heated at 80° for three or four hours. In one case a part stood for $4^1/_2$ months before carbonation. In no experiment was a trace of an isomer found among the carboxylic acids. The products were solely those of carboxyl in the place originally occupied by chlorine.

These tests were supplemented by metalation of each *tert*-butylphenylsodium with amylsodium in the presence of *tert*-pentoxide in order to obtain, if possible, disodio products, in addition to noting any rearrangement. The *meta* isomer gave, as expected from equation (1), 5-*tert*-butylisophthalic acid after carbonation. For the related *para* isomer to have



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[1] This work was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] Morton, *Chem. Revs.*, **35**, 1 (1944).

[3] Morton and Cluff, *J. Am. Chem. Soc.*, **74**, 4056 (1952).

[4] Truce and Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951).

[5] Morton, Massengale, and Brown, *J. Am. Chem. Soc.*, **67**, 1620 (1945).

[6] Morton and Little, Jr., *J. Am. Chem. Soc.*, **71**, 487 (1949).

[7] Morton, Little, Jr., and Strong, Jr., *J. Am. Chem. Soc.*, **65**, 1339 (1943).

[8] Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

[9] Claff and Morton, *J. Org. Chem.*, **20**, 981 (1955).

[10] Morton and Ramsden, *J. Am. Chem. Soc.*, **70**, 3132 (1948).

[11] Morton, Claff, Jr., and Kagan, *J. Am. Chem. Soc.*, **76**, 4556 (1954).

[12] Morton, Claff, Jr., and Collins, *J. Org. Chem.*, **20**, 428 (1955).

produced a disodium compound, the second sodium atom would have had to enter *ortho* to sodium or to the *tert*-butyl group, or sodium would have had to shift from *para* to *meta* so that the second sodium could enter the other *meta* position. Neither change occurred because no dicarboxylic acid was obtained from the attempted metalation of the *p*-sodio isomer. Moreover the mono-acid fraction from the metalation of each sodium compound showed no trace of the other isomer. These experiments confirm the results of the first series and show that a *tert*-pentoxide is not effective in inducing an intramolecular change.

These facts show that all the dicarboxylic acid ultimately produced from the metalation of *tert*-butylbenzene under these and the previous[12] conditions came from an initial metalation in one *meta* position followed by a second metalation in the other *meta* position. Once a sodium atom entered either a *meta* or *para* position no intramolecular interchange with the hydrogen on an adjoining carbon took place. Neither did two *m-tert*-butylphenylsodium compounds disproportionate to 5-*tert*-butylphenyldisodium-1.3 and *tert*-butylbenzene.

EXPERIMENTS

p-tert-Butylchlorobenzene. A mixture of 359 g. (4.85 moles) of *tert*-butyl alcohol and 1090 g. (9.75 moles) of chlorobenzene was stirred magnetically in a 4 l. flask while 260 g. (1.95 moles) of anhydrous aluminum chloride was added in small portions, according to the general method of Tsukervanik.[13] The mixture then was heated on the steam-bath for 90 minutes. Water was added cautiously and the organic layer was washed with dilute sodium hydroxide and with water. Fractionation of the dried product yielded 422 g. (65%) which boiled from 202–230° and was approximately 27% *meta-* and 73% *para-tert*-butylbenzene, as judged later by an infrared comparison with the pure chloro hydrocarbons. A trace of the *ortho* isomer was probably present also.

The pure *para* isomer was obtained from this mixture by fractionation of 400 g. through a 6 × 900 mm. Podbielniak spinning band column and then crystallizing the final 120 ml. from an equal volume of pentane cooled in an acetone bath by solid carbon dioxide. After the third crystallization and a distillation through a ten inch Holtzman column, the pure *p-tert*-butylchlorobenzene boiled at 217°, melted at 23.0–24.5° and had $n_{\rm D}^{25}$ 1.5081. No infrared absorption occurred at 13.1 microns. The sample was accordingly judged free of the *meta* isomer. In subsequent purifications the fractionation was omitted because crystallization, even from the crude mixture, proved comparatively easy at very low temperatures.

p-tert-Butylphenylsodium. *p-tert*-Butylchlorobenzene (0.077 mole) was added dropwise to 0.154 g.-atom of sodium sand in heptane in the manner common for preparing these sodium reagents.[12] The mixture then was stirred for one hour at 30°. Approximately 100 ml. of the suspension was carbonated at once and another 100 ml. was withdrawn and stored in a bottle under nitrogen atmosphere for $4^1/_2$ months. Heptane was added to the remainder in order to restore the volume in the flask to its original amount and the mixture was heated with stirring for four hours at 80°. Carbonation of the three portions yielded the same *p-tert*-butylbenzoic acid which melted at 167° (corr.). The freedom from any *meta* isomer was shown by the absence of an absorption peak at 9.2 microns.

m-tert-Butylchlorobenzene. *tert*-Butylbenzene was nitrated and the pure *para*-nitro-*tert*-butylbenzene (m.p. 28.50–30° from heptane) was reduced by iron powder in ethanol as described by Crawford and Stewart.[14] The *p-tert*-butylacetanilide (64 g. or 0.335 mole) was dissolved in 300 ml. of acetic acid with 28.6 g. of fused sodium acetate and was subjected to a slow stream of chlorine (24.8 g.). The reaction mixture then was poured into 500 ml. of water and the solid was recovered by filtration. After two crystallizations from ethanol, 2-chloro-4-*tert*-butylacetanilide melted at 152.4–154°. The yield was 36 g. (48%).

The above acetanilide (36 g.) was refluxed for three hours in 50 ml. of 95% ethanol and 50 ml. of concentrated hydrochloric acid. A solution of 35 g. of sodium hydroxide in 75 ml. of water was added to the cooled reaction mixture and the amine was separated, dried, and distilled at 102–104°/7 mm. The amine (19 g.) was dissolved in a mixture of 65 ml. of 95% ethanol and 15.5 ml. of concentrated sulfuric acid. A solution of 11.4 g. of sodium nitrite in 30 ml. of water was added slowly with stirring at 5–10°. The mixture was stirred 20 minutes more and 2.7 g. of copper bronze was added. When bubbling ceased, 150 ml. of water was added. The product was steam-distilled and extracted from the distillate with carbon tetrachloride, after which it was washed with alkali, dried and distilled through a Holtzmann column. The *m-tert*-butylchlorobenzene (10.1 g.) boiled at 212–216° and had $n_{\rm D}^{25}$ 1.5097. The infrared absorption showed no trace of the bands at 12.1 and 13.5 microns which are characteristic for the *para* isomer.

Anal. Calc'd for $C_{10}H_{13}Cl$: C, 71.21; H, 7.77; Cl, 21.04. Found: C, 71.62; H, 7.78; Cl, 21.13.

m-tert-Butylphenylsodium. *m-tert*-Butylchlorobenzene (6.5 g. or 0.04 mole) was added to 1.8 g. (0.08 g.-atom) of sodium sand in 300 ml. of heptane in the usual way. After one hour additional stirring at 30° the volume was made up to 400 ml. by addition of more heptane. One-fourth was carbonated at once and another fourth was heated to 80° for three hours. The yield of *m-tert*-butylbenzoic acid from the unheated portion was 1.3 g. (19%), m.p. 129–130 (corr.). Recorded: m.p. 127°.[5] The yield from the heated part was only 0.6 g., 4%, and the sample was colored. Nevertheless the two infrared spectra were identical save for a small peak at 8.2 μ. The freedom from the *para* isomer was shown by the absence of an absorption at 11.7 μ.

Metalation of p-tert-butylphenylsodium. The *para* isomer was prepared from 6.5 g. (0.04 mole) of *p-tert*-butylchlorobenzene and 1.8 g. (0.08 g.-atom) of sodium sand in 300 ml. heptane as described above. This mixture was diluted with heptane to make the volume 400 ml. One-fourth of this suspension was decanted twice and the volume each time was replaced by heptane. Any *tert*-butylbenzene which was formed by disproportionation during the preparation of the reagent thus was removed. This suspension then was added to a suspension of amylsodium and sodium *tert*-pentoxide made from 12.1 ml. (0.1 mole) of amyl chloride, 4.6 g. (0.2 g.-atom) of sodium, and 5.4 ml. (0.05 mole) of *tert*-amyl alcohol, as described in a previous paper.[12] The mixture was heated and stirred for two hours at 70°. Carbonation yielded no 5-*tert*-butylisophthalic acid which would have been insoluble in benzene. The dissolved acid contained 1.2 g. (69%) of *p-tert*-butylbenzoic acid. An infrared

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(13) Tsukervanik, *J. Gen. Chem. U.S.S.R.*, **8**, 1512 (1938); *Chem. Abstr.*, **33**, 4587 (1939).

(14) Crawford and Stewart, *J. Chem. Soc.*, 4443 (1952).

absorption showed the absence of any *meta* isomer. If decanting and washing were omitted from this preparation enough *tert*-butylbenzene was present to be dimetalated and yield 2% of the high-melting 5-*tert*-butylisophthalic acid.

Metalation of m-tert-butylphenylsodium. A similar metalation of *m*-*tert*-butylphenylsodium yielded 16% of the benzene-insoluble 5-*tert*-butylisophthalic acid which melted above 300° and was identical with that recorded from the experiments already published.[15]

Acknowledgment. The authors are greatly indebted to Mr. James Howard for technical assistance in the majority of the experiments. Measurements of infrared absorption were made by the courtesy of Dr. Nagy.

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[15] Gilman and Kyle, *J. Am. Chem. Soc.*, **70,** 3945 (1948).