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.

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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).

TABLE I

ALKYLATION OF BENZENE

Procedure	Alkylating agent[a,b]	Catalyst	g.	Promoter	Temp., °C.	Duration, min.	Pentylbenzene Composition, % I	II	Yield,[e] %
1	A	$AlCl_3$	27	HCl	21	34	55	45	42[g]
1	A	$AlCl_3$	27	HCl	0	30	75	25	54
1	A	$AlCl_3$	27	HCl	−40	50	100	0	39
1	B	$AlCl_3$	27	HCl	21	36	0	100	42
1	B	$AlCl_3$	27	HCl	0	41	55	45	38
1	B	$AlCl_3$	27	HCl	−40	52	100	0	[d]
1	B	$AlCl_3$	27	HCl	−60	41	100	0	[d]
4	B	HF	100		35	39	100	0	27
4	A	HF	100		100	34	70	30	32
4	A	BF_3	1 mole		28	39	100	0	10[g]
4	A	BF_3	1 mole		119	30	80	20	11[g]
4	A	HF BF_3	100 27		0	18	75	25	51[g]
4	B	HF BF_3	100 163		25	17	..	..	[f]
1	A	$AlCl_3$	27	HCl	0	180	35	65	45
3	A	$AlBr_3$	27	HBr	25	1 sec.	90	10	22[g]
1	A	$AlBr_3$	27	HBr	25	25	70	30	21[g]
2	C	$AlCl_3$	3.5		24	150	100	0	71
2	C	$AlCl_3$	27		0	37	35	65	57
1	A	BF_3 H_2O	105 36		24	29	100	0	54
2	A	H_2SO_4[c]	185		0	67	100	0	4

[a] 2-Methyl-2-butene (A), 3-methyl-1-butene (B), *t*-pentyl chloride (C). [b] In all cases one mole alkylating agent and 5 moles of benzene were used. [c] 96% concentration. [d] See footnote 4. [e] Based on alkylating agent charged. [f] Intractable mixture. [g] Plus some *t*-butylbenzene.

of temperature was even more striking. At 21° a 42% yield of pentylbenzene was obtained. This contained only II. At −40° only I was formed but the yield of pentylbenzene was very low,[4] compared to 39% for the alkylation with 2-methyl-2-butene. At 0° the yield of pentylbenzene was 38% and it consisted of 55% I and 45% II. It seems evident that a decrease in the total severity of the conditions, in this case a decrease in temperature, served to favor the formation (and/or survival) of the tertiary alkylate.

This temperature effect was also studied using catalysts which heretofore had been known to give only tertiary alkylation. The reaction of benzene with 3-methyl-1-butene at 35° in the presence of hydrogen fluoride resulted in the formation of only one pentylbenzene, namely, I. The hydrogen fluoride catalyzed reaction of benzene at 100° with 2-methyl-2-butene, an olefin less prone to give secondary alkylation than 3-methyl-1-butene gave a 70/30 mixture of I and II. Schmerling[3] observed only tertiary alkylation at 0° in the alkylation of benzene with 2,3-dimethyl-2-butene in the presence of this catalyst. At 28° the boron fluoride catalyzed alkylation of benzene with 2-methyl-2-butene gave a 10% yield of pentylbenzene containing 80% I and 20% II.

An attempt also was made to investigate the temperature effect using the catalyst couple, hydrogen fluoride/boron fluoride. At 0° with 3-methyl-1-butene there was formed a 51% yield of pentylbenzenes consisting of 75% I and 25% II. At 25°, however, an intractable mixture of alkyl aromatics was formed.

Effect of Reaction Time.—Another factor which appeared to affect the extent of secondary alkylation was the reaction time. When benzene was alkylated with 2-methyl-2-butene at 0° in the presence of aluminum chloride/hydrogen chloride, the ratio of I to II in a 30-minute reaction product was 75/25, whereas in a 180-minute reaction product the ratio was 35/65. In the presence of aluminum bromide/hydrogen bromide at 25°, one-second reaction time, the pentylbenzene fraction contained a 90/10 ratio of I to II, whereas with a reaction time of 25 minutes, the yield was about the same but the ratio fell to 70/30.

Effect of Catalyst Ratio.—The extent of secondary alkylation also appeared to be affected by the amount of catalyst used. When benzene was alkylated with *t*-pentyl chloride at 0° using a catalyst to alkyl chloride ratio of 0.2, 65% of the pentylbenzene formed was II. However, when the catalyst to alkyl chloride ratio was 0.025 (temperature 25°), the only pentylbenzene formed was I.

In several instances, particularly at low ratios of aluminum chloride, and even with high ratios of aluminum bromide, *t*-butylbenzene is formed as one of the main products of the reaction between benzene and isoamylene. This phenomenon will be discussed in a subsequent paper.

Mechanism.—In conclusion, it must be stated that the data do not permit selection between the two mechanisms suggested by Schmerling and

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(4) The large amounts of polymer formed at these low temperatures so obscured the analyses that no valid estimate of the yields could be made. Infrared analysis, however, indicates that the only pentylbenzene present was *t*-pentylbenzene (I).

West: (a) S_N2 concerted molecular nucleophilic displacement or (b) S_E carbonium ion attack on benzene followed by isomerization of the intermediate *t*-alkylbenzene. It is evident that the S_N2 reaction, and the isomerization step in (b), both require higher temperatures than the carbonium ion reaction for appreciable conversion to take place. In addition, results obtained in studies of the reaction of isoamylenes with *p*-xylene (to be reported later) suggest that the reaction proceeds readily *via* some mechanism other than (b) since steric effects retard initial attack by the bulky *t*-carbonium ion.

Experimental

Materials.—2-Methyl-2-butene and 3-methyl-1-butene (99+ mole % minimum) were purchased from Phillips Petroleum Company and used as received. *t*-Pentyl chloride was purchased from the Matheson Company and found to be pure by infrared examination. The benzene used was Fisher ACS and Merck Reagent Grade.

Procedure 1.—A mixture comprising one mole alkylating agent and one mole benzene was added to a stirred mixture comprising four moles benzene, 3.4 moles of *n*-heptane, and the catalyst saturated with dry HCl. Stirring was continued for 5–10 minutes after the alkylating agent had been added, and the product was permitted to stand for about 10 minutes. The upper layer was separated from the catalyst layer, washed three times with water, stirred several hours with water at about 85 to 95°, dried, stirred with sodium sand at 130–150° for several hours, and distilled. The fractions were analyzed by means of their infrared spectra.[5]

Procedure 2.—The catalyst was added in several portions during the course of the reaction to a stirred mixture comprising 5 moles of benzene and 1 mole of alkylating agent. The products were worked up as in procedure 1.

Procedure 3.—A mixture of 4 moles of benzene and 27 g. of aluminum bromide in a large beaker was saturated with hydrogen bromide gas. At 25° a mixture comprising 1 mole of benzene and 1 mole of 2-methyl-2-butene was *dumped* into the vigorously stirred solution. This was followed by the immediate addition of 400 ml. of water. The estimated time of contact was 1 second. The products were worked up as in procedure 1.

Procedure 4.—Four moles of benzene was introduced under nitrogen pressure into an autoclave (containing 100 g. when employed, of hydrogen fluoride). When required, the boron fluoride gas was then introduced under its own pressure from a 2-liter cylinder. After the temperature had been brought to normal a mixture of 1 mole of benzene and 1 mole of alkylating agent was added with stirring. The product mixture was discharged into a mixture of ice and water. The products were worked up as in procedure 1.

Infrared Standards.—1-Phenyl-2-methylbutane was synthesized by well-known procedures (three steps from benzylmagnesium chloride and methyl ethyl ketone). Grateful acknowledgement is due to Universal Oil Products Company, Riverside, Illinois, for pure samples of 2-phenyl-3-methylbutane, 1-phenyl-3-methylbutane, 1-phenylpentane, 2-phenylpentane, 3-phenylpentane and neopentylbenzene. Pure *t*-pentylbenzene was obtained from the National Bureau of Standards.

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[5] The authors are indebted to F. L. Voelz and F. L. Boys of the Spectrometric Laboratory of Sinclair Research Laboratories, Inc., for the infrared absorption analyses.

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

Oxidation of Hindered Phenols. IV. Stable Phenoxy Radicals

BY CLINTON D. COOK, DAVID A. KUHN AND PETER FIANU

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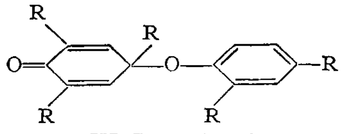
Stable phenoxy radicals are produced by the alkaline ferricyanide oxidation of 2,6-di-*t*-alkyl-4-alkoxy and -4-*t*-alkyl phenols. Properties of these radicals and of peroxides derived from them are reported.

We have suggested[1] that requirements for the formation of a stable mononuclear phenoxy radical are that the *ortho* and *para* positions be substituted by groups sufficiently large to prevent nuclear dimerization and that these groups must not have α-hydrogen atoms. This suggestion was based on the fact that 2,4,6-tri-*t*-butylphenol (I) is oxidized to 2,4,6-tri-*t*-butylphenoxy, a relatively stable radical,[1,2,2a,2b] and that 2,6-di-*t*-butyl-4-methylphenoxy rearranges to the corresponding benzyl radical and then dimerizes.[1]

We have now found that, similar to 2,4,6-tri-*t*-butylphenol, 2,4,6-tri-*t*-amylphenol (II) and 2,6-di-*t*-butyl-4-dimethylethoxymethyl (IX) and -4-dimethylmethoxymethyl (VIII) phenols are readily oxidized by alkaline ferricyanide or lead dioxide to produce the corresponding phenoxy radicals X. Like 2,4,6-tri-*t*-butylphenoxy, these radicals are of an intense blue color. Similar oxidation of 2,6-di-*t*-butyl-4-methoxy (V),[3] -4-ethoxy (VI), and -4-*t*-butoxyphenols (VII) and of 2,6-di-*t*-amyl-4-methoxy (IV) and -4-*t*-amyloxyphenols (III) gives bright red phenoxy radicals.

As compared to tri-*t*-butylphenoxy, 2,4,6-tri-*t*-amylphenoxy appears to disproportionate rather readily. While rate measurements were erratic, a rough indication of the rate is given by the fact that an 0.01 M solution of this radical underwent 70% decomposition in an hour. Study of this phenomenon is complicated by the difficulty of establishing the purity of 2,4,6-tri-*t*-amylphenol (II), a high boiling liquid which appears to dealkylate very readily.

Müller and co-workers[2b] have reported the formation of 2,4,6-tri-*t*-butylphenol on disproportionation of 2,4,6-tri-*t*-butylphenoxy. In addition to the phenol we have found that the disproportionation produces isobutylene and at least two dimeric products. The elemental analysis and infrared and ultraviolet spectra of one of the dimeric products are suggestive of a structure such as XI



XI, R = *t*-butyl

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[1] C. D. Cook, N. G. Nash and H. R. Flanagan, THIS JOURNAL, **77**, 1783 (1955).

[2] C. D. Cook and R. C. Woodworth, *ibid.*, **75**, 6242 (1953).

[2a] E. Müller and K. Ley, *Ber.*, **87**, 922 (1954).

[2b] E. Müller, K. Ley and W. Kiedaisch, *ibid.*, **87**, 1605 (1954).

[3] While this work was in progress Müller and Ley, (*Ber.*, **88**, 601 (1955)) published a discussion of the 2,6-di-*t*-butyl-4-methoxyphenoxy radical.