From the mother liquors from the recrystallization of the nitrile ester XXIV was obtained the **nitrile acid XXV**, by fractional crystallization. Three crystallizations from benzene–pentane gave the analytical sample of the acid XXV, m.p. 204–205°.

Anal. Calcd. for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67. Found: C, 67.43; H, 5.77.

5,6,7,8-Tetrahydro-2-hydroxy-3-carbethoxy-1-naphthaleneacetic Acid Ethyl Ester (XX).—The crude nitrile ester and acid (XXIV and XXV, 900 mg.) was refluxed for 5 hours with 2% absolute ethanolic hydrogen chloride. The excess ethanol was removed *in vacuo*, 30 cc. of water was added to the residue and it was warmed gently for 25 minutes. The mixture was cooled, extracted with ether and the ether extracts were washed a few times with 5% sodium carbonate, followed by washing with water until the washes were neutral. The ether solution was dried, the ether was removed *in vacuo*, and the semicrystalline residue was chromatographed on 25 g. of silica gel. Elution with 10% ether–petroleum ether gave 350 mg. of product, m.p. 83–87° and an additional 150 mg. melting at 88–89°. Repeated recrystallization from pentane did not raise the m.p.

The crude ester XX (350 mg.) was saponified by refluxing for 5 hr. with 10% alkali to yield 260 mg. of the crude diacid XVI, which after recrystallization from aqueous alcohol, melted with transition at 233–234°, final m.p. 294–295° dec. Esterification of 147 mg. of the crude acid with 2% alcoholic hydrogen chloride, followed by purification on silica gel and elution with 5% ether–petroleum ether gave 70 mg. of the diester XV, m.p. 96–97°. This was identical with the product obtained by hydrogenation of IX, as shown by mixed m.p. and the identity of the ultraviolet spectra.

4,5-Benzo-2,7-dicarbethoxycycloheptadienone (I) and By-product.—Phthalaldehyde (3.0 g.), 4.56 g. of diethyl acetonedicarboxylate, 0.2 cc. of dry piperidine and 0.8 cc. of acetic acid were refluxed in 15 cc. of dry benzene until 0.8 cc. of water (3.5 hr.) had collected in the water separator. The benzene was evaporated, 10 cc. of ethanol was added to the residue, and after standing some time, 4.3 g. of I, m.p. 96–97°, was obtained; the reported[3] m.p. is 95.5°. The mother liquors deposited 440 mg. of the by-product, m.p. 146–148°, unchanged by recrystallization from ethanol. The analysis corresponded to that of the benzenoid analog of VI.

Anal. Calcd. for $C_{26}H_{30}O_{10}$: C, 62.14; H, 6.02. Found: C, 61.89; H, 6.28.

The condensation to form I using a basic ion-exchange resin as catalyst was carried out as follows.[29] To a solution of 2 g. of phthalaldehyde dissolved in 30 cc. of dry benzene, were added 2.9 g. of diethyl acetonedicarboxylate and 500 mg. of Amberlite IR 4-B resin (washed with acetone and air-dried). The mixture was refluxed for 4 hours; after cooling, the catalyst was removed and washed a few times with dry benzene. The filtrates were combined and concentrated *in vacuo* to give a green oil, which was dissolved in alcohol, treated with norite and filtered. Concentration of the filtrate gave 1.8 g. of I, m.p. 93–96°.

4,5-Benzo-2,7-dicarbethoxycycloheptanone (VII).—To 250 mg. of prereduced Adams catalyst in 30 cc. of acetic acid was added 500 mg. of 4,5-benzo-2,7-dicarbethoxycycloheptadienone (I), and the mixture was hydrogenated until slightly over 2 moles of hydrogen was absorbed. The catalyst was removed, washed with ethanol, the filtrates were combined and the solvents removed *in vacuo*, to give 520 mg. of crude crystalline material. The product was chromatographed on 40 g. of silica gel, and elution with 30% ether–petroleum ether gave 103 mg. of the tetrahydro product VII, m.p. 99–102°. The m.p. was raised to 109–110° by three crystallizations from hexane; the infrared spectrum showed bands at 1731 (ester carbonyl) and 1690 cm.$^{-1}$ (keto carbonyl).

Anal. Calcd. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 67.22; H, 6.73.

Treatment of the By-product VI with Piperidine Acetate.—The by-product VI (630 mg.) was refluxed for 24 hours with 0.2 cc. of piperidine and 0.82 cc. of acetic acid. The solvent was removed *in vacuo*, the residue was taken up in ethanol, and the solution deposited 250 mg. of VI after standing. The m.p. of the product was raised to 180–182° by recrystallization from ethanol. The combined mother liquors were chromatographed on 50 g. of silica gel, and eluted with 10% ether–petroleum ether, which would have yielded the dihydronaphthalene IX if it was present. Elution with 30% ether–petroleum ether gave an additional 195 mg. of VI, m.p. 178–180°. Further elution with 40 and 50% ether–petroleum ether gave 28 mg. of non-crystallizable oil. Elution with 70% ether–petroleum ether gave 100 mg. of product, m.p. 188–190°; the m.p. was not raised by crystallization from ethanol. A mixed m.p. with VI gave a slight depression, 174–176°. The 190° compound gave a single absorption peak at 250 mμ, similar to VI. The total recovery of material from the reaction was 573 mg.

ROCHESTER, NEW YORK

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[29] For a review of the use of ion-exchange resins as catalysts in the Claisen and Knoevenagel condensations, see M. J. Astle and J. A. Zaslowsky, *Ind. Eng. Chem.*, **44**, 2867 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

The Action of Aluminum Chloride on Alkylbenzenes. IV

BY DOROTHY V. NIGHTINGALE AND JAMES M. SHACKELFORD[1]

RECEIVED JUNE 4, 1954

When 1,3-dimethyl-4-*n*-butylbenzene, 1,3-dimethyl-4-*sec*-butylbenzene and 1,3-dimethyl-4-isobutylbenzene are warmed with aluminum chloride, the butyl group migrates to the 5-position without isomerization. The alkylation of *m*-xylene with *n*-butyl chloride yields a mixture of 1,3-dimethyl-5-*n*-butylbenzene and 1,3-dimethyl-5-*sec*-butylbenzene. The alkylation of *m*-xylene with *sec*-butyl chloride yields 1,3-dimethyl-5-*sec*-butylbenzene.

In a previous publication from this Laboratory,[2] it was shown that the acetylation of *p*-di-*n*-butylbenzene and *p*-di-*sec*-butylbenzene by means of aluminum chloride in refluxing carbon disulfide yielded 2,4-di-*n*-butylacetophenone and 2,4-di-*sec*-butylacetophenone as the principal dialkylacetophenones. The fact that the migrating butyl groups were not isomerized led us to repeat the earlier rearrangement experiments of the senior author with the 1,3-dimethyl-4-butylbenzenes.[3]

It has now been established by both chemical and spectroscopic evidence that the principal changes which take place when these trialkylbenzenes are warmed on a steam-bath with aluminum chloride are

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[1] Abstracted from a portion of the dissertation to be submitted by J. M. Shackelford for the degree of Doctor of Philosophy.

[2] D. V. Nightingale and H. B. Hucker, *J. Org. Chem.*, **18**, 1529 (1953).

[3] D. V. Nightingale and L. I. Smith, THIS JOURNAL, **61**, 101 (1939).

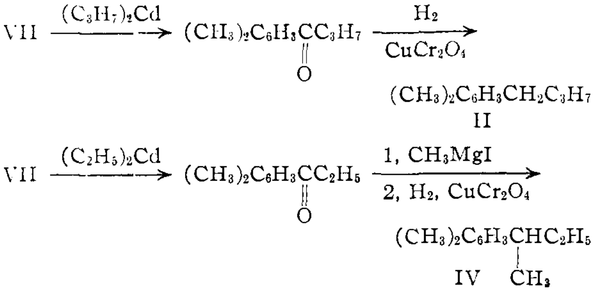
1,3-dimethyl-4-*n*-butylbenzene ⟶
I
1,3-dimethyl-5-*n*-butylbenzene
II
1,3-dimethyl-4-*sec*-butylbenzene ⟶
III
1,3-dimethyl-5-*sec*-butylbenzene
IV
1,3-dimethyl-4-isobutylbenzene ⟶
V
1,3-dimethyl-5-isobutylbenzene
VI

m-Xylene was the only other identified product of the reaction. Contrary to our earlier conclusions, the migrating *n*- and *sec*-butyl groups were not isomerized.

The identity of the rearrangement products II and IV was established by comparison of their infrared absorption spectra with the infrared spectra of authentic II and IV, and by mixture melting points of their trinitro derivatives and the same derivatives of authentic II and IV. The tribromo derivative of II was identical with the tribromo derivative of authentic II. Bromination of IV and authentic IV yielded tetrabromo-*m*-xylene.[4] The infrared spectra of II and IV indicate the presence of some unchanged 1,2,4-trialkylbenzene.

The product from the action of aluminum chloride on V was originally reported only as a mixture of hydrocarbons. The values from the carbon and hydrogen analyses of the trialkylbenzene fraction agreed with those calculated for a dimethylbutylbenzene. Authentic VI was not available, but the infrared spectrum of the trialkylbenzene fraction indicates that this material is a mixture of 1,3-dimethyl-5-isobutylbenzene (VI) and unchanged V.

Authentic II and IV were synthesized from 3,5-dimethylbenzoyl chloride (VII)



$$\text{VII} \xrightarrow{(C_3H_7)_2Cd} (CH_3)_2C_6H_3\underset{\underset{O}{\|}}{C}C_3H_7 \xrightarrow[CuCr_2O_4]{H_2} (CH_3)_2C_6H_3CH_2C_3H_7 \quad \text{II}$$

$$\text{VII} \xrightarrow{(C_2H_5)_2Cd} (CH_3)_2C_6H_3\underset{\underset{O}{\|}}{C}C_2H_5 \xrightarrow[2,\ H_2,\ CuCr_2O_4]{1,\ CH_3MgI} (CH_3)_2C_6H_3\underset{\underset{CH_3}{|}}{CH}C_2H_5 \quad \text{IV}$$

The 1,3-dimethyl-4-*sec*-butylbenzene (III) used in the current investigation was synthesized *via* the Grignard reaction so that there could be no question as to the structure of the butyl radical or the 1,3,4-orientation of the hydrocarbon.

The earlier conclusions as to the structure of the migrating *n*-butyl radical were based on the fact that the trinitro derivative of the isomerized trialkylbenzene did not depress the melting point of the trinitro derivative of the trialkylbenzene obtained from the alkylation of *m*-xylene with *n*-butyl chloride. The structure proof synthesis of II described above was not available at that time. Our assumption that the butyl radical in the alkylation product was secondary was based on the work of Shoesmith and McGechen[5] in which they established that the alkylation of toluene with *n*-butyl chloride in the presence of aluminum chloride yielded *m*- and *p*-*sec*-butyltoluene.[6]

The alkylation of *m*-xylene with *n*-butyl chloride was repeated. Careful fractionation of the product yielded II and IV in a ratio of 1.7:1 based on the weight of the compounds isolated.[7] These two trialkylbenzenes were identified by comparison of their infrared spectra with the spectra of authentic II and IV, and by their trinitro derivatives. In 1938, precision fractionation equipment was not available and we happened to isolate only the trinitro derivative of II and overlooked the other isomer.

The product from the alkylation of *m*-xylene with *sec*-butyl chloride, not previously reported, has been similarly identified as IV. The infrared spectrum of this trialkylbenzene was identical with that of IV obtained from *m*-xylene and *n*-butyl chloride.

Our earlier identification of the rearrangement product from II as 1,3-dimethyl-5-*t*-butylbenzene was based on the mixture melting point of the trinitro derivative with the same derivative of the authentic hydrocarbon and on freezing point data. It is quite possible that the butyl alcohol used in 1938 for the preparation of II was tertiary rather than secondary or contained considerable amounts of *t*-butyl alcohol, and that the trialkylbenzene obtained from it was a mixture of isomers.[8] The trinitro derivative, m.p. 107°, of this product may have beea a eutectic mixture.

To clarify this question, the alkylation of *m*-xylene with *sec*-butyl alcohol and 85% sulfuric acid was repeated, using pure *sec*-butyl alcohol. The values from the carbon and hydrogen analyses of the product agreed with the calculated values for a dimethylbutylbenzene, but comparison of its infrared spectrum with that of authentic III and the 1,3,5-trialkylbenzenes indicated that the material may be a mixture of III, a 1,3,5-trialkylbenzene and possibly a 1,2,3-trialkylbenzene. Nitra-

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[4] G. F. Hennion and J. C. Anderson, THIS JOURNAL, **68**, 424 (1946). Polybromo derivatives are frequently of little use in the identification of isomeric alkylbenzenes by means of mixture melting points, because mixtures often show little or no depression of the melting point. In this problem, however, they furnish additional confirmatory evidence that the migrating *n*-butyl group was not isomerized, since secondary and tertiary alkyl groups are replaced by bromine under the experimental conditions specified.

[5] J. B. Shoesmith and J. F. McGechen, *J. Chem. Soc.*, 2231 (1930).

[6] M. J. Schlatter and R. D. Clark, THIS JOURNAL, **75**, 363 (1953), have made a careful study by means of infrared spectra of the *t*-alkylation products of toluene, including the work of Shoesmith and McGechen with *t*-butyl chloride. They have shown that when chemical methods of analysis are used with mixtures of isomers, a minor constituent may be overlooked and that misleading data may be obtained due to migration of alkyl groups during the separation of hydrocarbons by procedures involving sulfonation. It is entirely possible that the *sec*-butyltoluene obtained by Shoesmith and McGechen contained some *m*- and *p*-*n*-butyltoluene.

[7] H. Gilman and R. N. Meals, *J. Org. Chem.*, **8**, 126 (1943), have shown that the alkylation of benzene with long straight chain primary alkyl halides by means of aluminum chloride yields mixtures of *n*- and *sec*-alkylbenzenes even at 0°. The paper contains the literature references to the alkylation of benzene with *n*-butyl chloride.

[8] Buu-Hoi and P. Cagniant, *Bull. soc chim.*, **9**, 887 (1942), state that the alkylation of *m*-xylene with both *sec*- and *t*-butyl alcohol yields 1,3-dimethyl-5-*t*-butylbenzene, but there is no mention in their experimental section of the use of *sec*-butyl alcohol or of derivatives of a trialkylbenzene obtained from it.

tion of this product and of authentic III even at ice-bath temperatures yielded only trinitro *m*-xylene. When this material was warmed with aluminum chloride the trialkylbenzene fraction obtained from the reaction was also a mixture as might be expected. Its nitration product melted over a wide range and finally yielded a small amount of the trinitro derivative of IV.

The results of our present rearrangement experiments are in agreement with the recently published data of Kinney and Hamilton[9] in which they have shown by infrared and mass spectrometric techniques that *n*-butylbenzene when treated with aluminum chloride at 100° forms some *m*-di-*n*-butylbenzene. McCaulay and Lien[10] found no isomerization of migrating *n*- or *sec*-butyl radicals when *n*- and *sec*-butylbenzene were treated with $HF-BF_3$ catalyst at room temperature.

Since the *n*-butyl radical migrates without isomerization in the presence of aluminum chloride, it is likely that Baddeley and Kenner[11] were correct in their statement that 1,2,4-tri-*n*-propylbenzene yielded 1,3,5-tri-*n*-propylbenzene when warmed with aluminum chloride. It is also likely that 1,3-dimethyl-4-*n*-propylbenzene rearranged to 1,3-dimethyl-5-*n*-propylbenzene under the same conditions. This and other rearrangement experiments reported from this laboratory are being repeated to clarify our earlier conclusions.

Experimental[12]

The *m*-xylene was Oronite 95.9% *m*-xylene, containing 1.4% each of *o*- and *p*-xylene. 1,3-Dimethyl-4-*n*-butylbenzene (I), 1,3-dimethyl-4-isobutylbenzene (V) and 1,3-dimethyl-4-*sec*-butylbenzene (III) were prepared by the catalytic hydrogenation of 2,4-dimethyl-*n*-butyrophenone, 2,4-dimethylisobutyrophenone, and methylethyl-(2,4-dimethylphenyl)-carbinol, respectively.[13] All acylations were carried out according to the procedure described in Organic Syntheses,[14] and unless otherwise specified all reaction products were fractionated through a medium-bore Todd Column at a reflux ratio of 10:1. Melting points were taken in a copper block and are uncorrected.

Alkylation of *m*-Xylene with *n*-Butyl Chloride.—In the usual equipment was placed 127 g. of *m*-xylene and 60 g. of aluminum chloride. To this mixture was added slowly with mechanical stirring 72 g. (1 mole) of *n*-butyl chloride at such a rate that the temperature did not rise above 35°. After the addition was complete, the mixture stood overnight at room temperature and then the complex was decomposed with iced hydrochloric acid. The solution was extracted with ether, the ether extracts combined, washed with water, dried and distilled. The reaction product was fractionated at 15 mm.: (a) 35 ml., 94–98°; (b) 10 ml., 98–101°; (c) 42 ml., 101–103°; (d) 21 ml., 103–104°; residue 12 ml.

Fraction (a) was redistilled to give 20 g. of 1,3-dimethyl-5-*sec*-butylbenzene (IV), b.p. 96–97° (15 mm.), $n^{25}D$ 1.4958. This fraction formed a trinitro derivative, m.p. 90–91°, mixed m.p. with the same derivative (m.p. 91°) of authentic IV, 90–91°.

Fractions (c) and (d) were combined and redistilled to give 35 g. of 1,3-dimethyl-5-*n*-butylbenzene (II), b.p. 103–104° (15 mm.), $n^{25}D$ 1.4947. The hydrocarbon formed a trinitro derivative, m.p. 93–94°, and mixed m.p. with the same derivative (m.p. 94°) of authentic II, 93–94°.

Anal. Calcd. for $C_{12}H_{15}N_3O_6$: C, 48.45; H, 5.08. Found: C, 48.62; H, 5.16.

A mixture of the trinitro derivatives of these two alkylation products softened at 72° and melted at 78–82°. The trinitro derivative of II obtained from this alkylation did not depress the melting point of the trinitro derivative (m.p. 96°) isolated in 1938 from the alkylation of *m*-xylene with *n*-butyl chloride and it has the same fibrous structure. The tribromo derivative of II melted at 52° and did not depress the melting point of the same derivative of authentic II.

Alkylation of *m*-Xylene with *sec*-Butyl Chloride.—*m*-Xylene (180 g.) was alkylated in the same way with 110 g. of freshly distilled *sec*-butyl chloride and 95 g. of aluminum chloride, to yield 125 g. of 1,3-dimethyl-5-*sec*-butylbenzene IV, b.p. 95–97° (15 mm.), $n^{25}D$ 1.4929.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 88.75; H, 11.26.

The hydrocarbon formed a trinitro derivative, m.p. and mixed m.p. with the same derivative (m.p. 91°) of authentic IV, 90–91°.

Anal. Calcd. for $C_{12}H_{15}N_3O_6$: C, 48.45; H, 5.08. Found: C, 48.26; H, 5.26.

Alkylation of *m*-Xylene with *sec*-Butyl Alcohol.—The procedure is essentially that of Kirrmann and Graves.[15] The *sec*-butyl alcohol was purified by fractionation through a Todd column. *m*-Xylene (250 ml.) and 61 ml. of *sec*-butyl alcohol were placed in the usual equipment in water cooled with a little ice. A mixture of 330 ml. of concd. sulfuric acid and 70 ml. of water was added slowly with stirring. The mixture was stirred an additional seven hours at room temperature. The hydrocarbon layer was separated, washed, dried and distilled to yield 68 g. (42%) of trialkylbenzene, b.p. 106–108° (28 mm.), $n^{24}D$ 1.4967.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 88.90; H, 11.19.

Nitration of this product yielded only trinitro-*m*-xylene, m.p. 181–182°.

This trialkylbenzene (35 g.) was warmed with 8.5 g. of aluminum chloride for 3.5 hours. Fractionation of the product at 17 mm. yielded (a) 5 g., b.p. 88–94°; (b) 12 g., 94–97°. Fraction (a) did not form a solid trinitro derivative. Fraction (b) yielded a nitration product which melted over a wide range. Repeated recrystallization of this material yielded a small amount of the trinitro derivative of IV. The infrared spectrum also indicated that this fraction was a mixture.

Preparation of Authentic 1,3-Dimethyl-5-*n*-butylbenzene (II).—The 3,5-dimethyl-*n*-butyrophenone was prepared from 3,5-dimethylbenzoyl chloride[16] (VII) and di-*n*-propylcadmium by a modification of the method of Cason.[17] *n*-Propylmagnesium bromide was prepared from 98 g. (0.80 mole) of *n*-propyl bromide in 200 ml. of ether, then 100 ml. of ether was removed by distillation and 100 ml. of benzene added. The solution was cooled and 160 g. (0.88 mole) of cadmium chloride was added as rapidly as possible. The solution was refluxed for one hour, then 72 g. (0.43 mole) of acid chloride VII was added and the refluxing continued for one hour. The complex was decomposed in the usual manner and the product extracted with ether. The benzene–ether solution was extracted with sodium carbonate, washed till neutral, dried and distilled; yield of 3,5-dimethyl-*n*-butyrophenone, 31 g., b.p. 139° (16 mm.), $n^{25}D$ 1.5169.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.87; H, 9.13. Found: C, 81.97; H, 9.27.

The ketone formed a semicarbazone, m.p. 157°.

Anal. Calcd. for $C_{13}H_{19}N_3O$: C, 66.97; H, 8.20. Found: C, 67.09; H, 8.25.

Reduction of this ketone with hydrogen and copper–chromium oxide catalyst yielded 1,3-dimethyl-5-*n*-butylbenzene (II), b.p. 102–104° (15 mm.), $n^{25}D$ 1.4937. The hydrocarbon formed a trinitro derivative, m.p. 95°.

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[9] R. E. Kinney and L. A. Hamilton, THIS JOURNAL, **76**, 786 (1954).

[10] D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953).

[11] G. Baddeley and J. Kenner, *J. Chem. Soc.*, 303 (1935).

[12] The carbon and hydrogen analyses were by R. E. Bolin.

[13] D. V. Nightingale and H. D. Radford, *J. Org. Chem.*, **14**, 1089 (1948).

[14] "Org. Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

[15] Am. Kirrmann and M. Graves, *Bull. soc chim.*, [5] **1**, 1494 (1934).

[16] 3,5-Dimethylbenzoic acid was prepared by the oxidation of mesitylene with dilute nitric acid (H. R. Snyder, R. R. Adams and A. V. McIntosh, THIS JOURNAL, **63**, 3280 (1941)) and converted to the acid chloride by means of thionyl chloride.

[17] J. Cason and F. S. Prout, *ibid.*, **66**, 46 (1944).

Anal. Calcd. for $C_{12}H_{15}N_3O_6$: C, 48.45; H, 5.08. Found: C, 48.48; H, 5.46.

Preparation of Authentic 1,3-Dimethyl-5-*sec*-butylbenzene (IV).—The 3,5-dimethylpropiophenone was synthesized from 3,5-dimethylbenzoyl chloride and diethylcadmium as described for the preparation of 3,5-dimethyl-*n*-butyrophenone. The yield of ketone was 48%, b.p. 110° (15 mm.), n^{25}_{D} 1.5143.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.54; H, 8.64. Found: C, 81.18; H, 9.12.

The ketone formed a semicarbazone, m.p. 167°.

Anal. Calcd. for $C_{12}H_{17}N_3O$: C, 65.72; H, 7.81. Found: C, 65.64; H, 7.89.

Methylethyl-(3,5-dimethylphenyl)-carbinol was prepared from 45 g. of 3,5-dimethyl-*n*-propiophenone and methylmagnesium iodide in the usual manner, b.p. 109–111° (15 mm.), yield 24 g. (48%), n^{24}_{D} 1.5148. This carbinol was reduced with hydrogen and copper chromium oxide catalyst to yield 21 g. of 1,3-dimethyl-5-*sec*-butylbenzene (IV), b.p. 95–96° (16 mm.), n^{24}_{D} 1.4929.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 88.96; H, 11.50.

The trinitro derivative crystallized from alcohol in granules, m.p. 91°.

Anal. Calcd. for $C_{12}H_{15}N_3O_6$: C, 48.45; H, 5.08. Found: C, 48.18; H, 5.07.

Rearrangements with Aluminum Chloride.—The aluminum chloride was added to the hydrocarbon and the mixture warmed with stirring on a steam-bath. After heating for 3.5 hours, the complex was decomposed with iced hydrochloric acid and the hydrocarbon isolated in the usual manner.

1,3-Dimethyl-4-*n*-butylbenzene (I).—The product from 102 g. of hydrocarbon and 23 g. of aluminum chloride was fractionated at 16 mm.: (a) 17 g., 30–70°; (b) 8.5 g., 70–100°; (c) 1 g., 100–103°; (d) 31 g., 103–105°. Fraction (a) was identified by its trinitro derivative as containing mainly *m*-xylene. The trinitro derivative of (c) and (d) crystallized from alcohol in fibers, m.p. 94°, and it did not depress the melting point of the trinitro derivative, m.p. 95° of authentic II. The tribromo derivative of (d) melted at 53° and did not depress the melting point (53°) of the same derivative of authentic II.

Anal. Calcd. for $C_{12}H_{15}Br_3$: C, 36.10; H, 3.79. Found: C, 35.73; H, 3.80.

The principal trialkylbenzene formed by rearrangement of I is therefore 1,3-dimethyl-5-*n*-butylbenzene (II). The infrared spectrum of a center cut from redistillation of (d) through a Podbielniak column indicated the presence of a small amount of unchanged I.

1,3-Dimethyl-4-*sec*-butylbenzene (III).—The product from 133 g. of hydrocarbon and 29 g. of aluminum chloride was fractionated at 16 mm.: (a) 12 g., 45–50°; (b) 7 g., 50–91°; (c) 18 g., 91–95°; 63 g., 95–96°. Fraction (a) was mainly *m*-xylene. The trinitro derivative of (c) and (d) crystallized from alcohol in granules, m.p. 91°, mixed m.p. with the same derivative (m.p. 91°) of authentic IV, 90–91°. This rearrangement product was therefore 1,3-dimethyl-5-*sec*-butylbenzene. The infrared spectrum of a center cut of (d) indicated the presence of a small amount of unchanged III.

1,3-Dimethyl-4-isobutylbenzene (V).—The product from 100 g. of hydrocarbon and 20 g. of aluminum chloride was fractionated at 17 mm.: (a) 12 g., 50–65°; (b) 6 g., 80–91°; (c) 5 g., 91–98°; (d) 20 g., 98–101°.

Fraction (a) was mainly *m*-xylene. Carbon and hydrogen analyses of (d) agreed with the values of a dimethylbutylbenzene, and the infrared spectrum indicated a mixture of unchanged V and VI.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.81; H, 11.19. Found: C, 88.66; H, 11.46.

The trinitro derivative of fraction (d) melted at 85–86°, and may be either the derivative of VI or a eutectic mixture.

Anal. Calcd. for $C_{12}H_{15}N_3O_6$: C, 48.45; H, 5.08. Found: C, 48.50; H, 5.37.

Nitrations.—The trinitro derivatives of the hydrocarbons were prepared by adding 2 ml. of the hydrocarbon slowly with shaking to an ice-cold mixture of 10 ml. of concd. sulfuric acid and 5 ml. of fuming nitric acid. After all of the hydrocarbon had been added, the mixture was warmed on a water-bath at 60–80° and then poured onto ice. The nitro compound was separated, washed with water and recrystallized from alcohol.

The trinitro derivative of 1,3-dimethyl-4-isobutylbenzene, not previously reported, melted at 115–116°. A mixture of this derivative and trinitro-1,3-dimethyl-5-*t*-butylbenzene (m.p. 112°) softened at 80–85° and melted at 86°.

Anal. Calcd. for $C_{12}H_{15}N_3O_6$: C, 48.45; H, 5.08. Found: C, 48.76; H, 5.22.

Brominations.—The brominations were all carried out with liquid bromine in the presence of iron powder as described by Hennion and Anderson.[4]

Infrared Absorption Spectra.—The absorption spectra were determined by Dr. E. E. Pickett of the spectrographic laboratory of the University of Missouri and by J. M. Shackelford, on a Beckman Infrared Spectrophotometer, Model IR-2, cell length 0.025 mm. The samples for spectroscopic analysis were center cuts obtained by redistillation of the trialkylbenzene fractions through a Podbielniak column.

COLUMBIA, MO.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Conjugation in the Biphenyl System

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The dissociation constants of 3-hydroxybiphenyl, 4-hydroxybiphenyl, 3′-nitro-4-hydroxybiphenyl, 4′-nitro-4-hydroxybiphenyl, 2-hydroxyfluorene and 2-hydroxy-7-nitrofluorene have been measured by a spectrophotometric method in aqueous borate–boric acid buffers. The data are interpreted as indicating a lack of significant contribution by contributing structures involving conjugation between the two benzene rings to the electronic structures of the ground states of the conjugate bases of these compounds. An explanation of this conclusion is given.

Recent studies of the effect of a group X in the 3′- or 4′-position on the reactivity of a substituent Y in the 4-position of a substituted biphenyl have raised some question as to the ability of the biphenyl system to transmit substituent effects by resonance hybridization involving the quinonoid structure I.[1] The studies thus far reported[1a,2] have been concerned with substituted biphenyls of type II, where X = Br or NO_2 and Y = COOR (R = H or alkyl). While these studies demonstrated that substituent effects are transmitted through the biphenyl system, the substituents were of such a nature that strong resonance interactions of type III would not be expected.

We have prepared 3′- and 4′-nitro-4-hydroxybiphenyl (II, X = NO_2, Y = OH) and measured their dissociation constants. These have been com-

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[1] For reviews see (a) E. Berliner and E. Blommers, THIS JOURNAL, **73**, 2479 (1951), and (b) G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 854 (1952).

[2] N. N. Lichtin and H. P. Leftin, THIS JOURNAL, **74**, 4207 (1952).