TABLE VI

*GEM*-DEHYDRATION OF $\alpha$-BUTOXYALLYL HYDROPEROXIDE

| Perox. Concn., % | Catalyst | Solv. | Temp. | Yield, % Butyl Acrylate | High Boiler, Wt. % | Loss, Wt. % |
|---|---|---|---|---|---|---|
| 31.3 | $FeSO_4$ | $H_2O$ | 100 | 27.4 | 0.0 | 23 |
| 12.8 | $FeSO_4$ | $H_2O$ | 20 | 12.8 | 11.6 | 26 |
| 71.0 | $FeSO_4$ | $H_2O$ | 100 | 12.8 | 5.9 | 12 |
| 17.9 | $Ac_2O$, pyr. | — | 30 | 11.9 | 7.4 | 42 |
| 67.7 | $C_9H_{13}N$[a] | $C_6H_6$ | 25 | 1.6 | 12.9 | 31 |
| 12.9 | KOH | BuOH | 25 | 0.0 | 24.0 | 0.0 |
| 16.6 | $H_2SO_4$ | HOAc | 80 | 5.7 | 10.9 | 10.5 |
| 11.4 | $C_5H_{11}N$[b] | — | 40 | [c] | 11.0 | 33 |

[a] *N,N*-Dimethylbenzylamine. [b] Piperidine. [c] No acrylate obtained; workup yielded 0.11 mole of $\beta$-(*N*-piperidino)propionic acid, yield *ca.* 30%.

taining 21.3% $\alpha$-butoxyallyl hydroperoxide was added dropwise to a vigorously boiling solution of 20 g. of ferrous sulfate heptahydrate and 2.0 g. of hydroquinone in 500 ml. of water. Steam distillate was collected rapidly during the half-hour addition time, and thereafter until the distillate no longer contained oily drops. The distillate organic layer was separated, 0.1 g. of hydroquinone was added, the layer was dried 3 hr. over Drierite, then distilled at reduced pressure. There was collected 68 g. of allyl butyl ether, b.p. 38.5–48.0°/40 mm., $d_4^{20}$ 0.787–0.791, $n_D^{25}$ 1.4031–1.4050, and 9.5 g. of butyl acrylate, b.p. 63.0–68.0°/40 mm., $d_4^{20}$ 0.895–0.900, $n_D^{25}$ 1.4160–1.4168 (listed,[13] b.p. 145–146° (nomograph interpolation gives b.p. 62°/40 mm.), $d_4^{20}$ 0.898, $n_D^{20}$ 1.4185). Residue and other losses amounted to 23% of the original charge to the oxidation.

Various modifications of the so-called ionic dehydrations were tried,[6,7] with little success. The essentials of these experiments are summarized in Table VI. Several of these runs were with hydroperoxide concentrates, up to 71% obtained by vacuum stripping to 35° maximum.

The piperidine experiment is of interest, since a 30% yield of "acrylate" was recovered as a Michael addition product, namely, $\beta$-(*N*-piperidino)propionic acid. In this case 34 ml. of piperidine was added to 90.5 g. of oxidized allyl butyl ether containing 11.4 wt. % $\alpha$-butoxyallyl hydroperoxide. Extraction of the organic layer with aqueous hydrochloric acid gave, on reduction in volume, 21 g. of a solid, m.p. 189–195°, which recrystallized well from ethanol, m.p. 215–217°.

*Anal.* Calcd. for $C_8H_{16}ClNO_2$: C, 49.61; H, 8.33; Cl, 18.31; N, 7.23; neut. equiv., 193.5. Found: C, 49.87; H, 8.00; Cl, 17.84; N, 7.13; neut. equiv., 190, 191; sapon. equiv., 196, 189.

The calculated structure is $\beta$-(*N*-piperidino)propionic acid hydrochloride; this compound gives an immediate and copious precipitate of silver chloride when added to aqueous silver nitrate. The organic layer was distilled giving 42 g. recovery of ether and 10 g. of residue.

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[CONTRIBUTION FROM THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

# Reduction of Azobenzenes by Benzoin

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4-Dimethylaminoazobenzene and related compounds as well as azobenzene are reduced by benzoin in the absence of catalysts and solvents to amines, while benzoin is oxidized to benzil, the final products being azomethine compounds formed by condensation of amines with benzil. There were some indications that the amines were produced through disproportionation, but not by direct reduction, of hydrazo compounds formed at the first stage of reduction.

In an attempt to synthesize azo derivatives of indole from aromatic aminoazo compounds and $\alpha$-hydroxy ketones, it was found that the reaction did not lead to the expected products, but resulted in reduction of azo compounds, if benzoin was used as a hydroxy ketone.

Recently a variety of organic as well as biochemical reagents have been utilized for the reduction of azo compounds,[1–4] but no example of reduction by benzoin seems to have been reported. Although aromatic nitro compounds are reduced by benzoin the reduction stops at azoxy or azo stage,[5] and benzoin is ineffective for chlorophyll- or pheophytin-sensitized photochemical reduction of 2′-carboxy-4-dimethylaminoazobenzene.[2] In this

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[3] W. C. J. Ross and G. P. Warwick, *J. Chem. Soc.*, 1724 (1956).

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TABLE I

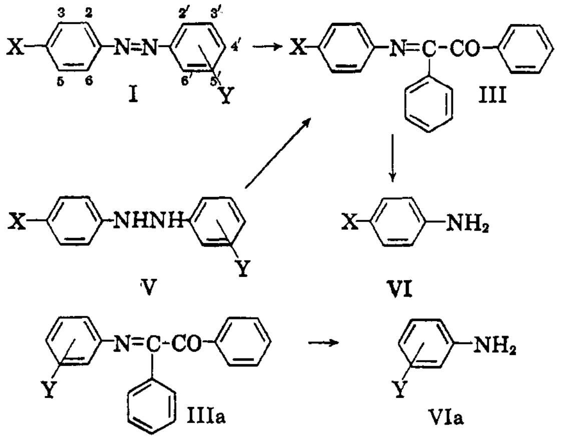
REACTION OF AZO AND HYDRAZO COMPOUNDS WITH BENZOIN AND BENZIL

| Run | Mole Ratio, II/I | Azo Compd. (I) | | Reactn. Condn. | | Products[a] Yield, % |
|---|---|---|---|---|---|---|
| | | X | Y | Temp. | Time, hr. | |
| 1 | 1 | $(CH_3)_2N$ | H | 185 | 6 | I, 11[b]; III, 6 |
| 2 | 1 | $(CH_3)_2N$ | H | 130 | 6 | I, 36[b]; III, 26 |
| 3 | 2 | $(CH_3)_2N$ | H | 130 | 6 | III, 64; IIIa, 14; IV, 7 |
| 4 | 3 | $(CH_3)_2N$ | H | 130 | 6 | III, 46 |
| 5 | 2 | $(CH_3)_2N$ | H | 130 | 1 | III, 18; IV, 32 |
| 6[c] | 2 | $(CH_3)_2N$ | H | 130 | 1 | III, 18; IV, 29 |
| 7[c] | 2 | $(CH_3)_2N$ | H | 130 | 6 | III, 61 |
| 11 | 2 | $(CH_3)_2N$ | 4'-$CH_3$ | 130 | 6 | III, 43 |
| 12 | 2 | $(CH_3)_2N$ | 4'-Cl | 130 | 6 | III, 43 |
| 13 | 2 | $(CH_3)_2N$ | 4'-$CF_3$ | 130 | 6 | III, 49 |
| 14 | 2 | $(CH_3)_2N$ | 2'-$CO_2H$ | 130 | 6 | III, 43 |
| 21 | 2 | $CH_3HN$ | H | 130 | 6 | III, 57 |
| 22 | 2 | $H_2N$ | H | 130 | 6 | III,[d] 53 |
| 23 | 2 | $CH_3O$ | H | 130 | 6 | I, 81[b]; II, 86 |
| 31 | 1 | H | H | 185 | 6 | I, 8[b]; IV, 2 |
| 32 | 2 | H | H | 130 | 6 | I, 33[b]; II, 14; IV, 10; V,[e] (11); VI (= VIa),[f] (1) |
| 33[c] | 2 | H | H | 130 | 6 | I, 33[b]; II, 32; IV, 29 |
| 34 | 2 | H | H | 150 | 12 | IV, 43; V,[e] (6); VI (= VIa),[f] (2) |
| 35 | 2 | H | H | 195 | 6 | III (= IIIa), 14 |
| 36 | 2 | H | H | 195 | 12 | III (= IIIa), 19 |
| | II/V | Hydrazo Compd. (V) | | | | |
| 41 | 1 | H | H | 130 | 6 | I, 66[g] |
| 42 | 1 | H | H | 195 | 4 | —[h] |
| 43 | 1 | H | H | 195 | 12 | III (= IIIa), 18 |
| | IV/V | | (V) | | | |
| 51 | 1 | H | H | 195 | 12 | I, 56[g]; III (= IIIa), 16 |

[a] Unless otherwise noted, Symbol I, III, IIIa, V, or VI denotes the structure with appropriate substituents (X and Y) corresponding to azo compound (I), one of the starting materials. [b] The yield is calculated by regarding I as directly recovered. [c] In these experiments, reaction flasks were irradiated throughout reaction with ultraviolet light from an Acme-type mercury lamp of 3 amp. capacity, placed 15 cm. apart from the flasks. [d] The product is *N*,*N'*-didesylidene-*p*-phenylenediamine (III), X = ($C_6H_5COC_6H_5C{=}N$). [e] Hydrazobenzene (V, X = Y = H) was determined as benzidine, the yield of which was given in parentheses. [f] Aniline (VI, X = H) was determined as acetanilide, the yield of which was given in parentheses. [g] The yield is based on disproportionation scheme (Step 2 in the reaction sequence indicated below). [h] Viscous reddish brown material was obtained from which no crystallizable substance was separated by repeated recrystallization.

paper the reduction of azobenzene and its nuclear-substituted derivatives is investigated, and a plausible course of the reaction is suggested from the consideration of effects of substituents on reducibility.

When 4-dimethylaminoazobenzene (I, X = $(CH_3)_2N$; Y = H) was heated with an equimolar amount of benzoin(II), an orange-red substance was obtained together with recovered I (X = $(CH_3)_2N$; Y = H) (runs 1 and 2, Table I). This substance is *p*-dimethylamino-*N*-desylideneaniline (III, X = $(CH_3)_2N$), the structure of which was determined by hydrolysis with hydrochloric acid to benzil(IV) and *N*,*N*-dimethyl-*p*-phenylenediamine (VI, X = $(CH_3)_2N$) and by comparison with an authentic specimen. By using two equivalents of II the yield of III(X = $(CH_3)_2N$) was greatly increased (run 3), but increase was no longer observed even if more than two equivalents were used (run 4).



Some derivatives of I (X = $(CH_3)_2N$) having substituents Y on the primed rings also gave III (X = $(CH_3)_2N$), the yields of which were, although on an average lower (43–49%) than that of the unsubstituted substance (64%), nearly equal irrespective of the nature of extra substituents (runs 11–14).

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In contrast to this, the reactivity of 4-substituted azobenzenes (I,Y = H) is largely influenced by substituents X. Thus 4-methylaminoazobenzene (I, X = $CH_3HN$; Y = H) and 4-aminoazobenzene (I, X = $H_2N$; Y = H) gave corresponding anils (runs 21 and 22), while 4-methoxyazobenzene (I, X = $CH_3O$; Y = H) and azobenzene (I, X = Y = H) did not, a part of benzoin and azo compounds being recovered. However, azobenzene does give a small yield of *N*-desylideneaniline (III, X = H) if subjected to more drastic reaction conditions (runs 35 and 36). Hydrazobenzene (V, X = Y = H) also gave III (X = H) by heating either with benzoin (run 43) or with benzil (run 51) under the same conditions as above.

A study of titanous chloride reduction of I (X = Y = H) in alcoholic hydrochloric acid[6] showed that the rate of reduction of *cis*-azobenzene was far greater than that of *trans*-isomer. To find the difference, if any, in the reactivities of both isomers towards benzoin reduction, the reaction mixture was irradiated with ultraviolet light, by which isomerization of *trans*-azobenzene derivatives to *cis*-isomers was to be accomplished.[7] However no appreciable difference was observed between the irradiated and the unirradiated reactions both for I(X = $(CH_3)_2N$; Y = H)(runs 3, 5, 6, and 7) and for I (X = Y = H)(runs 32 and 33).

It is suggested from the examination of the above experimental results that a most probable course of the reaction will be as follows:

$$(1)\quad ArN{=}NAr' + C_6H_5CHOHCOC_6H_5 \longrightarrow ArNHNHAr' + C_6H_5COCOC_6H_5$$

$$(2)\quad 2\ ArNHNHAr' \longrightarrow ArNH_2 + H_2NAr' + ArN{=}NAr'$$

$$(3)\quad ArNH_2 + C_6H_5COCOC_6H_5 \longrightarrow ArN{=}CC_6H_5COC_6H_5$$

$$(3a)\quad Ar'NH_2 + C_6H_5COCOC_6H_5 \longrightarrow Ar'N{=}CC_6H_5COC_6H_5$$

Isolation of IV and V (runs 32 and 34) may be an evidence for the hydrogen transfer between I and II (Step 1), and formation of III from V (run 43) shows that V is a true intermediate of the reduction. The final product III will be formed by the condensation of IV and VI (Step 3 and 3a), which may be confirmed by isolation of VI (runs 32 and 34) as well as by a direct condensation of IV and anilines. VI seems to be produced by the disproportionation[8,9] (Step 2), rather than by direct reduction, of V since III is also obtained from IV and V (runs 51). The yields of III in this reaction are generally poor (64% at best), which may be attributed partly to the reoxidation of V to I in the presence of air[8,10] and partly to a loss of VI due to decomposition.

The comparison of the results of runs 3, 21–23, and 32 shows that the effect of 4-substituent X on the reducibility as measured by the yield of III is in the increasing order: $OCH_3 < H < NH_2 \sim NHCH_3 \sim N(CH_3)_2$. According to the studies on polarography[11] and chemical reduction[8] of azobenzene derivatives, the more electronegative the substituent, the more reducible is the azo compound. The deactivation by 4-methoxy group in the present results is coincident with the above evidence, but the accelerating effect of 4-dimethylamino group seems somewhat anomalous. However, it will be pointed out in this connection that in enzymatic reduction by baker's yeast[4] I(X = $(CH_3)_2N$; Y = H) has a greater reactivity over that of I (X = Y = H). The variation in the order of reducibility might be considered as the consequence of different reaction mechanisms due to different reducing agents.

## EXPERIMENTAL[12]

*Materials.* Preparation and purification of azo compounds were previously reported.[13] 4-Methoxyazobenzene (I, X = $CH_3O$; Y = H) (m.p. 56°),[14] benzoin (II) (m.p. 134°),[15] benzil (IV) (m.p. 95°),[16] hydrazobenzene (V, X = Y = H) (m.p. 126°), and *N,N*-dimethyl-*p*-phenylenediamine (VI. X = $(CH_3)_2N$) (m.p. 41°)[17] were purified by recrystallization. *N*-Methyl-*p*-phenylenediamine (VI. X = $CH_3HN$) (b.p. 144–145° (14 mm.); m.p. 35°) was prepared by reduction[17] of *p*-nitroso-*N*-methylaniline. Several authentic specimens of anils (III) were prepared as follows.

*p-Dimethylamino-N-desylideneaniline* (III. X = $(CH_3)_2N$). A mixture of 1.4 g. (0.01 mole) of VI (X = $(CH_3)_2N$), 2.1 g. (0.01 mole) of IV, 0.2 g. of 50% potassium hydroxide solution, and 15 ml. of 95% ethanol was refluxed for 3.5 hr.

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(12) All melting points are uncorrected. Numbers of runs refer to those in Table 1.

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After the solution was cooled, the resulting precipitate was filtered and recrystallized from benzene-ethanol to give 3.1 g. (94%) of III (X = $(CH_3)_2N$), m.p. 140° (reported[18] m.p. 137–138°).

*p-Methylamino-N-desylideneaniline* (III. X = $CH_3HN$). One and two tenths grams (0.01 mole) of VI (X = $CH_3HN$) and 2.1 g. (0.01 mole) of IV were treated similarly as above. Yield of III (X = $CH_3HN$), scarlet needles, m.p. 142°, was 2.8 g. (89%).

*Anal.* Calcd. for $C_{21}H_{18}ON_2$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.31; H, 5.79; N, 8.96.

*N,N'-Didesylidene-p-phenylenediamine* (III. X = $C_6H_5COC_6H_5C{=}N$). A mixture of 0.5 g. (0.005 mole) of *p*-phenylenediamine, 2.1 g. (0.01 mole) of IV, 0.2 g. of 50% potassium hydroxide solution, and 10 ml. of 95% ethanol was refluxed for 5 hr. After the solution was cooled, the precipitate was filtered and recrystallized from dioxane-ethanol to give 2.0 g. (81%) of III (X = $C_6H_5COC_6H_5C{=}N$), yellow platelets, m.p. 221°.

*Anal.* Calcd. for $C_{34}H_{24}O_2N_2$: C, 82.90; H, 4.91; N, 5.69. Found: C, 83.05; H, 4.99; N, 5.73.

*N-Desylideneaniline* (III. X = H). A mixture of 0.9 g. (0.01 mole) of VI (X = H) and 2.1 g. (0.01 mole) of IV was heated in an oil bath at 195° for 6 hr., and, after cooling, triturated with 50 ml. of 5% hydrochloric acid. The precipitate was filtered, washed with water, dried, and recrystallized from benzene-ethanol to yield 1.5 g. (55%) of III (X = H), m.p. 106° (reported m.p. 103–106°,[19] 106–107°[20]).

*Reaction of 4-dimethylaminoazobenzene* (I. X = $(CH_3)_2N$; Y = H). *Run 3.* A mixture of 2.3 g. (0.01 mole) of I (X = $(CH_3)_2N$; Y = H), and 4.2 g. (0.02 mole) of II was heated in an oil bath at 130° for 6 hr. The reaction mixture was immediately extracted with boiling petroleum ether (b.p. 75–120°), the extract being treated with Norit S.X.30 and filtered hot. The solvent was removed *in vacuo*, and the residue was dissolved in benzene-ethanol. After standing overnight at room temperature, the precipitate was filtered and recrystallized from benzene-ethanol to give 2.1 g. (64%) of III (X = $(CH_3)_2N$), m.p. 140°. The melting point was not depressed by admixture with an authentic specimen prepared above.

The mother liquor from which crude III was separated was evaporated to dryness, and the residue was again dissolved in boiling petroleum ether and treated with Norit. After removal of the solvent *in vacuo*, the residue was recrystallized from methanol to give crude IIIa (Y = H) which, after further recrystallizations from benzene-ethanol, yielded 0.4 g (14%) of pure IIIa (Y = H), m.p. and mixed m.p. 106°.

Concentration of the above methanolic filtrate yielded precipitate which on recrystallizations from methanol gave 0.3 g. (7%) of IV, m.p. and mixed m.p. 95°.

Other runs (1–14) of I (X = $(CH_3)_2N$; Y = H) and its derivatives were treated similarly, 0.01 mole of an azo compound and an appropriate amount of benzoin being used.

*Hydrolysis of p-dimethylamino-N-desylideneaniline* (III. X = $(CH_3)_2N$). Six and a half grams (0.02 mole) of III (X = $(CH_3)_2N$) obtained in the above experiments was mixed with 50 ml. of 10% hydrochloric acid and heated on a water bath for 15 min. After the solution was cooled, insoluble solid was filtered, washed with water, and dried. After recrystallizations from carbon tetrachloride, it gave 3.6 g. (86%) of IV, m.p. and mixed m.p. 95°.

The combined hydrochloric acid filtrate and water washings were concentrated *in vacuo*, neutralized with 10% sodium hydroxide solution, and extracted with ether. Ether was distilled, the residue being fractionated *in vacuo* to give 2.1 g. (77%) of VI (X = $(CH_3)_2N$), b.p. 133–136° (15 mm.), m.p. and mixed m.p. 41°.

A sample of this material was mixed with water and treated with acetic anhydride. The resulting precipitate was filtered and recrystallized from water to yield *p*-dimethylaminoacetanilide, m.p. 134° (reported[21] m.p. 134–135°).

*Reaction of 4-methylaminoazobenzene* (I. X = $CH_3HN$; Y = H). *Run 21.* A mixture of 2.1 g. (0.01 mole) of I (X = $CH_3HN$; Y = H) and 4.2 g. (0.02 mole) of II was heated at 130° for 6 hr. The reaction mixture was treated similarly as in run 3 to yield 1.8 g. (57%) of III (X = $CH_3HN$), m.p. 142°, undepressed by admixture with an authentic specimen.

*Anal.* Calcd. for $C_{21}H_{18}ON_2$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.28; H, 5.80; N, 8.93.

*Reaction of 4-aminoazobenzene* (I. X = $H_2N$; Y = H). *Run 22.* A mixture of 2.0 g. (0.01 mole) of I (X = $H_2N$; Y = H) and 4.2 g. (0.02 mole) of II was heated at 130° for 6 hr. The reaction mixture was immediately dissolved in benzene and stood overnight in an ice box. The precipitate was filtered, washed with benzene, and recrystallized from dioxane-ethanol to yield 2.6 g. (53%) of III (X = $C_6H_5CO$-$C_6H_5C{=}N$), m.p. 221°, undepressed on mixing with an authentic specimen.

*Anal.* Calcd. for $C_{34}H_{24}O_2N_2$: C, 82.90; H, 4.91; N, 5.69. Found: C, 82.98; H, 4.91; N, 5.76.

*Reaction of 4-methoxyazobenzene* (I, X = $CH_3O$; Y = H). *Run 23.* A mixture of 2.1 g. (0.01 mole) of I (X = $CH_3O$; Y = H) and 4.2 g. (0.02 mole) of II was heated at 130° for 6 hr. By recrystallization of the reaction mixture from ethanol was recovered 3.6 g. (86%) of II, m.p. and mixed m.p. 134°. The mother liquor was concentrated, and the resulting precipitate was filtered and recrystallized from ethanol to give 1.7 g. (81%) of recovered I (X = $CH_3O$; Y = H), m.p. and mixed m.p. 56°.

*Reaction of azobenzene* (I. X = Y = H) *at lower temperature. Run 32.* A mixture of 1.8 g. (0.01 mole) of I (X = Y = H) and 4.2 g. (0.02 mole) of II was heated at 130° for 6 hr. After the mixture was cooled, it was triturated with 100 ml. of warm 5% hydrochloric acid, and the solid material was filtered and washed with water. Recrystallization of this solid from ethanol gave 0.6 g. (14%) of recovered II, m.p. and mixed m.p. 133–134°.

The mother liquor from which II was separated was concentrated, and the resulting precipitate was filtered and recrystallized from methanol to give 0.4 g. (10%) of IV, m.p. and mixed m.p. 95°.

The ethanolic filtrate from which crude IV was separated and the methanolic mother liquor separated from purified IV were combined and evaporated to dryness, the residue being recrystallized from water-ethanol to yield 0.6 g. (33%) of recovered I (X = Y = H), m.p. and mixed m.p. 68°.

The combined hydrochloric acid filtrate and water washings were neutralized with cold 10% sodium hydroxide solution. The resulting precipitate was filtered, washed with water, dried, and recrystallized from petroleum ether-isopropyl alcohol to yield 0.2 g. (11%) of benzidine, m.p. and mixed m.p. 124–126°. The filtrate from which benzidine was separated was extracted with ether, and the ether was evaporated. The residue was treated with acetic anhydride, the resulting solid being recrystallized from water to give 0.03 g. (1%) of acetanilide, m.p. and mixed m.p. 114°.

Other runs (32–34) of I (X = Y = H) were similarly treated, 0.01 mole of I (X = Y = H) being used in combination with an appropriate amount of benzoin.

*Reaction of azobenzene* (I. X = Y = H) *at high temperature. Run 35.* A mixture of 1.8 g. (0.01 mole) of I (X = Y = H) and 4.2 g. (0.02 mole) of II was heated at 195° for 6 hr.

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The reaction mixture was extracted with petroleum ether, the extract being treated with Norit. The solvent was removed *in vacuo*, and the residue was recrystallized from benzene-ethanol to yield 0.8 g. (14%) of III (X = H), m.p. and mixed m.p. 106°.

Run 36 was similar except that the reaction time was 12 hr.

*Reaction of hydrazobenzene* (V. X = Y = H) *at low temperature. Run 41.* A mixture of 1.8 g. (0.01 mole) of V (X = Y = H) and 2.1 g. (0.01 mole) of II was heated at 130° for 6 hr. The reaction mixture was dissolved in benzene-ethanol, and was allowed to stand for several days in an ice box. The precipitate was filtered and recrystallized from water-ethanol to give 0.6 g. (66% yield based on Step 2) of I (X = Y = H), m.p. and mixed m.p. 68°.

*Reaction of hydrazobenzene* (V. X = Y = H) *at high temperature. Run 43.* One and eight-tenth grams (0.01 mole) of V (X = Y = H) was heated with 2.1 g. (0.01 mole) of II at 195° for 12 hr. The reaction mixture was treated similarly as in run 35, and the resulting mass was recrystallized from benzene-ethanol to give 0.5 g. (18%) of III (X = H), m.p. and mixed m.p. 106°.

*Reaction of hydrazobenzene* (V. X = Y = H) *with benzil* (IV). *Run 51.* A mixture of 1.8 g. (0.01 mole) of V (X = Y = H) and 2.1 g. (0.01 mole) of IV was heated at 195° for 12 hr., and the reaction mixture was treated with petroleum ether and Norit similarly as in run 35. Recrystallization of the resulting mass afforded 0.45 g. (16%) of III, m.p. and mixed m.p. 106°, and 0.5 g. (56% based on Step 2) of I (X = Y = H), m.p. and mixed m.p. 68°.

*Condensation of aniline* (VI. X = H) and *N,N-dimethyl-p-phenylenediamine* (VI. X = $(CH_3)_2N$) *with benzil* (IV). A mixture of 0.01 mole of amine (VI) and 2.1 g. (0.01 mole) of IV was heated at 130° for 6 hr. The reaction mixture for VI (X = H) was at once recrystallized from benzene-ethanol to give 1.2 g. (42%) of III (X = H), m.p. and mixed m.p. 106°.

The reaction mixture for VI (X = $(CH_3)_2N$) was treated with petroleum ether and Norit, and recrystallized from benzene-ethanol to yield 2.0 g. (61%) of III (X = $(CH_3)_2N$), m.p. and mixed m.p. 140°.

KYOTO, JAPAN

[CONTRIBUTION FROM THE PLASTICS & RESINS DIVISION STAMFORD RESEARCH LABORATORIES, AMERICAN CYANAMID CO.]

# The Synthesis of 2,2-Ditolylpropane from α,*p*-Dimethylstyrene[1]

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2,2-Di(*p*-tolyl)propane has been obtained in high yields for the first time by the alkylation of toluene with 2-chloro-2-(*p*-tolyl)propane, a derivative of α,*p*-dimethylstyrene. Complexes of aluminum chloride with nitromethane or nitrobenzene were found to be specific catalysts for this reaction. Other Lewis acids and complexes were found to favor the competing reaction—*i.e.*, the formation of 1,3,3,6-tetramethyl-1-(*p*-tolyl)indane and other dimers of α,*p*-dimethylstyrene.

1,1-Diarylalkanes are readily prepared by the acid catalyzed alkylation of aromatic compounds with aldehydes[2] or with styrenes.[3] On the other hand, alkylations leading to non-terminal diarylalkanes which employ simple ketones or α-methylstyrenes, have been limited to active aromatic compounds such as phenols[4] and aniline.[5] Toluene, for example, has not been alkylated in high yields with acetone or with α-methylstyrenes.[6] The alkylating agents appear to condense with themselves rather than with toluene under the conditions investigated.

The present work is a study of conditions which led to the successful alkylation of toluene by a derivative of α,*p*-dimethylstyrene, 2-chloro-2-(*p*-tolyl) propane to give 2,2-ditolylpropane in high yield.

## DISCUSSION OF EXPERIMENTAL RESULTS

As early as 1890 Spiller and co-workers alkylated toluene with styrene in the presence of sulfuric acid to give a 1,1-diarylalkane.[3] We have found that when this reaction is carried out using α,*p*-dimethylstyrene (DMS) in place of the styrene, the major product (80%) is the dimer, [1,3,3,6-tetramethyl-1-(p-tolyl)]indane.[7] Only a small quantity (4%) of the desired product, 2,2-ditolylpropane (DTP) is obtained. The course for these reactions is shown below. Apparently the carbonium ion derived from α,*p*-dimethylstyrene (in contrast to the styryl carbonium ion) attacks the double bond of another α,*p*-dimethylstyrene molecule in preference to the toluene ring, $k_1 << k_2 + (k_3, k_4$, or $k_5)$.

In an effort to suppress dimerization other reaction conditions and catalysts were studied.

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(1) Presented at the 135th Meeting of the American Chemical Society, Boston, Massachusetts, April 10, 1959.

(2)(a) A. Baeyer, *Ber.*, **6**, 220 (1873); (b) O. Fischer, *Ber.* **7**, 1193 (1874).

(3)(a) G. Kraemer, A. Spiller, and P. Eberhardt, *Ber.*, **23**, 3269 (1890); (b) A. Spiller and W. Schade, *Ber.*, **65B**, 1686 (1932).

(4)(a) Th. Zincke and M. Grueters, *Ann.*, **343**, 85 (1905); (b) J. B. Niederl, *J. Am. Chem. Soc.*, **50**, 2230 (1928); (c) J. B. Niederl and R. Casty, *Monatsh.*, **51**, 86 (1929).

(5) J. von Braun, *Ann.*, **472**, 1 (1929).

(6) A. B. Bakalar in U.S. Pat. **2,455,643** (Dec. 7, 1948) reports the isolation of a product of molecular weight 224 (corresponds to 2,2-ditolylpropane) by the condensation of toluene with acetone in the presence of sulfuric acid. However, several independent attempts in these laboratories to condense acetone with toluene using a variety of acid catalysts, including sulfuric acid, were unsuccessful.

(7) For a discussion of the acid catalyzed dimerization of the styrene see A. Muller, *J. Org. Chem.*, **17**, 1077 (1952), and J. C. Petropoulos and J. J. Fisher, *J. Am. Chem. Soc.*, **80**, 1938 (1958).