bands at 5.83(v.w.) and at 8.77(m-i) that are not shown by the diphenyline III. Both II and III give bands at 7.42 (v.w.), 9.92(w-m), 11.78(m) and 11.95(m-i) where none exist in the spectrum of IV. Both III and IV show bands at 8.84(m) and at 10.19–10.22(w-m) that II does not possess.

The benzidine II possesses unique bands at 7.64(w) and 7.74(i); the diphenyline III shows unique bands at 7.66(m), 13.28(m) and 13.52(m); and the 2,2′-diaminobiphenyl IV has unique bands at 7.68(i), 11.86(i, s) and 13.44(m).

PITTSBURGH, PENNSYLVANIA

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

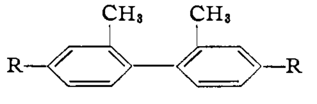
Ullmann Synthesis of Six Dimethyldinitrobiphenyls and their Reduction to the Corresponding Diaminodimethylbiphenyls[1]

BY ROBERT B. CARLIN AND GEORGE E. FOLTZ[2]

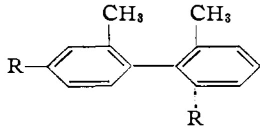
RECEIVED SEPTEMBER 30, 1955

Six dimethyldinitrobiphenyls (I–VI) were prepared by simple and mixed Ullmann reactions. Catalytic reduction of these afforded six corresponding diaminodimethylbiphenyls (VII–XII), all of which were converted to diacetyl and bis-salicylal derivatives. Comparison of the diamines and of their derivatives with three diaminodimethylbiphenyls and their derivatives obtained by catalytic reductive debromination of the rearrangement products of 3,3′-dibromo-5,5′-dimethylhydrazobenzene showed VII, IX and XII to be the structures of the compounds derived from the rearrangement and thereby proved the structures of the rearrangement products themselves. Some aspects of the behavior of halonitrotoluenes in mixed Ullmann reactions is reminiscent of the behavior of monomer mixtures in copolymerization. This analogy may prove useful in the development of a satisfactory mechanism for the Ullmann reaction.

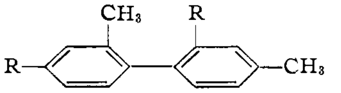
The rearrangement of 3,3′-dibromo-5,5′-dimethylhydrazobenzene[3] conceivably could lead to six different diaminodibromodimethylbiphenyls. Catalytic reductive debromination of these rearrangement products could in turn yield six diaminodimethylbiphenyls (VII–XII). In order that all of the rearrangement products could be identified by comparison of their debrominated derivatives with synthetic specimens, the preparations of VII–XII were carried out. This report is concerned with these preparations, all of which were achieved by Ullmann coupling of appropriate halonitrotoluenes and subsequent reduction of the resulting dimethyldinitrobiphenyls.



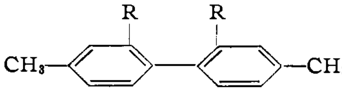
I, R = NO_2
VII, R = NH_2
VIIa, R = NHAc
VIIb, R = NC_7H_7O



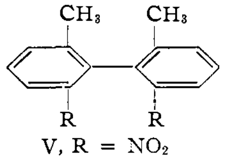
II, R = NO_2
VIII, R = NH_2
VIIIa, R = NHAc
VIIIb, R = NC_7H_7O



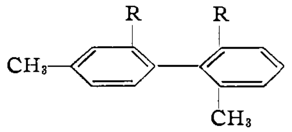
III, R = NO_2
IX, R = NH_2
IXa, R = NHAc
IXb, R = NC_7H_7O



IV, R = NO_2
X, R = NH_2
Xa, R = NHAc
Xb, R = NC_7H_7O

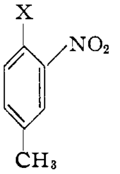


V, R = NO_2
XI, R = NH_2
XIa, R = NHAc
XIb, R = NC_7H_7O

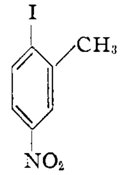


VI, R = NO_2
XII, R = NH_2
XIIa, R = NHAc
XIIb, R = NC_7H_7O

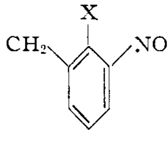
The known compounds I, IV and V were obtained in 25, 46 and 79% yields, respectively, by the symmetrical Ullmann coupling of 2-iodo-5-nitrotoluene, 4-iodo-3-nitrotoluene and 2-iodo-3-nitrotoluene respectively. Each of the three unsymmetrical dimethyldinitrobiphenyls II, III and VI was prepared by a mixed Ullmann reaction. Only one of these (II) was obtained in crystalline form; III and VI were isolated as oils which probably were not entirely free of isomers. The synthesis of III affords a typical example of the behavior encountered in all three mixed Ullmann couplings. A 35% yield of III was realized by treating equal weights of 4-bromo-3-nitrotoluene (XIII) and 2-iodo-5-nitrotoluene (XV) with copper at elevated temperatures. A 4% yield of IV, from the symmetrical coupling product I (from XV) was detected. When 4-iodo-3-nitrotoluene (XIV) was used in place of its bromine analog XIII in an attempted synthesis of III, only IV and unchanged XV were obtained from the mixture. The unsymmetrical dimethyldinitrobiphenyl II was prepared in a similar way in 16% yield from XV and 2-bromo-3-nitrotoluene (XVI); II was accompanied in the mixture by a 12% yield of V, from the self-coupling of XVI, but again no self-coupling product of XV was detected. Finally, a 32% yield of VI was obtained by coupling



XIII, X = Br
XIV, X = I



XV



XVI, X = Br
XVII, X = I

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(1) Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

(2) Institute Graduate Fellow in Organic Chemistry, 1951–1952.

(3) R. B. Carlin and G. E. Foltz, THIS JOURNAL, **78**, 1992 (1956).

XIV with 2-iodo-3-nitrotoluene (XVII); this time both of the symmetrical biphenyls, IV from XIV and V from XVII, were also isolated in 13 and 16% yields, respectively.

The formation of symmetrical IV and V, but not of I, as by-products of the mixed Ullmann reactions is worth noting. The precursors of IV (XIII and XIV) and of V (XVI and XVII) all have the *ortho* orientation of nitro and halogen, and IV and V were isolated whenever their precursors were used in a mixed Ullmann reaction. On the other hand, no I was obtained from either mixed Ullmann coupling in which XV, with its *para* orientation of nitro and halogen, was employed. Although the possibility of the presence of some I among the products cannot be excluded, its properties suggest that if present it should be isolated more readily than either IV or V. Together with the observations that the simple coupling of XV to I occurs with difficulty and in poor yield and that XV was recovered unchanged from one attempted mixed Ullmann reaction, the foregoing experiences are consistent with the belief that no more than traces of I were formed as by-products of the two mixed Ullmann reactions in which XV was a component. It therefore appears that XV is considerably more active in Ullmann reactions with different aryl halides than it is in coupling with other molecules of its own kind. For example, toward XIII, XV appears about eight times more reactive than other XIII molecules; yet XV is far less reactive toward molecules of its own kind than toward XIII molecules.

$$\mathrm{XIII}\left\{\begin{array}{l} + \mathrm{XV} \longrightarrow \mathrm{III}\ (35\%) \\ + \mathrm{XIII} \longrightarrow \mathrm{IV}\ (4.5\%) \end{array}\right.$$

$$\mathrm{XV}\left\{\begin{array}{l} + \mathrm{XV} \longrightarrow 0 \\ + \mathrm{XIII} \longrightarrow \mathrm{III}\ (35\%) \end{array}\right.$$

The mixed coupling of XV and XVI constitutes an entirely similar, if less striking, example. Such behavior of two components in a mixed Ullmann reaction bears some formal resemblance to certain copolymerization phenomena, in which monomer A may polymerize much more rapidly with monomer B than the latter does with itself in the monomer mixture, and yet A may be very sluggish in self-polymerization. Inasmuch as copolymerization behavior of this type is now quite well rationalized, the analogy may prove useful in developing a satisfactory mechanism for the Ullmann reaction.

Each of the dimethyldinitrobiphenyls I–VI was converted to the corresponding diaminodimethylbiphenyl VII–XII by hydrogenation at room temperature over Raney nickel either in ethanol or in benzene solution. All but one (IX) of the six diamines was a crystalline solid, and the three symmetrical ones (VII, X, XI) had already been reported in the literature. An unstable crystalline hydrate apparently formed when crystallization of IX was attempted, for the solid that separated from solution changed to an oil when it was dried or subjected to the action of anhydrous solvents in efforts to recrystallize it. One of the products of rearrangement of 3,3′-dibromo-5,5′-dimethylhydrazobenzene, on catalytic reductive debromination, yielded a substance that exhibited the same behavior. All six of the diaminodimethylbiphenyls were characterized as their diacetyl derivatives (VIIa-XIIa) and as their bis-salicylal derivatives (VIIb-XIIb). The three unsymmetrical diacetyl derivatives (VIIa, IXa, XIIa) and all but one (VIIb) of the bis-salicylal derivatives are reported here for the first time.

Comparison by melting point and mixed melting point determinations of the diamines VII–XII, where these were crystalline solids, and of their crystalline derivatives with the three diamines and their derivatives obtained by catalytic reductive debromination of the rearrangement products of 3,3′-dibromo-5,5′-dimethylhydrazobenzene[3] showed that VII, IX and XII were identical with the compounds derived from the rearrangement. The bis-salicylal derivative XIIb derived from the rearrangement melted at 171–172°, while a sample originating from the Ullmann reaction melted at 208–210°; however, these were shown to be dimorphs and not different compounds when a mixture of the two at first melted at 170–210° and then, after being held in molten condition at 220° for a few minutes and cooled until it solidified, melted again at 208–210°. The proofs of structure for the rearrangement products was therefore complete.

Experimental[4]

2-Iodo-3-nitrotoluene (XVII).—A solution of 50.0 g. of 2-amino-3-nitrotoluene[5] in 400 ml. of hot glacial acetic acid was cooled to 15° and treated with an ice-cold solution prepared by adding 33 g. of sodium nitrite to 185 ml. of nearly frozen concentrated sulfuric acid, heating the mixture to 75° and then cooling again. The mixture was kept below 25° during the addition; then it was stirred and diluted to 1500 ml. with ice and water. The solution was stirred and treated successively with 33 g. of urea, with a solution of 79 g. of potassium iodide in 400 ml. of water, and then with sodium bisulfite until there was a distinct odor of sulfur dioxide. The crude solid product was collected by filtration and recrystallized from aqueous ethanol, from which it formed 59.0 g. (68.2%) of pale yellow cubes, m.p. 66–68°. The m.p. 67–68° has been reported.[6]

4-Iodo-3-nitrotoluene (XIV) and 2-iodo-5-nitrotoluene (XV) were prepared in 70 and 72% yields, respectively, from the corresponding aminonitrotoluenes (both from Eastman Kodak Co.) by the procedure described in the preceding paragraph: XIV, light yellow needles from petroleum ether (b.p. 30–60°), m.p. 55–56°, reported m.p. 55°[7]; XV, small white needles from ethanol, m.p. 103–105°, reported m.p. 103–104°.[8]

4-Bromo-3-nitrotoluene (XIII).—A solution prepared by stirring 50.0 g. of 4-amino-3-nitrotoluene into 200 ml. of 1:1 (by volume) sulfuric acid was cooled to 15° and treated with a nitrosylsulfuric acid solution obtained just as described in the procedure for the preparation of XVI, above. A suspension of cuprous bromide was prepared by mixing solutions of 60 g. of cupric sulfate in 200 ml. of water, 30 g. of potassium bromide in 70 ml. of water and 110 ml. of 48% hydrobromic acid and then saturating the mixed solution with sulfur dioxide. After the cuprous bromide had been added to the diazonium solution, the mixture was subjected to steam distillation, and the distillate was extracted with ether. The ether solution was washed with sodium hydroxide and with water and was then dried over calcium chloride. Distillation of the ether left 31.5 g. (44.0%) of a residual oil, b.p. 97–103° (1 mm.). The distilled oil solidified and the solid was recrystallized from ethanol, from which it formed yellow prisms, m.p. 32–33°, reported m.p. 33°.[9]

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[4] Melting points are corrected.

[5] J. H. Hadfield and J. Kenner, *Proc. Chem. Soc. London*, **28**, 253 (1914).

[6] H. L. Wheeler and L. M. Liddle, *Am. Chem. J.*, **42**, 441 (1909).

[7] C. Willgerodt and M. Simonis, *Ber.*, **39**, 269 (1906).

[8] F. Reverdin and K. Kacer, *ibid.*, **30**, 3000 (1897).

[9] A. F. Hollemann, *Rec. trav. chim.*, **34**, 285 (1914).

2-Bromo-3-nitrotoluene (XVI).—A diazonium solution was prepared from 25.0 g. of 2-amino-3-nitrotoluene by means of the same procedure used in the preparation of XVII, above. The diazonium solution was treated with 12 g. of urea and then with a cuprous bromide suspension obtained by mixing solutions of 40 g. of cupric sulfate and 20 g. of potassium bromide in 120 ml. of water with 8.2 g. of sodium metabisulfite and 5.4 g. of sodium hydroxide in 60 ml. of water, the temperature being maintained at 50°, and then adding 80 ml. of 48% hydrobromic acid. The mixture was heated to 85°, allowed to stand about 12 hours and then extracted with ether. The ether extract was washed with water and with 10% aqueous sodium hydroxide and then dried over anhydrous potassium carbonate. Distillation of the ether left an oily residue, from which 25.6 g. (72%) of XVI distilled, b.p. 78–84° (1 mm.). The distillate formed pale yellow plates, m.p. 38–40°, from ethanol. The reported m.p. is 41–42°.[10]

4,6′-Dimethyl-2,2′-dinitrobiphenyl (VI).—An intimate mixture of 19.0 g. of 2-iodo-3-nitrotoluene (XVII), 17.0 g. of 4-iodo-3-nitrotoluene (XIV) and 36.0 g. of copper bronze powder (O. Hommel Co., Pittsburgh, Pa., Extra-fine Copper No. 5743—hereafter to be referred to simply as "copper powder") was heated for two hours at 110° and then gradually heated to 200°. The cooled mixture was extracted with benzene; removal of the benzene from the extract left a dark residual oil which on vacuum distillation yielded 15.2 g. of an orange oil, b.p. 164–166° (1 mm.). A solution of the oil in ethanol when cooled deposited 2.4 g. (12.9%) of 4,4′-dimethyl-2,2′-dinitrobiphenyl (IV), m.p. 142–143° after recrystallization from ethanol. The ethanol was removed from the mother liquor from IV, and the residual oil was dissolved in ether–petroleum ether (b.p. 30–60°). When cooled this solution deposited 5.8 g. of material from which 2.9 g. (15.6%) of 6,6′-dimethyl-2,2′-dinitrobiphenyl (V), m.p. 110–111°, was obtained by recrystallization from the same solvent mixture. Removal of solvents from the filtrate from V left a liquid which gave 6.0 g. (32%) of an oil, b.p. 166–168° (1 mm.), after vacuum distillation. Although this oil must have consisted chiefly of VI, it probably also contained small amounts of isomers.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44. Found: C, 62.36; H, 4.51.

2,4′-Dimethyl-2,4′-dinitrobiphenyl (III).—A mixture of 20.0 g. of 2-iodo-5-nitrotoluene (XV), 20.0 g. of 3-nitro-4-bromotoluene (XIII) and 40.0 g. of copper powder was heated to 145°, when the temperature suddenly surged to 275°. The mixture was allowed to cool to about 200° and then heated to 240°, when the temperature again surged, this time to 320°. The cooled mixture was extracted with benzene; distillation of the benzene left a dark brown oil from which 10.0 g. of a heavy orange oil, b.p. 215–217° (3 mm.) was obtained by vacuum distillation. A solution of this oil in ether–petroleum ether (b.p. 30–60°) deposited 1.0 g. (4.4%) of 4,4′-dimethyl-2,2′-dinitrobiphenyl (IV), m.p. 141–142° after recrystallization from ethanol, when it was cooled in Dry Ice. Removal of the solvents from the filtrates from IV left a liquid from which 8.0 g. (35.2%) of a yellow oil, b.p. 204–206° (1 mm.), was obtained by vacuum distillation. Although the transformation products IX, IXa and IXb from this oil showed that it must have consisted principally of III, the presence in it of one or more isomers of III is highly probable.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44. Found: C, 62.36; H, 4.78.

2,2′-Dimethyl-4,6′-dinitrobiphenyl (II).—A mixture of 18.3 g. of 2-iodo-5-nitrotoluene (XV), 15.0 g. of 2-bromo-3-nitrotoluene (XVI) and 30.0 g. of copper powder was heated until the luster of the copper powder disappeared and the powder became dark in color. Treatment of the resulting mixture exactly like that described in the preceding section gave first 2.2 g. (11.6%) of 6,6′-dimethyl-2,2′-dinitrobiphenyl (V), m.p. 109–111° after two recrystallizations from methanol, and then 3.0 g. (15.8%) of 2,2′-dimethyl-4,6′-dinitrobiphenyl (III) as an oil after distillation. A solution of this oil in ether–petroleum ether (b.p. 30–60°) was kept at 5° for a week, during which time small amounts of petroleum ether were added. This treatment caused the separation of short yellow needles, which after recrystallization from aqueous methanol had the m.p. 84–85°.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44. Found: C, 61.37; H, 4.57.

2,2′-Dimethyl-4,4′-dinitrobiphenyl (I).—A mixture of 10.0 g. of 2-iodo-5-nitrotoluene (XV) and 10.0 g. of copper powder was heated for a half-hour at 280°. The cooled mixture was extracted with benzene. Distillation of the benzene from the extract left 5.3 g. of tar which contained some crystalline material. Much of the dark colored contamination was removed by dissolving the residue from the benzene solution in acetone and then precipitating some of the tar by adding boiling petroleum ether (b.p. 65–110°). The solvents were removed from the resulting solution, and unchanged XV was removed from the residue by sublimation at 100° (10 mm.). When the residue from the sublimation was washed with a small amount of cold ether, the tar dissolved and a yellow powder remained which yielded 1.27 g. (25%) of 2,2′-dimethyl-4,4′-dinitrobiphenyl (I) by sublimation at 150–160° (1 mm.). Ethanol recrystallization afforded small yellow cubes, m.p. 170°, reported m.p. 170°.[11]

The substantial improvement in yield over previous efforts to carry out this same reaction[12] is attributed to the higher temperatures employed in the present work.

2,2′-Dimethyl-6,6′-dinitrobiphenyl (V) and 4,4′-Dimethyl-2,2′-dinitrobiphenyl (IV).—A mixture of the appropriate iodonitrotoluene with an equal weight of copper powder (and, in the case of the preparation of IV, twice its weight of clean sand) was heated to 180° for the preparation of IV and 200° for V. The mixture was extracted with benzene, the benzene was removed from the extract by distillation, and

TABLE I

PROPERTIES AND ANALYTICAL DATA FOR DIAMINODIMETHYLBIPHENYLS AND FOR THEIR DIACETYL AND THEIR BIS-SALICYLAL DERIVATIVES

Compound	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
		Diamines[a]			
VII	105–106[d]	...	...	..	..
VIII	88–89	79.21	79.62	7.60	7.81
IX	Oil[e]	79.21	78.64	7.60	7.28
X	125–126[f]	...	...	..	..
XI	135–136[g]	...	...	..	..
XII	106–107	79.21	79.41	7.60	7.71
		Diacetyl deriv.[b]			
VIIa	284–285[h]	...	...	..	..
VIIIa	181–182	72.95	72.67	6.80	6.99
IXa	183–184	72.95	73.09	6.80	6.84
Xa	192–193[i]	...	...	..	..
XIa	206–207[j]	...	...	..	..
XIIa	174–175	72.95	73.17	6.80	6.36
		Bis-salicylal deriv.[c]			
VIIb	200–202[k]	...	...	..	..
VIIIb	134–136	79.97	80.09	5.75	5.94
IXb	170–172	79.97	79.70	5.75	5.71
Xb	168–170	79.97	79.86	5.75	6.09
XIb	234–235	79.97	80.15	5.75	5.78
XIIb	208–210[l]	79.97	80.17	5.75	5.75

[a] Formula: $C_{14}H_{16}N_2$. [b] Formula: $C_{18}H_{20}N_2O_2$. [c] Formula: $C_{28}H_{24}N_2O_2$. [d] Reported m.p. 106–107°, P. Jacobson and O. Fabian, *Ber.*, 28, 2553 (1895). [e] Forms hydrochloride, m.p. 260° dec. *Anal.* Calcd. for $C_{14}H_{18}N_2Cl_2$: C, 58.95; H, 6.36. Found: C, 59.35; H, 6.25. [f] Reported m.p. 120°.[14] [g] Reported for DL-form, m.p. 136°; J. Kenner and W. V. Stubbings, *J. Chem. Soc.*, 119, 600 (1921). [h] As reported.[12] [i] Reported m.p. 189°.[14] [j] Reported for DL-form, m.p. 205°; *cf.* ref. under *g*. [k] Reported m.p. 200–201°.[12] [l] Dimorphic form, m.p. 171–172° obtained by catalytic reductive debromination of one of rearrangement products of 3,3′-dibromo-5,5′-dimethylhydrazobenzene. See last paragraph of Introductory section.

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(10) C. S. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, 1229 (1929).

(11) F. Ullmann and L. Frentzel, *Ber.*, **38**, 729 (1905).

(12) R. B. Carlin and R. C. Odioso, THIS JOURNAL, **76**, 2345 (1954).

the residue was crystallized from ethanol. In this way, 2-iodo-3-nitrotoluene (XVII) gave a 79% yield of V, yellow needles, m.p. 109–110°; and 4-iodo-3-nitrotoluene (XIV) afforded IV, yellow needles, m.p. 141–142°, in 46% yield. The reported m.p.'s are 110°[13] for DL-V and 142–143°[14] for IV.

Hydrogenation of Dimethyldinitrobiphenyls to Diaminodimethylbiphenyls.—The dimethyldinitrobiphenyls were treated with hydrogen at 45–50 p.s.i. at room temperature in the presence of Raney nickel for 4 hours (except for IV (1 hour) and V (2 hours)). Solvents were benzene for the preparations of IX and X and absolute ethanol for the other four. The hydrochlorides of IX and X were precipitated from the benzene solutions by treating the benzene solutions of the bases with dry hydrogen chloride, the hydrochlorides were dissolved in water, and the bases were precipitated by treating the solutions with aqueous sodium hydroxide. The diamine IX was an oil which was extracted into ether. Evaporation of the ether left an oil which gave a solid, m.p. 56–64°, from aqueous ethanol. This solid, probably an unstable hydrate, reverted to an oil when dried or when attempts were made to recrystallize it from non-aqueous solvents.

The other four diamines (VII, VIII, XI and XII) were precipitated from their solutions in ethanol by concentrating the solution and then diluting with water.

All of the diamines were recrystallized from aqueous ethanol except for IX (see above) and VIII, which was recrystallized from aqueous methanol. Properties of and analytical data for the six bases are recorded in Table I.

Diacetyl Derivatives.—All of the diacetyl derivatives except VIIa were prepared by bubbling ketene into ether solutions of the corresponding diamines. The diacetyl derivatives, which precipitated from the solutions as they formed, were collected by filtration. The diamine VII was converted to VIIa by means of acetic anhydride, in accordance with procedure A for the acetylation of diamines described in the preceding paper.[3] All but one of the diacetyl derivatives were recrystallized from aqueous ethanol; VIIIa was recrystallized from water. Table I includes the properties and analytical data for VIIa–XIIa.

Bis-salicylal Derivatives.—The diamines were heated with excess salicylaldehyde at 100° for 0.5–2 hours (VII, IX, XII) or at 190° for 5 minutes (VIII, X, XI); then most of the excess salicylaldehyde was removed by distillation. Except for VIIb, all of the derivatives were recrystallized from ethanol; petroleum ether (b.p. 65–110°) was the solvent for VIIb. Properties and analytical data for these compounds are reported in Table I.

PITTSBURGH 13, PENNSYLVANIA

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[13] W. Dethloff and H. Mix, *Chem. Ber.*, **82**, 534 (1949).

[14] St. von Niementowski, *ibid.*, **34**, 3325 (1901).

[CONTRIBUTIONS FROM SINCLAIR RESEARCH LABORATORIES, INC.]

The Alkylation of Benzene with Isoamylenes and with *t*-Pentyl Chloride[1]

BY B. S. FRIEDMAN AND F. L. MORRITZ[2]

RECEIVED OCTOBER 13, 1955

As reported by others, the ratio of *t*-pentylbenzene (I) to 2-phenyl-3-methylbutane (II) obtained by the reaction of benzene with *t*-pentyl chloride is dependent on the type and activity of catalyst employed. This applies also to the reaction of benzene with (A) 2-methyl-2-butene and (B) 3-methyl-1-butene. However, other factors of reaction severity also affect the course of the reaction. Thus, an increase in temperature, contact time or amount of catalyst decreases the ratio of I to II obtained with a given catalyst. The type of olefin used also affects the ratio, *e.g.*, aluminum chloride produces pure I at −40° and pure II at 21° from (B), but gives a mixture of I and II at 21° with (A). The mechanism of the reaction is discussed.

Boord[2] and his co-workers reported on the specificity of catalyst action when benzene was alkylated with *t*-pentyl chloride. The strong Friedel–Crafts catalyst, aluminum chloride, gave a mixture of isomeric pentylbenzenes. On the other hand, ferric chloride or aluminum chloride dissolved in nitromethane, produced pure *t*-pentylbenzene.

In the alkylation of benzene with branched chain hexyl chloride, or branched hexenes, Schmerling and West[3] demonstrated that the type of substitution was greatly dependent upon the catalyst. At 0° the aluminum chloride-catalyzed alkylation of benzene with 1-chloro-3,3-dimethylbutane or 2-chloro-2,3-dimethylbutane resulted only in the formation of the secondary isomer, 2-phenyl-3,3-dimethylbutane, in the monoalkylated product. Aluminum bromide and zirconium chloride, the latter at 85°, gave very similar results. The other Friedel–Crafts catalysts investigated, *e.g.*, aluminum chloride dissolved in nitromethane, catalyzed the reaction to give only the *t*-hexylbenzene, 2-phenyl-2,3-dimethylbutane, in the monoalkylated product.

Two mechanisms have been proposed[3] for the seemingly anomalous formation of secondary alkylate. One mechanism assumes that the reaction occurs *via* concerted bimolecular nucleophilic displacements (S_N2) with the benzene acting upon a complex of the alkyl chloride and the catalyst. The other mechanism postulates initial tertiary alkylation and subsequent isomerization to give secondary alkylate. There appears to be a correlation between the isomerizing ability of the catalyst and the extent to which secondary alkylation occurs.

It is the purpose of the present investigation to show that the extent to which secondary alkylate is formed is dependent upon the total severity of the reaction. Higher operating temperatures, longer reaction times and increased catalyst ratios appear to favor the formation of secondary alkylate.

Effect of Temperature.—As shown in Table I, alkylation of benzene with 2-methyl-2-butene at 21° in the presence of aluminum chloride resulted in a 42% yield of pentylbenzenes. The composition of this product was 55% *t*-pentylbenzene (I) and 45% 2-phenyl-3-methylbutane (II). The yield of pentylbenzenes was not much lower at 0° and at −40°, but at 0° the ratio of I to II was 75/25, and at −40° only I was formed. When 3-methyl-1-butene was used as the alkylating agent, the effect

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[1] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September, 1955.

[2] M. Inatome, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **74**, 292 (1952).

[3] L. Schmerling and J. P. West, *ibid.*, **76**, 1917 (1954).