[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS CO.]

Reaction of Benzene with Dichloroalkanes Containing Tertiary Carbon Atoms[1]

BY LOUIS SCHMERLING, ROBERT W. WELCH AND JAMES P. WEST

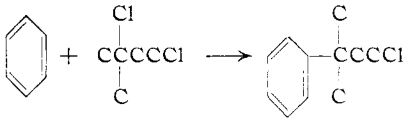
RECEIVED JUNE 4, 1956

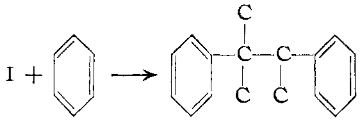
Hydrogen transfer occurs when benzene is condensed with 1,3-dichloro-3-methylbutane in the presence of aluminum chloride and a saturated hydrocarbon, isobutane or methylcyclopentane, yielding chiefly (3-chloro-1,1-dimethylpropyl)-benzene (I) and *t*-butylbenzene or (methylcyclopentyl)-benzene, respectively. In the absence of a saturated hydrocarbon, I and a diphenylpentane (II) are obtained in equal yield. On the other hand, no chloro-*t*-butylbenzene (corresponding to I) is produced by the reaction of benzene with 1,2-dichloro-2-methylpropane in the presence or absence of saturated hydrocarbons. When methylcyclohexane is used, the principal products are isobutylbenzene and (methylcyclohexyl)-benzene; when none is added, diphenylbutane, chiefly 1,2-diphenyl-2-methylpropane (VI) containing a small amount of *meso*-2,3-diphenylbutane, is obtained with only a trace of isobutylbenzene. The mechanism of the reactions is discussed.

It was shown recently[2] that the aluminum chloride catalyzed reaction of benzene with 1,1-dichloro-3,3-dimethylbutane yields 1,1-diphenyl-3,3-dimethylbutane (26–28%) together with a primary alkylbenzene, 1-phenyl-3,3-dimethylbutane (19–20%). The yield of the latter may be increased markedly (to 60%) at the expense of the former (yield, 6%) by carrying out the reaction in the presence of methylcyclopentane which serves as a hydrogen donor and is converted to (methylcyclopentyl)-benzene (48%). This reaction thus offers a simple means for obtaining a primary alkylbenzene containing a *gem*-dialkyl group.

The reaction of benzene with dichloroalkanes (*i.e.*, 1,2-dichloro-2-methylpropane and 1,3-dichloro-3-methylbutane) in which one chlorine atom is attached to a primary and the other to a tertiary carbon atom is described in the present paper. Means of controlling the reaction to give condensation at the tertiary carbon atom only were investigated. The effect of saturated hydrocarbons on the reaction was determined.

1,3-Dichloro-3-methylbutane.—Alkylation of benzene with 1,3-dichloro-3-methylbutane (isoprene dihydrochloride) in the presence of aluminum chloride at 2–4° resulted in the formation of a (chloropentyl)-benzene and a diphenylpentane in about equal yield, 28–29%. The former, (3-chloro-1,1-dimethylpropyl)-benzene (I), resulted from the condensation of benzene at the tertiary carbon atom, presumably *via* a carbonium ion mechanism. The latter, II, was apparently 2,3-diphenyl-2-methylbutane, formed *via* conversion of I to a secondary carbonium ion, rather than 1,3-diphenyl-3-methyl-butane formed by the bimolecular nucleophilic displacement (S_N2 reaction) of the chlorine atom attached to the primary carbon atom of I.[3]


I


II

The structure of I was proved by hydrolyzing its Grignard reagent. Pure *t*-pentylbenzene was obtained. That the diphenylpentane was II rather than 1,3-diphenyl-3-methylbutane was indicated by the fact that 2-methyl-3-phenylbutane rather than isopentylbenzene was formed by its partial dephenylation under hydrogen transfer conditions.

Hydrogen transfer occurred when benzene was treated with 1,3-dichloro-3-methylbutane at −2 to 0° in the presence of isobutane and aluminum chloride. The chloropentylbenzene (I, 33%) was still a major product, but even more *t*-butylbenzene (48%) was obtained. The dichloride and II (or an intermediate) served as the hydrogen acceptors producing, respectively, isopentyl chloride which was isolated in 11% yield and pentylbenzene (pure 2-methyl-3-phenylbutane) obtained in 14% yield. Isopentane was probably also formed, but was not recovered.

Similarly, the reaction of the isoprene dihydrochloride with benzene and methylcyclopentane gave I (44%) and (methylcyclopentyl)-benzene (IV, 38%). Isopentane was isolated in 8% yield, accounting for almost half of the hydrogen abstracted from the cycloalkane which reacted to form the cycloalkylbenzene. Isopentyl chloride (not isolated) and 2-methyl-3-phenylbutane (7%) accounted for the remainder.

The (methylcyclopentyl)-benzene (IV) consisted of secondary cycloalkylbenzenes, (2-[and 3-]methylcyclopentyl)-benzene, rather than the tertiary isomer, (1-methylcyclopentyl)-benzene. It has been shown that, contrary to general belief, alkylation of benzene with tertiary alkyl chlorides (other than *t*-butyl chloride) in the presence of aluminum chloride yields chiefly secondary rather than tertiary alkylbenzenes.[4]

Reaction of the chlorine atom in the chloropentylbenzene (I) was practically prevented by modifying the activity of the aluminum chloride by dissolving it in nitromethane.[5] Compound I was obtained in 55% yield by the gradual addition of the dichloride to a benzene solution of aluminum chloride and nitromethane at room temperature. The principal by-product (22%) was crystalline *p*-bis-(3-chloro-1,1-dimethylpropyl)-benzene (III)

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[1] Presented before the Division of Organic Chemistry of the American Chemical Society at the Dallas Meeting, April, 1956.

[2] L. Schmerling, J. P. Luvisi and R. W. Welch, THIS JOURNAL, **77**, 1774 (1955).

[3] L. Schmerling, *Ind. Eng. Chem.*, **45**, 1447 (1953); H. C. Brown, L. P. Eddy, W. J. Wallace, M. Grayson and K. L. Nelson, *ibid.*, **45**, 1462 (1953).

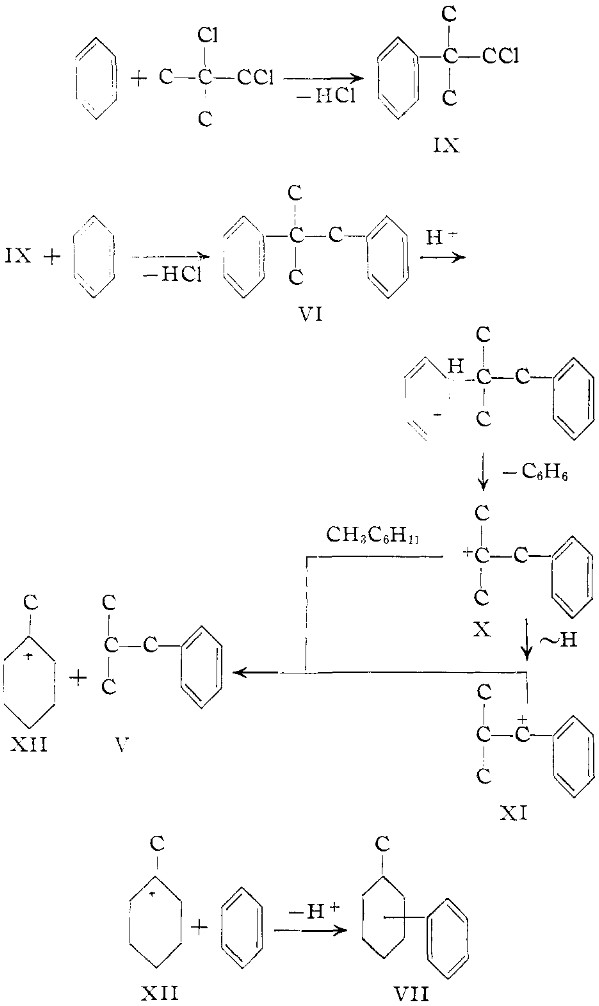
[4] L. Schmerling and J. P. West, THIS JOURNAL, **76**, 1917 (1954).

[5] L. Schmerling, *Ind. Eng. Chem.*, **40**, 2072 (1948).

formed by the further reaction of I with the dichloromethylbutane.

1,2-Dichloro-2-methylpropane.—The condensation of 1,2-dibromo-2-methylpropane (isobutylene dibromide) with benzene in the presence of aluminum chloride has been described by Bodroux.[6] From the product of two experiments in each of which 20 g. of aluminum chloride was added to a solution of 75 g. (0.35 mole) of the dibromide in 150 g. (1.9 moles) of benzene, there was obtained 21 g. (14%) of 1,2-diphenyl-2-methylpropane (VI), 11 g. (12%) of isobutylbenzene, and a small amount of crystalline compound which was not identified but which was later shown[7] to be *meso*-2,3-diphenylbutane.

In the present investigation it was found that the reaction of 0.5 mole of 1,2-dichloro-2-methylpropane with 2.6 moles of benzene in the presence of 5 g. of aluminum chloride at wet ice temperature resulted in a 50% yield of diphenylbutane (chiefly 1,2-diphenyl-2-methylpropane, VI) and less than 1% of isobutylbenzene. The diphenylbutane deposited a small amount (about 2.5% of the fraction) of crystals, m.p. 123–125°, which consisted of *meso*-2,3-diphenylbutane (XIII).



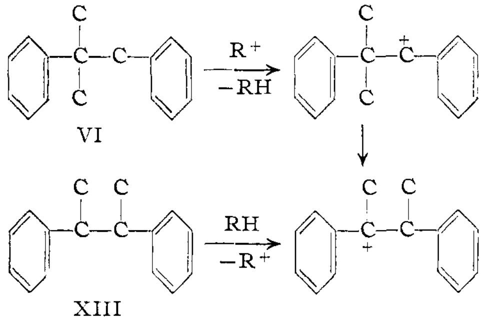
The reaction was markedly modified by carrying it out in the presence of methylcyclohexane, no diphenylbutane being isolated. Pure isobutylbenzene (V) was obtained in 57% yield together with a 70% yield of (methylcyclohexyl)-benzene (VII) and a 14% yield of (methylcyclohexyl)-isobutylbenzene (VIII), largely the *para* isomer. Compound VII (and, presumably, VIII) was practically completely secondary rather than tertiary cycloalkyl derivative.

With zirconium chloride as catalyst at room temperature, both normal alkylation and hydrogen transfer occurred in the presence of the saturated hydrocarbon. The chief products were V, VI and VII, each of which was obtained in about 30% yield.

Mechanism.—It seems quite probable that the first step in the reaction of benzene with either of the dichlorides is the formation of a chloro-*t*-alkylbenzene. The reaction with the isobutylene dichloride, for example, might be indicated in terms of classical carbonium ion theory (see chart).

Addition of cation XII to isobutylbenzene (V) results in the cycloalkylisobutylbenzene, VIII.

Formation of crystalline *meso*-2,3-diphenylbutane (XIII) involves isomerization of VI.[8] Thus, the reaction of VI with benzene in the presence of aluminum chloride yielded 1–17% of XIII and 2–11% of V, depending on the relative amount of catalyst and the reaction temperature.[8]



That the diphenyl compound VI is formed by the reaction of the chlorobutylbenzene (IX) with benzene was observed by Somerville and Spoerri.[8] The reaction of 10 moles of IX with 100 moles of benzene in the presence of 1 mole of aluminum chloride at 10–12° gave a 48% yield of VI and a 4% yield of *meso*-2,3-diphenylbutane (XIII).

The ready conversion VI to isobutylbenzene (V) in the presence of methylcyclohexane has now been shown by carrying out the reaction of the diphenylbutane and the saturated hydrocarbon in the presence of aluminum chloride and a minor amount of isopropyl chloride (added as a convenient source of hydrogen chloride). A 37% yield of V and a 17% yield of the (methylcyclohexyl)-isobutylbenzene (VIII) was obtained. About 1% of the 24% recovered VI was the crystalline isomer XIII. Presumably, ions X and XI are formed as above indicated; these are converted to V by abstraction of hydride ions from the methylcyclohexane, yielding XII which adds to V to yield VIII.

The chloro-*t*-butylbenzene (IX) also reacted

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[6] F. Bodroux, *Compt. rend.*, **132**, 1333 (1901).

[7] W. T. Somerville and P. E. Spoerri, THIS JOURNAL, **72**, 2185 (1950).

[8] W. T. Somerville and P. E. Spoerri, *ibid.*, **74**, 3803 (1952).

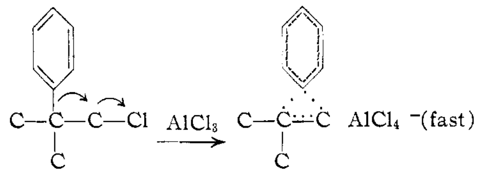
TABLE I

REACTION OF BENZENE WITH CHLORO-*t*-ALKYL CHLORIDES

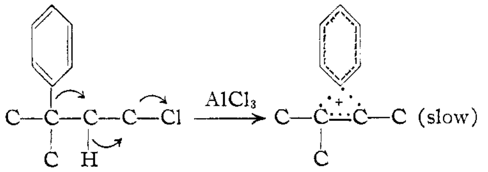
Expt.	Method	Reactants, moles C_6H_6	RCl_2	Satd.	Catalyst Kind	G.	Ave. temp., °C.	Chief products Compd.	Yield, %
				1,3-Dichloro-3-methylbutane					
1	S	1.2	0.2	..	$AlCl_3$	2	2 to 4[a]	I	28
								II	29
2	A	6.2	1.0	..	$AlCl_3$	10	25 to 27	I	55
					CH_3NO_2	10		III	22
3	E	1.0	0.18	..	$FeCl_3$	1	20 to 22	I	19
4	A	2.6	.5	2.1[b]	$AlCl_3$	5	−2 to 0	I	33
								PhBu-*t*	48
								PhC_5H_{11}[c]	14
								i-$C_5H_{11}Cl$	11
5	A	2.6	.5	1.5[d]	$AlCl_3$	5	2 to 4	I	44
								IV	38
								PhC_5H_{11}[c]	3
								i-C_5H_{12}	8
				1,2-Dichloro-2-methylpropane					
6	A	2.6	0.5	..	$AlCl_3$	5	2 to 4	V	1
								VI	50
7	A	2.6	.5	1.5[e]	$AlCl_3$	5	3 to 4	V	57
								VII	70
								VIII	14
8	A	1.3	.25	0.75[e]	$ZrCl_4$	6	26 to 30	V	30
								VII	34
								VI	30

[a] See description of procedure for method S. [b] Isobutane. [c] 2-Methyl-3-phenylbutane. [d] Methylcyclopentane. [e] Methylcyclohexane.

with methylcyclohexane at about 0° to yield V (22%) and VIII (25%), as well as higher boiling material. This might be explained by assuming that the primary cation derived from IX rearranges *via* phenyl migration to the more reactive ions X and XI. However, the fact that no chlorobutylbenzene was isolated from the product of the reaction of benzene with 1,2-dichloro-2-methylpropane whereas chloropentylbenzene (I) was always a major product of the reaction with 1,3-dichloro-3-methylbutane seems very significant and leads to the proposal that, especially with the 1,2-dichloride, participation of the neighboring phenyl group (anchimeric assistance[9]) is involved in the displacement of the chlorine atom resulting in a cyclic bridged (phenonium) ion rather than the classical carbonium ion as outlined above. In other words, the chorobutylbenzene (IX) is far more reactive than the chloropentylbenzene (I) because the presence of a phenyl group on the carbon atom adjacent to the carbon atom holding the chlorine aids in the elimination of the chloride ion

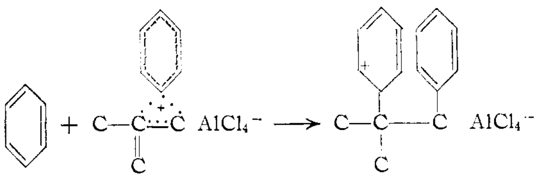


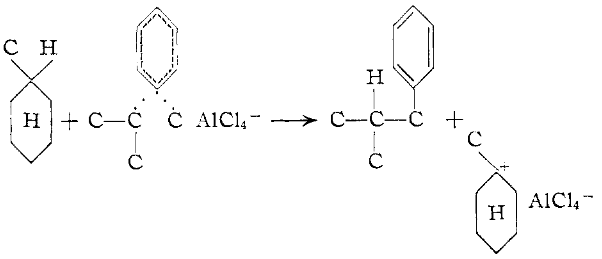
IX



I

When the phenonium ion adds to benzene or abstracts hydrogen from a saturated hydrocarbon, the reaction occurs at the tertiary carbon atom, yielding the diphenylalkane (VI or II) or alkylbenzene (V or 2-methyl-3-phenylbutane), respectively, as final products.





Experimental

Materials.[10]—1,3-Dichloro-3-methylbutane was obtained in 86% yield by the reaction of isoprene with hydrogen chloride at room temperature under 30 atm. initial pressure, b.p. 60° (30 mm.), n^{20}_D 1.4465. **1,2-Dichloro-2-methylpropane** was prepared in similar manner by the addition of hydrogen chloride to methallyl chloride, 83% yield, b.p. 105–106°, n^{20}_D 1.4378.

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(9) S. Winstein, C. R. Lindgren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

(10) L. Schmerling, *ibid.*, **74**, 2887 (1952).

Table II

Properties of the Condensation Products

Compd.	Formula	B.p., °C.	Mm.	$n^{20}D$	Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found Cl
I	$PhCMe_2CH_2CH_2Cl$	76–78	3	1.5197	72.30	8.28	19.24	72.63	8.50	19.24
II	$PhCMe_2CHPHMe$	129–131	2	1.5619	91.01	8.99		90.72	9.00	
III	p-$C_6H_4(CMe_2CH_2CH_2Cl)_2$	171–173	2.5	[a]	66.88	8.42	24.70	66.63	8.39	24.98
IV	PhC_5H_8Me[b]	67–69	3	1.5183						
V	$PhCH_2CHMe_2$	37–38	7	1.4870						
VI	$PhCH_2C(Me)_2Ph$[c]	114–115[d]	5	1.5589						
VII	$PhC_6H_{10}Me$	90–92	6	1.5125	89.59	10.41		90.10	10.21	
VIII	p-$Me_2CHCH_2C_6H_4C_6H_{10}Me$[e]	133–134	7	1.5070	88.62	11.38		89.11	11.30	

[a] Crystalline; m.p. 67–68°. [b] L. Schmerling, J. P. Luvisi and R. W. Welch, This Journal, **77**, 1774 (1955). [c] F. Bodroux, *Compt. rend.*, **132**, 1333 (1901). [d] Deposits about 2.5% of crystalline *meso*-2,3-diphenylbutane, m.p. 121–123°. [e] Oxidation with chromium trioxide dissolved in dilute sulfuric acid and acetic acid yielded terephthalic acid.

Procedures.—Three general procedures were used, resulting in the data summarized in Table I.

Method A.—A solution of the dichloride in about one-third of the total amount of benzene used was added gradually to a stirred mixture of the catalyst and the remainder of the benzene. Stirring was continued for about 0.5–1.0 hour after all the solution had been added, the product was permitted to stand for about 10 minutes, and the upper layer was separated from the catalyst layer, washed with dilute alkali and with water, dried over anhydrous potassium carbonate and distilled.

Method E.—The mixture of reactants and catalyst in an erlenmeyer flask was permitted to stand for 18 hours.

Method S.—The mixture of reactants and catalyst was stirred at ice-bath temperature for 8 hours. The product was then allowed to stand at room temperature overnight before being treated in the above described method. Most, if not all, of the hydrogen chloride produced was evolved at the lower temperature.

The reaction products were identified by means of their infrared spectra as well as their physical and chemical properties.

1-Chloro-3-phenyl-3-methylbutane (I).—Hydrolysis of the Grignard reagent prepared from 20 g. of I yielded 13 g. (18%) of pentylbenzene, b.p. 59.5° at 6 mm., $n^{20}D$ 1.4929. Infrared analysis indicated that the product was pure *t*-pentylbenzene.

Reaction of β-Chloro-*t*-butylbenzene (IX) with Methylcyclohexane.—Thirty-four grams (0.2 mole) of IX[11] was added during 45 min. to a stirred mixture of 100 g. (1.0 mole) of methylcyclohexane and 5 g. of aluminum chloride. Stirring was continued for an additional hour. About 3 g. (0.08 mole) of hydrogen chloride was absorbed in a soda lime tower in the exit line. Distillation of the washed upper layer liquid product yielded 6 g. (22%) of isobutylbenzene (V), 8 g. (25%) of the (methylcyclohexyl)-isobutylbenzene (VIII), and 10 g. of higher boiling product.

Reaction of 1,2-Diphenyl-2-methylpropane (VI) with Methylcyclohexane.—A solution of 1 g. of isopropyl chloride in 21 g. (0.1 mole) of VI was added to a stirred mixture 60 g. (0.6 mole) of methylcyclohexane and 2 g. of aluminum chloride at 4° during 6 min. After being stirred for an additional hour, the product was worked up in the usual manner. There was obtained 5 g. (37%) of isobutylbenzene (V), 3 g. (17%) of the (methylcyclohexyl)-isobutylbenzene (VIII), 5 g. (24%) of unreacted diphenylmethylpropane (VI) which deposited 0.035 g. of crystalline *meso*-2,3-diphenylbutane (XIII) on standing, and 5 g. of higher boiling product.

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[11] F. C. Whitmore, C. A. Weisberger and A. C. Shabica, Jr., This Journal, **65**, 1469 (1943); L. Schmerling and V. N. Ipatieff, *ibid.*, **67**, 1862 (1945).

Des Plaines, Illinois

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

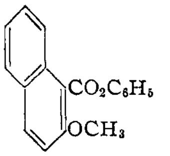
The Reaction of Phenyl 2-Methoxy-1-naphthoate with Grignard Reagents. A New Route to Fluorenones

By Reynold C. Fuson and F. W. Wassmundt[1]

Received May 28, 1956

Phenyl 2-methoxy-1-naphthoate has been found to undergo displacement of the methoxyl group when treated with the phenyl, *o*- and *p*-tolyl and 1- and 2-naphthyl Grignard reagents. The resulting phenyl 2-aryl-1-naphthoates have been cyclized, by the action of cold concentrated sulfuric acid, to the corresponding fluorenones. Benzylmagnesium chloride converts the methoxy ester to phenyl 2-benzyl-1-naphthoate, which undergoes ring closure to give a compound presumed to be 1,2-benzanthrone. Treatment of the impure product with benzoyl chloride converted it to the enol benzoate. Oxidation of the anthrone produced 1,2-benzanthraquinone.

Displacement of nuclear methoxyl groups by the action of Grignard reagents on highly hindered ketones[2] led us to test the effect of such reagents on the corresponding hindered esters. Phenyl 2-methoxy-1-naphthoate I was selected partly because of its convenient melting point and partly because of the great facility with which methoxyl group displacement occurs with the corresponding ketone, II.



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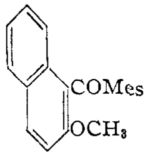

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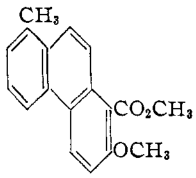

III

It should be mentioned that Richtzenhain and Nippus[3] had suggested a similar possibility with

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(1) Standard Oil Co. of Indiana Fellow, 1954–1955.

(2) R. C. Fuson and S. B. Speck, This Journal, **64**, 2446 (1942).

(3) H. Richtzenhain and P. Nippus, *Chem. Ber.*, **82**, 408 (1949).