xylylene. The compound was recrystallized from methyl alcohol in the form of lemon yellow needles (m.p. 152.0–154.5° dec.). *Anal.* Calcd. for $C_9H_{10}I_2$: C, 29.04; H, 2.71; I, 68.23; mol. wt., 372.1. Found: C, 28.8; H, 2.65; I, 68.3; mol. wt., 345.

WESTFIELD, N. J.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF FRIBOURG. SWITZERLAND, AND ST. JOSEPH'S COLLEGE, INDIANA]

Reactivity of Methyl Groups in Some Derivatives of *m*-Xylene and Toluene

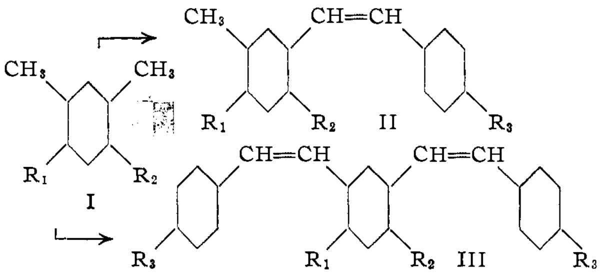
BY LOUIS CHARDONNENS AND WILLIAM J. KRAMER[1]

RECEIVED APRIL 22, 1957

Several *o*- and *p*-substituted *m*-xylenes were condensed with aromatic aldehydes. Included are condensations of some substituted toluenes, particularly some not bearing nitro groups.

It is well known that the methyl group, which is relatively inert in pure hydrocarbon compounds, becomes more reactive in the vicinity of certain substituents in the molecule. Among the rich possibilities in this field are the condensations of substituted toluene and *m*-xylene with aromatic aldehydes in the catalytic presence of piperidine to produce substituted stilbenes.[2] The present paper extends the study of these condensations in two ways: it investigates some derivatives of *m*-xylene, a study begun by Borsche[3]; and it establishes the possibility of carrying out such condensations in both toluene and *m*-xylene derivatives without the presence of the nitro group as an activating substituent.

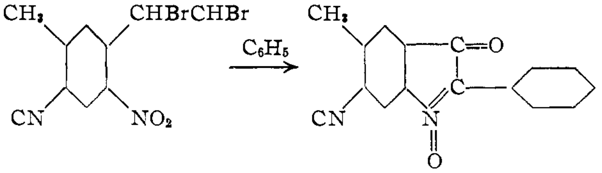
The *m*-xylene derivatives employed bore activating substituents (R_1, R_2) in *o*- and *p*-positions relative to a methyl group, the *m*-position being of little value.[4] Among the most likely substituents nitro, nitrile, benzenesulfonyl, benzoyl, *p*-nitrobenzoyl, only the first three were used with success. When R_1 and R_2 are different, two isomeric monocondensation products are possible, but only one was ever found in a particular reaction. Consistently better yields were obtained from *p*-dimethylaminobenzaldehyde than from benzaldehyde. Yields were for the most part considerably poorer than those obtained from the corresponding toluene derivatives.



Borsche had condensed 5-nitro-2,4-dimethylbenzonitrile (I, R_1 = CN, R_2 = NO_2) with benzaldehyde at 190–200° and obtained a 6% yield of a monocondensation product for which he did not establish the relative positions of the substituents. Subsequent experience has shown that better results are obtained with a longer reaction time at lower temperatures and by a more generous use of the catalyst piperidine. The reaction was therefore repeated at 145–150°, and it yielded 15% of a monocondensation product together with 4% of a double condensation product, the latter being 5-nitro-2,4-distyrylbenzonitrile.

The monocondensation product proved identical by mixed melting point with that obtained by following Borsche's directions. Its formula was determined by its ultraviolet absorption spectrum, which was compared with those of the two possible homologs 2-nitro-4-stilbenecarbonitrile[5] and 4-nitro-2-stilbenecarbonitrile.[5] The inverted chromophores –CN and –NO_2 in these two substances produce widely differing spectra, whereas the methyl group in the substance in question affected the spectrum but slightly. Borsche's compound, corresponding to the former of the two homologs, is therefore 2-nitro-5-methyl-4-stilbenecarbonitrile (II, R_1 = CN, R_2 = NO_2, R_3 = H).

It was possible in this case to check the method of proof by a reaction requiring a nitro and styryl group adjacent to each other. Addition of bromine to the stilbene double bond and exposure of the product to sunlight in pyridine produced an isatogen[6] derivative, 2-phenyl-5-methyl-6-cyanoisatogen.



The condensation of 5-nitro-2,4-dimethylbenzonitrile with *p*-dimethylaminobenzaldehyde gave a 14% yield of the double condensation product, 5-nitro-2,4-bis-(*p*-dimethylaminostyryl)-benzonitrile (III, R_3 = NMe_2). In addition there was a 13% yield of a monocondensation product. Analogy with the product just described would suggest that the methyl group adjacent to the nitro group had reacted. That the contrary had taken

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[2] *Cf.* L. Chardonnens and H. Thomann, *Helv. Chim. Acta*, **39**, 1892 (1956), for the most recent publication on this subject.

[3] W. Borsche, *Ann.*, **386**, 351 (1912); *cf.* P. Ruggli, A. Zimmermann and R. Thouvay, *Helv. Chim. Acta*, **14**, 1250 (1931).

[4] L. Chardonnens and P. Heinrich, *ibid.*, **22**, 1471 (1939).

[5] F. Ullmann and M. Gschwind, *Ber.*, **41**, 2291 (1908).

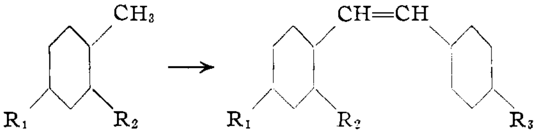
[6] P. Pfeiffer, *ibid.*, **45**, 1810, 1819 (1912); *Ann.*, **411**, 72 (1916); P. Ruggli and R. Thouvay, *Helv. Chim. Acta*, **14**, 1256 (1931); *cf.* J. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955).

place was shown by comparing the spectrum in the ultraviolet and visible range with those of the two possible homologs derived from toluene, 4-nitro-4'-dimethylamino-2-stilbenecarbonitrile[7] and 2-nitro-4'-dimethylamino-4-stilbenecarbonitrile.[7] This conclusion is confirmed when the three products are matched by external appearance and especially by fluorescence in benzene solution. The formula is, therefore, 4-nitro-5-methyl-4'-dimethylamino-2-stilbenecarbonitrile (II, $R_1 = NO_2$, $R_2 = CN$, $R_3 = NMe_2$).

Condensation of 2,4-dimethyl-5-nitro-diphenylsulfone (I, $R_1 = SO_2Ph$, $R_2 = NO_2$) with benzaldehyde yielded exclusively the double condensation product 5-nitro-2,4-distyryl-diphenylsulfone (III, $R_3 = H$). With *p*-dimethylaminobenzaldehyde two products again were formed: a 38% yield of a doubly condensed 5-nitro-2,4-bis-(*p*-dimethylamino-styryl)-diphenylsulfone (III, $R_1 = SO_2Ph$, $R_2 = NO_2$, $R_3 = NMe_2$) and a 5% yield of a singly condensed product. The absorption spectrum shows that the chromophores are arranged as in 3-nitro-4-(*p*-dimethylaminostyryl)-diphenylsulfone[8] rather than 5-nitro-2-(*p*-dimethylaminostyryl)-diphenylsulfone.[8] The formula is therefore 5-nitro-2-methyl-4-(*p*-dimethylaminostyryl)-diphenylsulfone (II, $R_1 = SO_2Ph$, $R_2 = NO_2$, $R_3 = NMe_2$).

Similar reaction procedures with 5-nitro-2,4-dimethylbenzophenone and 5,3'-dinitro-2,4-dimethylbenzophenone yielded no identifiable products.

Hitherto it has been tacitly admitted or tentatively expressed[3,8] that at least one nitro group is needed as activating substituent for this type of reaction. This point of view is based upon experience with benzaldehyde. It has been shown[9] that *p*-dimethylaminobenzaldehyde gives better results with less reactive methyl groups. In confirmation we add the condensation of 5-nitro-2-methylbenzophenone (IV, $R_1 = NO_2$, $R_2 = COPh$) with both *p*-dimethyl- and *p*-diethylaminobenzaldehydes, which produced 5-nitro-2-(*p*-dimethylaminostyryl)-benzophenone (37%) (V, $R_3 = NMe_2$) and 5-nitro-2-(*p*-diethylaminostyryl)-benzophenone (30%) (V, $R_3 = NEt_2$). The attempt with benzaldehyde had produced nothing.[8]



IV V

Accordingly 4,6-bis-(benzenesulfonyl)-1,3-dimethylbenzene (I, R_1, $R_2 = SO_2Ph$) was prepared and condensed with *p*-dimethylaminobenzaldehyde with a 46% yield. Only the monocondensation product was formed, 2,4-bis-(benzenesulfonyl)-5-methyl-4'-dimethylaminostilbene (II, $R_3 = NMe_2$).

4-Methylisophthalonitrile (IV, R_1, $R_2 = CN$), reported as not condensing with benzaldehyde,[3] was condensed with *p*-dimethylaminobenzaldehyde and yielded 4-(*p*-dimethylaminostyryl)-isophthalonitrile (34%)(V, $R_3 = NMe_2$). Condensed with *p*-diethylaminobenzaldehyde it gave a 37% yield of 4-(*p*-diethylaminostyryl)-isophthalonitrile (V, $R_3 = NEt_2$).

Reported as not condensing with benzaldehyde,[8] 2,4-bis-(benzenesulfonyl)-toluene (IV, R_1, $R_2 = SO_2Ph$) was condensed with *p*-dimethylaminobenzaldehyde and it produced a 48% yield of 2,4-bis-(benzenesulfonyl)-4'-dimethylaminostilbene (V, $R_3 = NMe_2$).

Experimental

I. **5-Nitro-2,4-dimethylbenzonitrile.**[3]—A cleaner product was obtained by nitrating 20 g. of 2,4-dimethylbenzonitrile dissolved in 200 ml. of sulfuric acid with 16 g. of potassium nitrate dissolved in 50 ml. of sulfuric acid; yield 55%, m.p. 108°.[10]

1. **Condensation with *p*-Dimethylaminobenzaldehyde.**—The experiments were carried out by heating 3.52 g. (0.02 mole) of the above product with double the molecular quantity of aldehyde and 15 drops of piperidine mixed in an open test-tube. A temperature of 135–140° was maintained for 2 hr. by means of a paraffin-bath or, better, by a refluxing mixture of glycerol and water. As the reaction neared completion, the dark reaction mixture ceased to give off bubbles of steam when it was stirred. The partially cooled mass was mixed with an equal volume of methanol and allowed to precipitate overnight. The precipitate was filtered, washed with alcohol and ether and dried at 80° (4.5 g.).

The two products contained in the black powder were separated by two crystallizations from pyridine. The crystals obtained were recrystallized twice from benzene. The product, 4-nitro-5-methyl-4'-dimethylamino-2-stilbenecarbonitrile (0.8 g., 13%, m.p. 228°), forms black needles of metallic sheen, grinds to a violet-brown powder and dissolves in acetone and glacial acetic acid with a red color. The color in benzene ranges from red in concentrated solutions to orange with orange fluorescence in dilute solutions; $\lambda_{\max}^{\text{MeOH}}$ 213, 295 and 448 mμ, ϵ 25400, 10900 and 30200. For 4-nitro-4'-dimethylamino-2-stilbenecarbonitrile,[7] $\lambda_{\max}^{\text{MeOH}}$ 214, 302 and 464 mμ, ϵ 28400, 12700 and 29100. For 2-nitro-4'-dimethylamino-4-stilbenecarbonitrile,[7] $\lambda_{\max}^{\text{MeOH}}$ 213, 258 and 426 mμ, ϵ 20900, 14400 and 22200.

Anal.[11] Calcd. for $C_{18}H_{17}O_2N_3$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.30; H, 5.51; N, 13.57.

The product retained by the pyridine was dried, dissolved in benzene and purified in a column of alumina. The top layer of adsorbent containing resinous material was lifted and the remainder eluted with benzene containing 10% pyridine. The column remained reddish-brown, but subsequent complete elution with acetone yielded only a small amount of resin. The eluted product was crystallized twice from a mixture of dioxane and amyl alcohol and formed long violet-brown crystals of 5-nitro-2,4-bis-(*p*-dimethylaminostyryl)-benzonitrile (1.2 g., 14%, m.p. 210°).

Anal. Calcd. for $C_{27}H_{26}O_2N_4$: C, 73.95; H, 5.98; N, 12.78. Found: C, 73.68; H, 6.06; N, 12.43.

2. **Condensation with Benzaldehyde.**—The reaction was carried out as above: 3.52 g. (0.02 mole) of nitrile was heated 2 hr. at 145–150° with 16 drops of piperidine and 0.04 mole of freshly distilled benzaldehyde. The resulting dark mass was treated with acetic acid and, after crystallization had been primed by scratching with a glass rod, was left overnight, filtered, washed with ether and dried (1.8 g.).

The two products formed were again separated by two crystallizations from pyridine. The crystals obtained were recrystallized twice from ethanol containing 20% benzene. The yellow needles of 2-nitro-5-methyl-4-stilbenecarbonitrile (0.8 g., 15%, m.p. 190°) were identified by mixed melting point with those obtained by following Borsche's directions; namely, condensing at 190–200° for ten minutes; $\lambda_{\max}^{\text{MeOH}}$ 222 and 315 mμ, ϵ 18300 and 22000. For 2-nitro-4-stilbenecarbonitrile,[5] $\lambda_{\max}^{\text{MeOH}}$ 220 and 314 mμ, ϵ 17500 and 20600. For 4-nitro-2-stilbenecarbonitrile,[5] $\lambda_{\max}^{\text{MeOH}}$ 212, 252 and 351 mμ, ϵ 25000, 11400 and 16500.

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(7) P. Pfeiffer, *Ber.*, **48**, 1808 (1915).

(8) L. Chardonnens and J. Venetz, *Helv. Chim. Acta*, **22**, 853 (1939).

(9) J. Dippy, L. Hogarth, H. Watson and F. Williams, *C. A.*, **32**, 1681^9 (1938).

(10) All melting points are corrected.

(11) Microanalyses for this part by Peisker-Ritter, Brugg, Switzerland.

Anal. Calcd. for $C_{16}H_{12}O_2N_2$: C, 72.71; H, 4.58; N, 10.60. Found: C, 72.89; H, 4.56; N, 10.39.

The pyridine solution containing the product of double condensation, 5-nitro-2,4-distyrylbenzonitrile, was evaporated and the product purified over alumina in benzene solution. It was crystallized twice from acetic acid containing a little benzene. Golden rhombohedrons formed at the bottom of the receptacle and yellow needles at the surface. The mixed melting point proved them identical in composition (m.p. 186°). Mixed with the above monocondensation product, they melted between 155–160°. There was no third product.

Anal. Calcd. for $C_{23}H_{16}O_2N_2$: C, 78.39; H, 4.58; N, 7.95. Found: C, 78.24; H, 4.67; N, 8.12.

3. **Isatogen Derivative.**—One gram of the above monocondensation product was dissolved in 50 ml. of acetic acid and treated dropwise with 0.8 g. of bromine. The solution was heated 0.5 hr. on the water-bath, concentrated and left to crystallize; 0.4 g. of crystals was obtained, which after recrystallization in alcohol formed almost colorless needles melting at 192–193° dec. There was also 0.8 g. of isomeric dibromide which crystallized poorly.[6] The product was dried at room temperature over phosphorus pentoxide at 14 mm.

Anal. Calcd. for $C_{16}H_{12}O_2N_2Br_2$: Br, 37.69. Found: Br, 37.70.

This dibromide was placed on a water glass, covered with pyridine and exposed to open sunlight for 8 to 10 hr. The pyridine was replenished till near the end, when it was allowed to evaporate to dryness. The red product was chromatographed in benzene over alumina, the residual dibromide coming through first. The red zone was extracted with acetone which, when evaporated, left bronze-red leaflets of 2-phenyl-5-methyl-6-cyanoisatogen (50 mg., 21%, m.p. 246°). Recrystallization from alcohol did not change the melting point. The uncrystallized dibromide also yielded the isatogen, together with some of the original stilbene.[6]

Anal. Calcd. for $C_{16}H_{10}O_2N_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.34; H, 3.96; N, 10.59.

II. **2,4-Dimethyl-5-nitro-diphenylsulfone** was prepared by Friedel–Crafts reaction on the chloride of 2,4-dimethyl-5-nitrobenzenesulfonic acid,[12] in a reaction time of about 4 hr. with moderate warming. After the usual treatment with ice, acid and steam, the product crystallized almost pure from the cooled distillation flask. It was further purified over alumina and crystallized from benzine of b.p. 120–180°. Colorless prisms were formed (m.p. 142°, 74%).

Anal. Calcd. for $C_{14}H_{13}O_4NS$: C, 57.72; H, 4.50; N, 4.81. Found: C, 57.83; H, 4.55; N, 4.91.

1. **Condensation with *p*-Dimethylaminobenzaldehyde.**—A mixture of 2.91 g. (0.01 mole) of the above product with 1 ml. of piperidine was melted at 120° and 0.02 mole of aldehyde mixed in at this temperature during 20 minutes. The temperature was then raised to 130–135° for an additional hour. The mass crystallized with metallic lustre on cooling. Washed with alcohol and dried, it weighed 3.6 g.

The products it contained were separated by repeated extraction with hot acetone, about 100 ml. in all. The residue, which contained the double-condensation product 2,4-bis-(*p*-dimethylaminostyryl)-5-nitro-diphenylsulfone, was crystallized from pyridine, then several times from benzene–alcohol until it formed tiny violet-black needles of m.p. 211° (2.1 g., 38%).

Anal. Calcd. for $C_{32}H_{31}O_4N_3S$: C, 69.43; H, 5.64; N, 7.59. Found: C, 69.49; H, 5.69; N, 7.52.

The acetone was evaporated and the residue, which contained 2-methyl-4-(*p*-dimethylaminostyryl)-5-nitro-diphenylsulfone, was chromatographed in benzene over alumina. After a brief development with benzene, the upper resinous layer of adsorbent was removed and the rest eluted with benzene containing 10% pyridine. Crystallization was from benzine of b.p. 120–180°, then acetone–ethanol. The substance forms dark red crystals, violet-red powder and red solutions (0.22 g., 5%, m.p. 187°); $\lambda_{\max}^{\mathrm{MeOH}}$ 240 and 430 mμ, ε 16800 and 21000. For 3-nitro-4-(*p*-dimethylaminostyryl)-diphenylsulfone, $\lambda_{\max}^{\mathrm{MeOH}}$ 239 and 430 mμ, ε 17,100 and 19,100. For 5-nitro-2-(*p*-dimethylaminostyryl)-diphenylsulfone, $\lambda_{\mathrm{Max}}^{\mathrm{MeOH}}$ 301 and 469 mμ, ε 20900 and 29000.

Anal. Calcd. for $C_{23}H_{22}O_4N_2S$: C, 65.38; H, 5.25; N, 6.63. Found: C, 65.51; H, 5.33; N, 6.91.

2. **Condensation with Benzaldehyde.**—The sulfone (2.91 g., 0.01 mole), 0.025 mole of benzaldehyde and 5 drops of piperidine were heated 8 hr. at 130–140°. The dark, warm mass was mixed with an equal volume of acetic acid, prodded with a glass rod until the yellow substance appeared and left overnight. After an ether wash the product crystallized well from acetic acid containing a little benzene but required further purification over alumina in benzene, finally forming light yellow needles of m.p. 201° (1.1 g., 24%). Analysis showed it to be the product of double condensation, 2,4-distyryl-5-nitro-diphenylsulfone. Further condensations with less aldehyde failed to yield a product of single condensation.

Anal. Calcd. for $C_{28}H_{21}O_4NS$: C, 71.93; H, 4.53; N, 3.00. Found: C, 71.85; H, 4.56; N, 3.12.

III. **4,6-Di-(benzenesulfonyl)-1,3-dimethylbenzene** was prepared with a 28% yield by Friedel–Crafts reaction, even though this method failed for the benzene and toluene homologs.[8,13] Nineteen grams of the dichloride of 1,3-dimethylbenzene-2,4-disulfonic acid in 150 ml. of benzene was added in portions to 150 ml. of boiling benzene containing 22 g. of aluminum chloride and boiling continued 6 hr. Crystallization was from nitrobenzene or a rather large quantity of chlorobenzene, the product being insoluble in the usual lighter solvents. It formed brilliant white leaflets of m.p. 243°.

Anal. Calcd. for $C_{20}H_{18}O_4S_2$: C, 62.15; H, 4.69; S, 16.59. Found: C, 62.18; H, 4.78; S, 16.35.

Condensation with *p*-Dimethylaminobenzaldehyde.—Some (1.93 g., 0.005 mole) of the above product was pulverized and maintained at 190–200° and 0.02 mole of aldehyde added in 15 portions, each with a drop of piperidine, over 2 hr. Heating was continued 4 hr. longer. The product was treated with ethanol and allowed to settle out, after which it was washed with alcohol and dried at 100°. It tends to precipitate in finely divided form. Four to five crystallizations from pyridine produced microscopic brick-red needles of constant m.p. 280–282°. Larger prismatic forms were obtained by slow crystallization from xylene. Only the monocondensation product was formed, 2,4-di-(benzenesulfonyl)-5-(*p*-dimethylaminostyryl)-toluene (1.2 g., 46%).

Anal. Calcd. for $C_{29}H_{27}O_4NS_2$: C, 67.29; H, 5.26; N, 2.71. Found: C, 67.53; H, 5.40; N, 2.88.

IV. **5-Nitro-2-methylbenzophenone.** 1. **Condensation with *p*-Dimethylaminobenzaldehyde.**—5-Nitro-2-methylbenzophenone (2.41 g., 0.01 mole) was heated 4 hr. at 125° with a slight excess of aldehyde and 10 drops of piperidine. A dark red powder precipitated from ethanol, and after it had been washed with alcohol and crystallized once from a benzene–ligroin mixture, there remained 1.36 g. (37%) of 5-nitro-2-(*p*-dimethylaminostyryl)-benzophenone in the form of dark red plates. After purification over alumina and recrystallization by evaporation of a cold acetone–alcohol solution, it formed large red prisms with a greenish sheen (m.p. 152°).

Anal.[14] Calcd. for $C_{23}H_{20}O_3N_2$: C, 74.17; H, 5.41; N, 7.52. Found: C, 74.14; H, 5.47; N, 7.81.

2. **Condensation with *p*-Diethylaminobenzaldehyde.**—Carried out as above, the reaction yielded 1.2 g. (30%) of 5-nitro-2-(*p*-diethylaminostyryl)-benzophenone after the first crystallization, which was from acetone–ethanol. It formed wine-red needles of m.p. 122°.

Anal. Calcd. for $C_{25}H_{24}O_3N_2$: C, 74.98; H, 6.04; N, 6.99. Found: C, 75.04; H, 6.09; N, 7.31.

V. **4-Methylisophthalonitrile.** 1. **Condensation with *p*-Dimethylaminobenzaldehyde.**—The dinitrile (1.42 g., 0.01 mole) was heated 4 hr. at 160–165° with an excess of aldehyde and 10 drops of piperidine. After preliminary purification with ethanol and one crystallization from acetone, 0.92 g. (34%) of 4-(*p*-dimethylaminostyryl)-isophthalonitrile was obtained. Purified over alumina and recrystal-

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(12) W. J. Karslake and P. A. Bond, THIS JOURNAL, **31**, 405 (1909).

(13) H. Beckurts and R. Otto, *Ber.*, **11**, 2070 (1878).

(14) Microanalyses from this point were done by Micro-Tech Laboratories, Skokie, Ill.

lized from benzene, it formed almost black needles with bluish lustre (m.p. 214°). The red benzene solution showed a green fluorescence.

Anal. Calcd. for $C_{18}H_{15}N_3$: C, 79.09; H, 5.53; N, 15.38. Found: C, 79.20; H, 5.28; N, 15.33.

2. **Condensation with *p*-Diethylaminobenzaldehyde.**—The dinitrile (1.42 g., 0.01 mole) was heated with an excess of aldehyde and 15 drops of piperidine for 4 hr. at 155°. After preliminary purification with ethanol and one crystallization from benzene–ethanol, 1.11 g. (37%) of 4-(*p*-diethylaminostyryl)-isophthalonitrile was obtained. Further purification over alumina and recrystallization from benzene–ethanol brought it to the form of orange prisms melting at 190°.

Anal. Calcd. for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.80; H, 6.33; N, 14.12.

VI. **2,4-Bis-(benzenesulfonyl)-toluene. Condensation with *p*-Dimethylaminobenzaldehyde.**—The sulfone (3.7 g., 0.01 mole) was heated 4 hr. at 145° with 2 g. of aldehyde and 10 drops of piperidine. Even at this temperature a solid crystalline mass formed, which after a washing with ethanol and crystallization from dioxane formed a brick-red powder (2.4 g., 48%). Recrystallized twice from pyridine, it formed wine-red prisms of 2,4-bis-(benzenesulfonyl)-4′-dimethylaminostilbene (m.p. 265°).

Anal. Calcd. for $C_{28}H_{25}O_4NS_2$: C, 66.77; H, 5.00; S, 12.73. Found: C, 66.68; H, 5.30; S, 12.52.

Absorption spectra were determined on a Beckman model DU spectrophotometer with 10-mm. quartz cells. All solutions were made up of 1 mg. of solute in 100 ml. of methanol.

FRIBOURG, SWITZERLAND
COLLEGEVILLE, INDIANA

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

High Pressure Thermal Alkylation of Monoalkylbenzenes by Simple Olefins[1]

BY HERMAN PINES AND JOSEPH T. ARRIGO[2]

RECEIVED MARCH 14, 1957

The thermal reactions of monoalkylbenzenes with simple olefins were studied in a flow-type system at 420 atm. pressure and in the temperature range of 400–485°. With respect to the formation of 1:1 adducts with the arenes, it was observed that the olefin reactivity decreased in the order propylene > isobutylene > 2-methyl-2-butene. Arene reactivity decreased in the sequence toluene > ethylbenzene > cumene. Selectivity in the addition of aralkyl radicals to unsymmetrical olefins was found to parallel the order of stability of free radicals, III > II > I. Intermediate radicals were found to undergo cyclization or 1,2-phenyl migration in certain cases. Free radical mechanisms for the various reactions are discussed.

The side-chain alkylation of alkylbenzenes by simple olefins at elevated temperatures and pressures has been reported recently.[3] Results of the reaction of toluene with propylene indicated that there was about a sevenfold predominance of *n*- to isobutylbenzene formed. In view of these data, the purpose of the present work was to make a

TABLE I

TOLUENE–PROPYLENE EXPERIMENTS

Experiment	1	2	3	4	5
Temperature, °C.	409	430	456	475	485
Reactants, moles					
Toluene	4.31	4.31	4.14	4.11	2.46
Propylene	0.85	0.85	0.82	0.85	0.50
Results: Propylene reacted, mole %	34	51	54	42	35
Yields based on propylene reacted, mole %					
Propylene dimers	24	21	19	19	16
Propylene trimers	10	11	7.4	3.8	4.1
Monoadducts	28	34	44	37	13
Toluene reacted, mole %	3.4	6.4	10.4	10.4	13.7
Yields based on toluene reacted, mole %[a]					
Benzene	0.7	0.2	0.8	1.3	4
Ethylbenzene	5	3	8	13.2	22.5
Cumene	0.3	0.1	0.3	0.6	0.5
n-Propylbenzene	....	....	1.8	4.2	3
Cymenes(*o*-, *m*-, and *p*-)	....	....	....	1	0.8
Isobutylbenzene	11	9.4	9.8	9.3	2.0
n-Butylbenzene	47	47.6	40.3	24	4.6
Diadduct[b]	36	27.2	12	8	3.6
Diarylalkanes	....	12.5	27	38.4	59[c]
Unsatn. of monoadducts, mole %	2	5.3	4.6	6.8	14

[a] Arenes boiling above the reactant and through the monoadduct range were analyzed after selective hydrogenation (see Experimental). [b] 1:2 arene–olefin products. [c] There was also isolated 0.04 g. of anthracene from expt. 5.

TABLE II

TOLUENE–ISOBUTYLENE EXPERIMENTS

Experiment	6	7	8
Temperature, °C.	411	432	456
Reactants, moles			
Toluene	4.40	4.88	4.72
Isobutylene	0.92	1.03	1.00
Results			
Isobutylene reacted, mole %	28	41	54
Yields based on isobutylene reacted, mole %			
Isobutylene dimers	40	48	47
Isobutylene trimers	10	9.7	7.3
Monoadducts	31	31	24
Toluene reacted, mole %	2.5	4.6	7.5
Yields based on toluene reacted, mole %			
Benzene	1.8	0.4	1.1
Ethylbenzene	5	5	8.1
Unident. butylbenzene (?)	....	....	3.7
Neopentylbenzene	1.6	1.6	1.7
Isopentylbenzene	71.8	56.3	35.4
Diadduct	19.8	9.4	11
Diarylalkanes	....	27.3	39
Unsatn. of monoadducts, mole %	5.5	5.7	10

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(1) Taken in part from a dissertation submitted by J. T. Arrigo to the Graduate School in partial fulfillment of the requirements for the Ph.D. degree, October, 1956.

(2) Universal Oil Products Co. Predoctoral Fellow, 1953–1956.

(3) V. N. Ipatieff, H. Pines and B. Kvetinskas, U. S. Patent 2,758,140 (1956).