The low-melting form of 9-mesitoyl-10-methyl-9,10-dihydrophenanthrene was obtained by submitting the ether-soluble portion of the product to a chromatographic separation on alumina. The major part of the material was eluted with a 10:1 ratio of cyclohexane to ether. Large needles, m.p. 109–110°, separated from a cooled aqueous ethanolic solution in a yield of 1.1 g.

Anal. Calcd. for $C_{25}H_{24}O$: C, 88.19; H, 7.11. Found: C, 87.83; H, 7.39.

The infrared spectrum of this compound is nearly superimposable on that of the higher-melting isomer.

Aromatization of 9-Mesitoyl-10-methyl-9,10-dihydrophenanthrene.—A solution of 0.24 g. of bromine in 10 ml. of carbon tetrachloride was added to 0.50 g. of 9-mesitoyl-10-methyl-9,10-dihydrophenanthrene dissolved in 25 ml. of carbon tetrachloride. The evolution of hydrogen bromide continued over a period of 5 hr. The reaction mixture was washed with sodium bisulfite and with water, and the solvent was removed. Chromatography of the pale yellow oil yielded a substance, m.p. 111–112°, which crystallized from ethanol. The combustion analysis agrees with that calculated for 9-mesitoyl-10-methylphenanthrene.

Anal. Calcd. for $C_{25}H_{22}O$: C, 88.72; H, 6.55. Found: C, 88.33; H, 6.64.

The infrared analysis of this compound is consistent with this structure. A conjugated carbonyl group (1658 cm.$^{-1}$), the mesityl nucleus (854 cm.$^{-1}$) and characteristic aromatic peaks (757, 726 cm.$^{-1}$) are found in the spectrum.

Aromatization of 9-Mesitoyl-10-phenyl-9,10-dihydrophenanthrene.—A solution of 3.0 g. of 9-mesitoyl-10-phenyl-9,10-dihydrophenanthrene in 60 ml. of carbon tetrachloride was treated with 1.19 g. of bromine. The solution was heated gently until the evolution of hydrogen bromide was complete. Removal of the solvent left a dark oil, which was triturated with ethanol. Crystals separated from the cooled solution in the form of hexagonal plates, m.p. 160–161°, yield 1.7 g. This compound proved to be 9-mesitoyl-10-phenylphenanthrene.

Anal. Calcd. for $C_{30}H_{24}O$: C, 89.96; H, 6.04. Found: C, 89.67; H, 6.13.

The infrared spectrum of this compound contains peaks characteristic of a conjugated carbonyl group (1660 cm.$^{-1}$), the mesitylene radical (850 cm.$^{-1}$), *o*-disubstituted (725 cm.$^{-1}$) and monosubstituted benzene (699, 761 cm.$^{-1}$).

The ethanol filtrate yielded an oil which was subjected to chromatography. A hydrocarbon was isolated from the cyclohexane eluent. An aqueous acetic acid solution of this substance deposited a white crystalline material in the form of rosettes, m.p. 104–105°, yield 0.5 g. Its picrate melts at 113–114°. Koelsch[5] reports a melting point of 105–106° for 9-phenylphenanthrene and a melting point of 115° for its picrate.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.51; H, 5.53.

The infrared spectrum is consistent with a hydrocarbon structure. The only significant peaks of absorption which occur indicate monosubstituted benzene (700 cm.$^{-1}$) and aromatic vibrations (745, 725 cm.$^{-1}$). The ultraviolet spectrum exhibits a maximum at 254 mμ (log ϵ 4.95) which is characteristic of the phenanthrene nucleus.

URBANA, ILLINOIS

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

Alkylation of Benzene with Polyhalides in the Presence of Saturated Hydrocarbons and Aluminum Chloride[1]

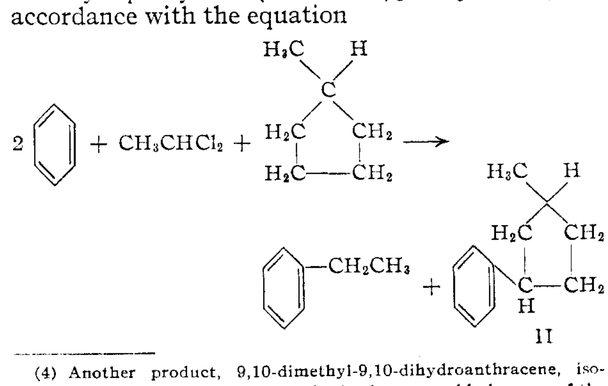
BY LOUIS SCHMERLING, ROBERT W. WELCH AND J. P. LUVISI

RECEIVED NOVEMBER 3, 1956

The aluminum chloride catalyzed condensation of a 1,1-dihaloalkane with benzene results in the formation of a primary alkylbenzene when the reaction is carried out in the presence of a hydrogen donor, namely a saturated hydrocarbon containing a tertiary carbon atom. Thus, for example, *n*-butylbenzene and (x-methylcyclohexyl)-benzene are produced in good yield by the reaction of benzene with 1,1-dichlorobutane in the presence of methylcyclohexane. Large amounts of hydrogen transfer products are also obtained with 2,3-dibromobutane and with 1,2-dichloro-2-methylpropane but not with 1,2-dichlorobutane. The mechanisms of these reactions and of the isomerization of tertiary alkylbenzenes is discussed.

In previous papers it was shown that excellent yields of primary monoalkylbenzenes (for example, isobutylbenzene[2] and 1-phenyl-3,3-dimethylbutane)[3] are obtained by the aluminum chloride catalyzed reaction of benzene with dichloroalkanes (1,2-dichloro-2-methylpropane and 1,1-dichloro-3,3-dimethylbutane, respectively) in the presence of a saturated hydrocarbon containing a tertiary carbon atom. The present paper describes the results of an investigation of the scope of this hydrogen transfer reaction, various polyhalides and saturated hydrocarbons being studied.

1,1-Dichloroethane.—The chief product obtained by the reaction of 1,1-dichloroethane with excess benzene in the presence of aluminum chloride at 3–4° was 1,1-diphenylethane (33% yield). Ethylbenzene was obtained in no more than 2% yield.[4] When the experiment was repeated, but with the addition of methylcyclopentane, practically no diphenylethane was produced. Instead, the chief reaction products were ethylbenzene and (methylcyclopentyl)-benzene isolated in approximately equal yields (42 and 38%, respectively) in accordance with the equation



II

(1) Presented before the Division of Organic Chemistry of the American Chemical Society at the Atlantic City Meeting, September, 1956.

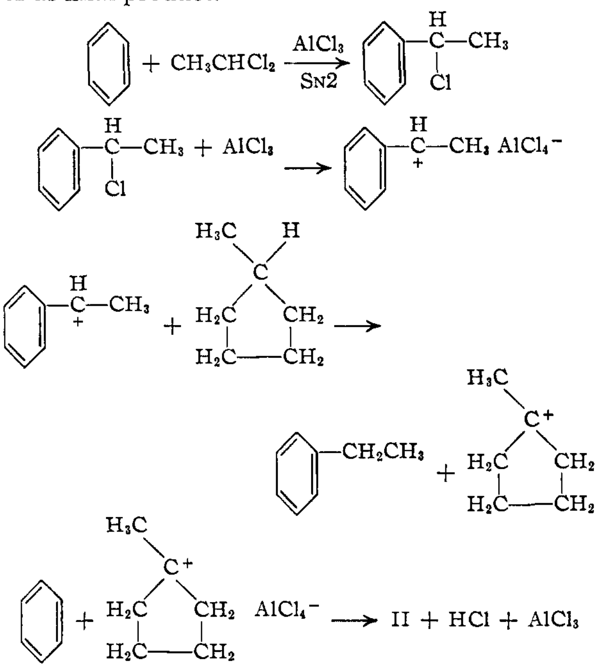
(2) L. Schmerling, R. W. Welch and J. P. West, THIS JOURNAL, **78**, 5406 (1956).

(3) L. Schmerling, J. P. Luvisi and R. W. Welch, *ibid.*, **77**, 1774 (1955).

(4) Another product, 9,10-dimethyl-9,10-dihydroanthracene, isolated by previous workers was not obtained, presumably because of the large excess of benzene (6.2:1) over dichloroethane; *cf.* A. Angelbis and R. Anschütz, *Ber.*, **17**, 165 (1884).

Infrared analysis showed that II contained little, if any, of the tertiary cycloalkylbenzene, (1-methylcyclopentyl)-benzene, further evidence that alkylation and cycloalkylation in the presence of aluminum chloride tends to yield secondary, rather than tertiary, alkyl and cycloalkylbenzenes.[5]

The reaction mechanism apparently involves the intermediate formation of the carbonium ion corresponding to (1-chloroethyl)-benzene, followed by the abstraction of the hydride ion attached to the tertiary carbon atom of methylcyclopentane to form ethylbenzene and the tertiary methylcyclopentyl cation, which reacts with benzene to yield II as final product.

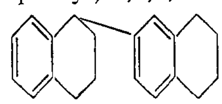


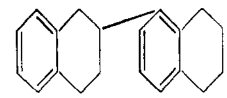
The yields of ethylbenzene and II were increased to about 60% each by carrying out the reaction at higher temperatures, 39–41°.

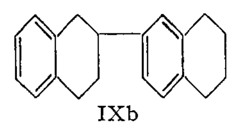
Use of a smaller ratio of benzene to dichloroethane (2:1 instead of 5.2:1) and of hydrogen donor (methylcyclohexane) to dichloroethane (1.6:1 instead of 4:1) resulted in the further reaction of the primary products with the formation of disubstituted benzenes. Besides ethylbenzene (42%) and methylcyclohexylbenzene (III, 31%), there was obtained diethylbenzene (9%) and (x-methylcyclohexyl)-ethylbenzene (IV, 9%).

Decahydronaphthalene was a more active hydrogen donor than methylcyclopentane. When it was used at 2–4°, phenyldecahydronaphthalene (V; chiefly the 2-phenyl isomer) was obtained in 70% yield. Ethylbenzene and a small amount (0.5%) of bis-(decahydronaphthyl)-benzene (VI) also were isolated.

1,2,3,4-Tetrahydronaphthalene served as both the aromatic hydrocarbon and the hydrogen donor when treated with 1,1-dichloroethane and aluminum chloride at 26–96°. "Self-alkylation" of the tetrahydronaphthalene occurred; tetrahydronaphthyltetrahydronaphthalene (IX) and ethyltetrahydronaphthalene (VII) were obtained in 40–45% yield. Dehydrogenation of a lower boiling fraction of IX gave 1,2′-binaphthyl, indicating that it was either or both 6-(1,2,3,4-tetrahydro-1-naphthyl)- and 5-(1,2,3,4-tetrahydro-2-naphthyl)-1,2,3,4-tetrahydronaphthalene (IXa and IXa′). The fact that alkylation of 1,2,3,4-tetrahydronaphthalene with alkyl chlorides in the presence of aluminum chloride gives 6-alkyl derivatives exclusively[6] indicates that the compound was IXa. Dehydrogenation of the higher boiling fraction, which was present in somewhat larger amount, to 2,2′-binaphthyl showed that it was 6-(1,2,3,4-tetrahydro-2-naphthyl)-1,2,3,4-tetrahydronaphthalene (IXb).


IXa


IXa′


IXb

Schroeter[7] obtained a 0.5–1.0% yield of a crystalline compound (m.p. 53–54°), to which he assigned the structure IXb, by the action of 1–2% aluminum chloride on tetrahydronaphthalene at 50–70° for 6–10 hr. Attempts to crystallize the product of the present investigation were unsuccessful.

A crystalline by-product (VIII, m.p. 71–72°) of lower boiling point than IX was isolated in 0.5% yield. Analysis and dehydrogenation indicated that it was an octahydroanthracene. Schroeter[7] found that 1,2,3,4,5,6,7,8-octahydroanthracene is a major product (obtained in about 2% yield) of the action of aluminum chloride on tetrahydronaphthalene. It is apparently formed *via* ring opening of the tetrahydronaphthalene to produce 4-phenylbutyl cation which condenses with tetrahydronaphthalene forming 6-(4-phenylbutyl)-1,2,3,4-tetrahydronaphthalene which undergoes dephenylation to 4-(1,2,3,4-tetrahydro-2-naphthyl)-butyl cation, ring closure of which yields *sym*-octahydroanthracene.[8]

1,1-Dibromoethane.—When 2,3-dimethylbutane was used as hydrogen transfer agent for the alkylation of benzene with 1,1-dibromoethane, the hexylbenzene, which was isolated in 21% yield together with a 34% yield of ethylbenzene, consisted chiefly of 3-phenyl-2,2-dimethylbutane, the isomer which is also the chief product of the alkylation of benzene with either 2-chloro-2,3-dimethylbutane or 1-chloro-3,3-dimethylbutane.[5]

Dichloromethane.—Bicyclohexyl produced an 18% yield of a mixture of 3- and 4-phenylbicyclohexyl (Xa and Xb, respectively) when present in a reacting mixture of methylene chloride and benzene in the presence of aluminum chloride. Toluene was obtained in 15% yield.

1,1-Dichlorobutane.—The behavior of 1,1-dichlorobutane was similar to that of 1,1-dichloroethane. In the absence of hydrogen donor, 1,1-diphenylbutane (36%) was the principal product; butylbenzene was obtained in no more than 3%

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

(6) A. Barbot, *Bull. soc. chim.*, [4] **47**, 1314 (1930).

(7) G. Schroeter, *Ber.*, **57**, 1990 (1924).

(8) *Cf.* references 6 and 7.

yield. In the presence of methylcyclohexane, *n*-butylbenzene and (methylcyclohexyl)-benzene were obtained in about 63–64% yield. On the other hand, the presence of cyclohexane had no effect on the reaction; the yields of products were identical to those obtained in the absence of donor. It is obvious that cyclohexane which does not contain a tertiary carbon atom was not a hydrogen donor under the reaction conditions (2–4°).

1,1-Dichloro-3-methylbutane.—Hydrogen transfer occurred with 1,1-dichloro-3-methylbutane, even in the absence of a saturated hydrocarbon; the product consisted of pentylbenzenes (27%), relatively little 1,1-diphenyl-3-methylbutane being produced. Infrared analysis showed that the pentylbenzene consisted of about 80% isopentylbenzene and 20% of 1,1-dimethylindan and/or 2-methyl-3-phenylbutane and *t*-pentylbenzene. Hydrogen attached to the tertiary carbon atom in the dichloride and/or the isopentylbenzene took part in the hydrogen exchange reaction in much the same manner as the analogous hydrogen atoms in the saturated hydrocarbons containing tertiary carbon atoms, yielding intermediates which reacted to yield the pentylbenzene isomers and/or the dimethylindan. It was not possible to distinguish between these hydrocarbons by means of infrared. The nature of the reaction, however, makes it seem most plausible that the by-product was the indan formed by ring closure at the tertiary carbon atom of isopentylbenzene. The dichloride which lost the hydride ion attached to the tertiary carbon atom was presumably converted to unsaturated product, making up the so-called "lower layer" catalyst complex, and to high boiling by-product.

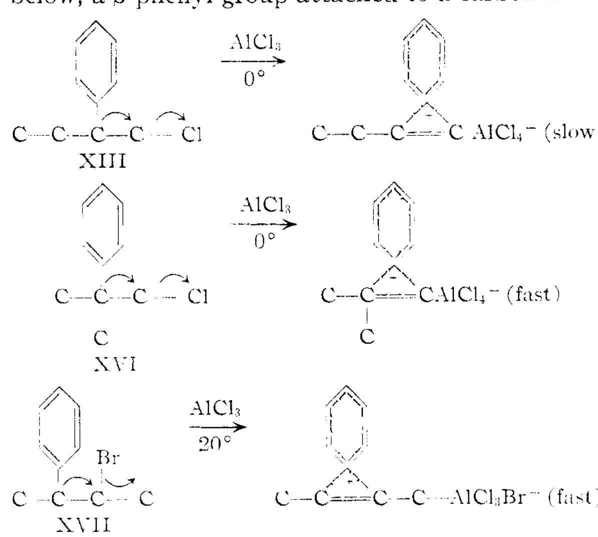
In the presence of methylcyclohexane, a higher yield (49%) of pentylbenzene (approximately 85–90% isopentylbenzene and 10–15% of other pentylbenzenes or dimethylindan) was obtained together with a 42% yield of (methylcyclohexyl)-benzene (III).

(2,2-Dibromoethyl)-cyclohexane.—Further evidence that the presence of a tertiary carbon atom in a dihalide results in comparatively high yields of monoalkylbenzene even in the absence of a saturated hydrocarbon was obtained by carrying out the reaction of 2,2-dibromoethyl)-cyclohexane with benzene in the presence of aluminum chloride. When no saturated hydrocarbon was used as a donor, 1-cyclohexyl-2-phenylethane (XII) was obtained in 37% yield. When isopentane was used, the yield of XII was 40%; there was a relatively low yield (12%) of pentylbenzene (85–90% 2-methyl-3-phenylbutane and 10–15% *t*-pentylbenzene) indicating that the hydrogen atom attached to the tertiary carbon atom in the dibromoethylcyclohexane is more readily abstracted than is that in isopentane.

1,2-Dichlorobutane.—The dihalides in the above-described experiments were those in which both halogen atoms are attached to the same carbon atom. Some dihalides in which the halogens are on adjacent carbon atoms were also tested: 1,2-dichlorobutane and 2,3-dibromobutane.

The reaction of 1,2-dichlorobutane with benzene in the presence of aluminum chloride at 4–6° resulted in a 37% yield of 1-chloro-2-phenylbutane[9] (XIII) and only 8% of diphenylbutane consisting of about 85% 1,2-diphenylbutane (XIV) and 15% of crystalline *meso*-2,3-diphenylbutane; formation of the crystalline isomer presumably involved rearrangement of XIII or XIV.

Formation of only 8% of the diphenylbutane was due apparently to the comparative inactivity of the chlorine atom attached to the primary carbon atom under the reaction conditions. This is somewhat analogous to the previously described[2] observation that the reaction of 1,3-dichloro-3-methylbutane with benzene in the presence of aluminum chloride at 2–4° produces as high a yield (28–29%) of the monophenyl compound 1-chloro-3-methyl-3-phenylbutane[10] (XV) as of the diphenyl derivative 2-methyl-2,3-diphenylbutane. On the other hand, the reaction of 1,2-dichloro-2-methylpropane (isobutylene dichloride) under the same conditions gave a 50% yield of 1,2-diphenyl-2-methylpropane, no 1-chloro-2-methyl-2-phenylpropane[11] (XVI) being isolated. In the case of XVI, participation of the neighboring phenyl group (anchimeric assistance[12]) probably was involved in the displacement of the chlorine atom,[2] resulting in a cyclic bridged (phenonium) ion. The markedly smaller yield of diphenylbutane with 1,2-dichlorobutane indicates that XIII is much less reactive than XVI because there is less anchimeric assistance in XIII than in XVI. A similar effect was noted in a study of the participation of β-phenyl groups in the solvolysis of some primary benzenesulfonates.[12] 2-Methyl-2-phenylpropyl *p*-bromobenzenesulfonate was 6.25 times as reactive in acetic acid as 2-phenylpropyl *p*-benzenesulfonate. It would seem that a methyl group attached to the β-carbon atom holding the phenyl group (thus making it a quaternary carbon) assists in the formation of a phenonium ion involving a primary carbon atom more than does hydrogen. As will be shown below, a β-phenyl group attached to a carbon atom



(9) Also named [1-(chloromethyl)-propyl]-benzene (*C. A.*).

(10) Also named (3-chloro-1,1-dimethylpropyl)-benzene (*C. A.*).

(11) Also named (2-chloro-1,1-dimethylethyl)-benzene (*C. A.*) and (chloro-*t*-butyl)-benzene.

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

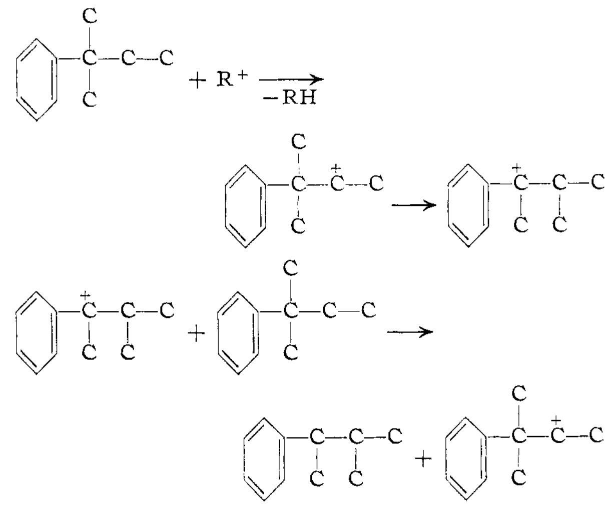
holding hydrogen does seem to participate in the reaction when the halogen is on a secondary carbon atom as in 2-bromo-3-phenylbutane.

The effect of saturated hydrocarbons on the reactions of these dihalides may be explained similarly. When the reaction of 1,2-dichlorobutane with benzene was carried out in the presence of methylcyclohexane, the hydrogen transfer reaction occurred to a relatively small extent, yielding 7% each of *sec*-butylbenzene and the cycloalkylbenzene (III). Diphenylbutane (about 93% 1,2- and 7% 2,3-isomer) and the chlorobutylbenzene XIII were obtained in approximately the same yields (7 and 50%, respectively) as in the absence of the saturated hydrocarbon. Formation of the phenonium ion from XIII was slow. The reaction was similar to that of 1,3-dichloro-3-methylbutane with benzene and methylcyclopentane or isobutane[2]; the chloropentylbenzene XV was obtained in good yields (44 and 33%, respectively) together with methylcyclopentylbenzene (II, 38%) or *t*-butylbenzene (48%) which were formed in part by the hydrogen transfer of the saturated hydrocarbon with the dihalide *before* it reacted with the benzene. On the other hand, hydrogen transfer with the intermediate chlorobutylbenzene (or ionic analog) was the chief reaction when isobutylene dichloride reacted with benzene in the presence of methylcyclohexane, yielding isobutylbenzene (57%), III (70%) and 1-(methylcyclohexyl)-4-isobutyl-benzene (14%).[2] Anchimeric assistance by the phenyl group occurred readily only with the latter chloride, there being little participation by the phenyl group in the chloropentylbenzene XV because it and the chlorine atom are not "neighbors."

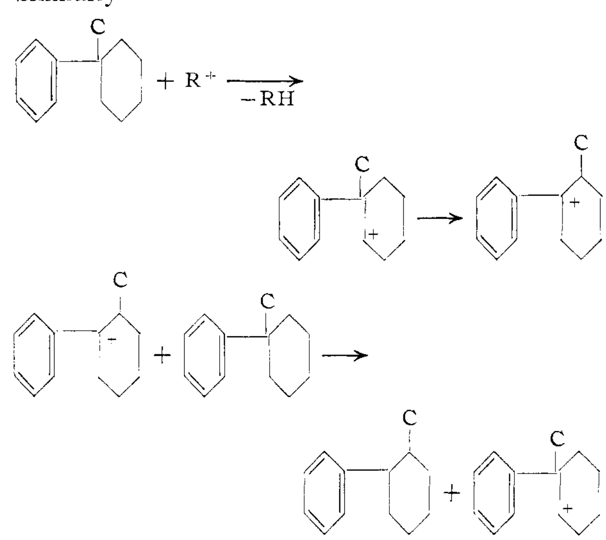
2,3-Dibromobutane.—In contrast to the results with the 1,2-dichlorobutane, high yields of hydrogen transfer product were obtained with a dihalide in which the halogen atoms were attached to adjacent secondary carbon atoms, namely 2,3-dibromobutane. In the presence of methylcyclopentane at room temperature, butylbenzene (95–96% *sec*-butylbenzene and 4–5% isobutylbenzene) and methylcyclopentylbenzene II were obtained in 68 and in 60% yield, respectively. In the absence of a saturated hydrocarbon, the chief product was *meso*-2,3-diphenylbutane (50%) together with a small amount of butylbenzene (6%).

The reaction may have involved the intermediate formation of 2-bromo-3-phenylbutane (XVII, not isolated) which under the influence of aluminum chloride and the neighboring group was converted to the cyclic bridged ion, reaction of which with benzene yielded diphenylbutane and with methylcyclopentane yielded *sec*-butylbenzene and methylcyclopentylbenzene II. The phenonium ion which is formed has been discussed in detail by Cram.[13] The small amount of isobutylbenzene which was formed can be explained by assuming a bridged ion involving the methyl group instead of the phenyl group.

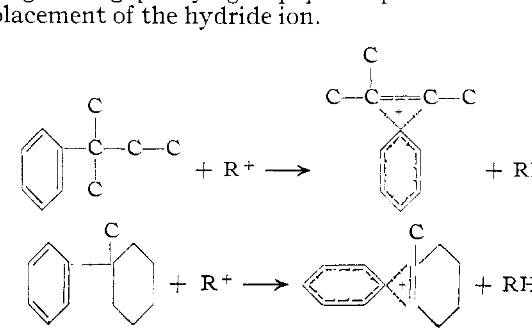
Anchimeric assistance also explains the fact that secondary, rather than tertiary, alkylbenzenes are produced in the presence of aluminum chloride.[5] It has been postulated[5] that the primary product is a tertiary alkylbenzene which is isomerized to the secondary alkylbenzene by way of a chain reaction involving the formation of a resonance stabilized benzyl cation



Similarly



An objection to this type of mechanism is that hydrogen atoms attached to secondary carbon atoms are not abstracted readily under the reaction conditions. For example, cyclohexane is not a hydrogen donor in the reaction of benzene with 1,1-dichlorobutane (expt. 11). However, the objection is plausibly overcome by postulating that the neighboring phenyl group participates in the displacement of the hydride ion.



(13) D. J. Cram, THIS JOURNAL, **71**, 3863 (1949); **74**, 2129, 2137, 2149 (1952); and **75**, 332 (1953).

TABLE I

REACTION OF BENZENE WITH 1,1-DICHLOROETHANE

Expt.	Reactants moles MeCHCl$_2$	C$_6$H$_6$	H donor	AlCl$_3$ Moles	g.	Temp., °C.	Chief products Compound	%[a]
1	0.50	2.6	None	..	5	3–4	PhEt	2[b]
							MeCHPh$_2$ (I)	33
2	.50	2.6	MCP[c]	2.0	5	3–4	PhEt	42
							MeC$_5$H$_8$Ph (II)	38
3	.50	2.6	MCP[c]	2.0	5	39–41	PhEt	62
							MeC$_5$H$_8$Ph (II)	60
4	.50	1.0	MCH[d]	0.8	5	38–51	PhEt	42
							PhEt$_2$	9
							MeC$_6$H$_{10}$Ph (III)	31
							MeC$_6$H$_{10}$PhEt (IV)	9
5	.50	2.6	DN[e]	1.1	5	2–4	PhEt	43
							C$_{10}$H$_{17}$Ph (V)	70
							(C$_{10}$H$_{17}$)$_2$Ph (VI)	0.5
6	.45	..	TN[f]	2.5	5	26–96	C$_{10}$H$_{11}$Et (VII)	44
							C$_{14}$H$_{18}$ (VIII)	0.5
							(C$_{10}$H$_{11}$)$_2$ (IX)	41
7	.50[g]	2.6	BIP[h]	1.5	5	2–32	PhEt	34
							PhCHMeCMe$_3$	21

[a] Based on the equation: $MeCHCl_2 + 2C_6H_6 + RH \rightarrow PhEt + PhR + 2HCl$, where RH is the diluent. [b] Maximum quantity present. [c] Methylcyclopentane. [d] Methylcyclohexane. [e] Decahydronaphthalene (67% *cis*-, 33% *trans*-). [f] 1,2,3,4-Tetrahydronaphthalene. [g] 1,1-Dibromoethane. [h] Biisopropyl (*i.e.*, 2,3-dimethylbutane).

TABLE II

REACTION OF BENZENE WITH POLYHALIDES

Expt.	Polyhalide Kind	Mole	C$_6$H$_6$, moles	H Donor Kind	Moles	AlCl$_3$, g.	Temp., °C.	Chief products Compound	%
8	CH$_2$Cl$_2$	0.50	2.6	BC[a]	2.0	5	25–27	PhMe	15
								C$_6$H$_{11}$C$_6$H$_{10}$Ph (X)	18
9	PrCHCl$_2$	.25	1.3	None	..	3	2–3	PhBu	3[b]
								PrCHPh$_2$ (XI)	36
10	PrCHCl$_2$	.25	1.3	MCH[c]	1.0	3	2–4	PhBu	63
								MeC$_6$H$_{10}$Ph (III)	64
11	PrCHCl$_2$	.25	1.3	CH[d]	1.0	3	2–4	PhBu	3[b]
								PrCHPh$_2$ (XI)	36
12	Me$_2$CHCH$_2$CHCl$_2$	.10	0.8	None	..	3	3–5	PhCH$_2$CH$_2$CHMe$_2$[e]	27
13	Me$_2$CHCH$_2$CHCl$_2$	.11	0.8	MCH[c]	0.6	3	3–3	PhCH$_2$CH$_2$CHMe$_2$[e]	49
								MeC$_6$H$_{10}$Ph (III)	42
14	C$_6$H$_{11}$CH$_2$CHBr$_2$	.17	1.3	None	..	5	5–25	PhCH$_2$CH$_2$C$_6$H$_{11}$ (XII)	37
15	C$_6$H$_{11}$CH$_2$CHBr$_2$	.17	1.3	*i*-C$_5$[f]	1.0	5	0–26	PhCH$_2$CH$_2$C$_6$H$_{11}$ (XII)	40
								PhC$_5$H$_{11}$[g]	12
16	EtCHClCH$_2$Cl	.50	2.6	None	..	5	4–6	PhCHEtCH$_2$Cl (XIII)	37
								EtCHPhCH$_2$Ph (XIV)	8[h]
17	EtCHClCH$_2$Cl	.50	2.6	MCH[c]	2.0	5	3–3	PhCHEtMe	7
								PhCHEtCH$_2$Cl (XIII)	50
								MeC$_6$H$_{10}$Ph (III)	7
								EtCHPhCH$_2$Ph (XIV)	7[i]
18	Me(CHBr)$_2$Me	.25	2.6	None	..	5	28–29	PhBu	6
								(MeCHPh)$_2$	50
19	Me(CHBr)$_2$Me	.25	2.6	MCP[j]	1.5	5	28–29	PhCHEtMe	68
								MeC$_5$H$_8$Ph (II)	60
20	ClCH$_2$CHCl$_2$	.26	2.6	MCH[c]	1.5	5	33–53	PhCH$_2$CH$_2$Ph	58
								MeC$_6$H$_{10}$Ph (III)	60
21	CCl$_4$	.25	2.5	*i*-C$_5$[e]	2.0	5	24–28	CH$_2$Ph$_2$	24
								PhC$_5$H$_{11}$[k]	30[l]

[a] Bicyclohexyl. [b] Maximum quantity present. [c] Methylcyclohexane. [d] Cyclohexane. [e] The infrared spectrum of the product boiling at about 190–195° indicated that it consisted of about 80% isopentylbenzene and 20% of what might have been 1,1-dimethylindan and/or 2-methyl-3-phenylbutane. [f] Isopentane. [g] Infrared analysis indicates 85–90% 2-methyl-3-phenylbutane and 10–15% *t*-pentylbenzene. [h] Includes about 15% crystalline 2,3-diphenylbutane. [i] Includes about 7% crystalline 2,3-diphenylbutane. [j] Methylcyclopentane. [k] Infrared analysis indicates 65–70% 2-methyl-3-phenylbutane and 30–35% *t*-pentylbenzene. [l] Based on a theoretical yield of 2 moles of product per mole of carbon tetrachloride.

TABLE III

PHYSICAL PROPERTIES OF THE REACTION PRODUCTS

	Compound	B.p., °C.	Mm.	B.p. at 760 mm., °C.[b]	$n^{20}D$	Analyses, %[a] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
I	$MeCHPh_2$[c]	123–124	10	260–261	1.5730				
II	MeC_5H_8Ph[d]	77–79	4	225–228	1.5190				
III	$MeC_6H_{10}Ph$[e]	95–99	7	235–240	1.5180				
IV	$MeC_6H_{10}PhEt$	110–115	4	270–277	1.5174				
V	$C_{10}H_{17}Ph$	134–135	4	300–302	1.5360	89.65	89.66	10.35	10.36
VI	$(C_{10}H_{17})_2Ph$	.....[g]				89.07	88.91	10.93	10.81
VII	$C_{10}H_{11}Et$	76–78	4	223–225	1.5373	89.94	90.20	10.06	10.05
VIII	$C_{14}H_{18}$[h]	113–126	3	283–299[i]	1.5664	90.46	90.32	9.54	9.78
IXa	$(C_{10}H_{11})_2$	176	3	370	1.5898	91.55	91.45	8.45	8.61
IXb	$(C_{10}H_{11})_2$	180	1	385	1.5960				
Xa	$C_6H_{11}C_6H_{10}Ph$	132–135	1	336–337	1.5310	89.19	89.16	10.81	10.77
Xb	$C_6H_{11}C_6H_{10}Ph$	173–174	4	350–352[j]	1.5350	89.19	89.33	10.81	10.66
XI	$PrCHPh_2$[k]	132	7	284	1.5570				
XII	$PhCH_2CH_2C_6H_{11}$	89–90	1	274–275	1.5183	89.29	89.09	10.71	10.82
XIII	$PhCHEtCH_2Cl$[l]	86–88	8	220–222	1.5174				
XIV	$EtCHPhCH_2Ph$[k]	124–128	8	270–275	1.5565				

[a] Analyses by Micro-Tech Laboratories, Skokie, Ill. [b] Calculated from boiling point under reduced pressure using Lippincott nomograph, *Ind. Eng. Chem.*, **38**, 320 (1946). [c] G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946, p. 347. [d] L. Schmerling, J. P. Luvisi and R. W. Welch, THIS JOURNAL, **77**, 1774 (1955). [e] L. Schmerling, R. W. Welch and J. P. West, paper presented before the Division of Organic Chemistry of the American Chemical Society at the Dallas Meeting, April 1956. [f] d^{20}_4 0.9729; mol. ref. calcd. 68.26, obsd. 68.69. [g] M.p. 158–160°. [h] An octahydroanthracene, *cf.* G. Egloff, ref. *c*, Vol. IV, p. 62. [i] Becomes partially crystalline on standing; m.p. 71–72°. [j] Crystallizes on standing; m.p. 83° (recrystallized from ethanol). [k] C. Egloff, ref. *c*, Vol. III, p. 358. [l] P. A. Levene, L. A. Mikeska and K. Passoth, *J. Biol. Chem.*, **88**, 27 (1930); G. J. VanZoeren, U. S. Patent 2,349,779.

When the phenonium ion abstracts a hydride ion from the tertiary alkyl- or cycloalkylbenzene, the reaction occurs at the tertiary carbon atom of the bridged ion, yielding secondary alkyl- or cycloalkylbenzene as the final product.

1,1,2-Trichloroethane.—Good yields (58–60% each) of bibenzyl and methylcyclohexylbenzene III were obtained by the reaction of 1,1,2-trichloroethane and benzene in the presence of methylcyclohexane and aluminum chloride at 33–53°. Bimolecular nucleophilic displacement of a chlorine on each carbon atom by benzene with the resultant formation of α-chlorobibenzyl occurred, followed by hydrogen–chlorine exchange involving the active benzylic chlorine atom. Alternatively, (2-chloroethyl)-benzene may have been formed first.

Bibenzyl was also a major product of the reaction in the absence of a saturated hydrocarbon.[14] Other products included diphenylmethane and anthracene. Hydrogen transfer reactions involving intermediate products, *e.g.*, 9,10-dihydroanthracene, apparently occurred.

Carbon Tetrachloride.—Hydrogen transfer occurred when carbon tetrachloride was contacted with benzene and isopentane in the presence of aluminum chloride at room temperature. Diphenylmethane was obtained in 24% yield and pentylbenzene (65–70% 2-methyl-3-phenylbutane and 30–35% *t*-pentylbenzene) in 30% yield, based on the theoretical yield of 2 moles of pentylbenzene per mole of carbon tetrachloride.

$$CCl_4 + 4C_6H_6 + 2C_5H_{12} \longrightarrow CH_2(C_6H_5)_2 + 2C_6H_5C_5H_{11} + 4HCl$$

In the absence of saturated hydrocarbon, the principal product of the reaction of carbon tetrachloride with benzene is either triphenylchloromethane or triphenylmethane depending on the reaction conditions.[15]

Experimental

Procedure.—A solution of the polyhalide in about 20–35% of the total amount of benzene used was added slowly (usually during about 1 to 2 hr.) to a stirred mixture of the remainder of the benzene, the saturated hydrocarbon and the catalyst. Stirring was continued for from approximately 1 to 3 hr. after all the mixture had been added (depending on the rate of hydrogen chloride evolution), after which the product was permitted to stand for about 10 minutes, and the upper layer was then separated from the catalyst layer, washed with dilute alkali and with water, dried over anhydrous potassium carbonate and distilled. The experiments are summarized in Tables I and II. The physical properties of the products are given in Table III.

Materials.—Most of the polyhalides were commercially available products. The 1,1-dichloro-3-methylbutane and the (2,2-dibromoethyl)-cyclohexane were prepared by condensing vinyl chloride and bromide with isopropyl chloride[16] and cyclohexyl bromide,[17] respectively.

Identification of Products.—The well-known alkylbenzenes were identified by their physical properties and by comparison of their infrared spectra with those of the authentic compounds. These included toluene, ethylbenzene, diethylbenzene, *n*- and *sec*-butylbenzene, isopentylbenzene, *t*-pentylbenzene, 2-methyl-3-phenylbutane and 2,2-dimethyl-3-phenylbutane.[5] Diphenylmethane was similarly identified. Bibenzyl (m.p. 52–53°) and 2,3-diphenylbutane (m.p. 123–125°) were characterized by melting point and by "mixed melting point" with authentic samples.

The infrared spectra of the methylcycloalkylbenzenes II and III indicated that the tertiary compounds 1-methyl-1-phenylcyclopentane and 1-methyl-1-phenylcyclohexane were not present. It is probable that II was (3-methylcyclopentyl)-benzene mixed with a smaller amount of (2-methylcyclopentyl)-benzene. Similarly, III was presumably a mixture of (3-methylcyclohexyl)- and (4-methylcyclohexyl)-benzene. It was identical to the product of the alkylation of benzene with 1-chloro-1-methylcyclohexane or with 3- or 4-

(14) A. Gardeur, *Bull. acad. roy. Belg.*, [3] **34**, 920 (1898).

(15) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 116–118.

(16) L. Schmerling, THIS JOURNAL, **68**, 1650 (1946).

(17) L. Schmerling, *ibid.*, **71**, 698 (1949).

methylcyclohexanol in the presence of aluminum chloride.[18]

The structures of several of the remaining polynuclear compounds were determined by dehydrogenation to known crystalline aromatic hydrocarbons using a platinum–alumina catalyst at 250–350°.

The **phenyldecahydronaphthalene V** yielded product, m.p. 92–95°, which on recrystallization from alcohol melted at 100–101°. 2-Phenylnaphthalene is reported to melt at 100–102°, 1-phenylnaphthalene at 84–86°.[19] Attempts to isolate product melting at about 85° by fractional crystallization were unsuccessful. Hence, V was apparently principally 2-phenyldecahydronaphthalene.

Compound VIII yielded yellow needles melting at 205–207° which did not depress the melting point of anthracene. Since analysis indicated that the formula of VIII was $C_{14}H_{18}$, it may be concluded that it was an octahydroanthracene.

The lower boiling **tetrahydronaphthyltetrahydronaphthalene (IXa)** gave yellow crystals, m.p. 73–74°. The higher boiling material (IXb) yielded product of m.p. 180–181°. The approximate melting points reported in the literature[20] for the binaphthyls are: 1,1′-, 156°; 1,2′-, 76°; and 2,2′-, 187°. Fractional crystallization of the products failed to yield any material melting near 156°. It may be concluded that IX consists of 6-(1,2,3,4-tetrahydro-2-naphthyl)-1,2,3,-4-tetrahydronaphthalene and either or both 6-(1,2,3,4-tetrahydro-1-naphthyl)- and 5-(1,2,3,4-tetrahydro-2-naphthyl)-1,2,3,4-tetrahydronaphthalene. While the relative amounts of these isomers were not determined, it appeared from the fractionation data that the 6-(1,2,3,4-tetrahydro-2-naphthyl)- isomer was present in largest amount.

The phenylbicyclohexyl (Xa) liquid fraction yielded a crystalline product which on fractional crystallization gave 2 parts of white flakes, m.p. 205–206°, and 8 parts of white needles, m.p. 83–85°. Dehydrogenation of the crystalline phenylbicyclohexyl Xb yielded product, m.p. 204–205°. The literature[21] values for the melting points of 1,2-, 1,3- and 1,4 diphenylbenzene are, respectively, 55–58°, 84–89° and 205–214°. Hence, X was a mixture of 3- and 4-phenylbicyclohexyl, the latter being a crystalline compound, Xb.

(18) L. Schmerling, unpublished results.

(19) G. Egloff, "Physical Constants of Hydrocarbons," Vol. IV, Reinhold Publishing Corp., New York, N. Y., 1947, p. 226.

(20) G. Egloff, ref. 19, Vol. IV, p. 317.

(21) G. Egloff, ref. 19, Vol. III, p. 473.

DES PLAINES, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Structure of Chloretyl, the Product of the Reaction between Chloral and Biacetyl

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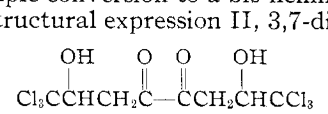
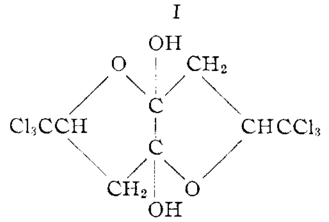
Spectral and chemical evidence has been presented to establish the structure of chloretyl, the product of the reaction between chloral and biacetyl, as 3,7-di-(trichloromethyl)-2,6-dioxabicyclo[3.3.0]octane-1,5-diol (II). The stereochemical structures of the α- and β-isomers of chloretyl (racemates) have been tentatively assigned as *cis–cis–cis* (VI) and *cis–cis–trans* (VII).

In 1952, a product of molecular formula $C_8H_8Cl_6O_4$ was obtained by Schlenk[3] from the reaction of chloral with biacetyl, in 2:1 molar proportion, in the presence of piperidinium acetate. The structure of the colorless solid, m.p. 199–201° dec., was not established, and the suggested formulations of the compound as a diketone dihydrate or a monohydrate of a hydroxyketone were not fully satisfactory. The property of the compound that was difficult to accommodate in postulated structures was the absence of absorption in the ultraviolet and visible regions. We reasoned that if the initial reaction product were conceived as normal (I), simple conversion to a bis-hemiketal would provide a structural expression II, 3,7-di-(trichloromethyl) - 2,6 - dioxabicyclo[3.3.0]octane - 1,5 - diol, which would satisfy the data presented by Schlenk for the $C_8H_8Cl_6O_4$ compound. Our postulate has been confirmed by infrared absorption and nuclear magnetic resonance studies and by additional chemical evidence. Moreover, we are in a position to consider the stereochemistry of the predominant product and its isomers.



I



II

We used conditions for the reaction between chloral and biacetyl similar to those of Schlenk. However, we were able to isolate two isomeric compounds, $C_8H_8Cl_6O_4$: an α-isomer capable of existing in readily interconvertible dimorphic forms, m.p. *ca.* 206° dec. and *ca.* 175° dec., and a β-isomer, m.p. 175–177°, in lower yield. As a convenience, we wish to use the name "chloretyl" (klôrĕtēl) for these products, or specifically, "α-chloretyl" and "β-chloretyl."

The infrared absorption spectra of the dimorphic forms of α-chloretyl were virtually identical as Nujol mulls and identical as 1% solutions in benzene. The spectrum of the β-isomer was similar but not identical to the α-chloretyl spectrum. The spectra of both isomers confirmed the absence of olefinic and carbonyl unsaturation and indicated the presence of hydroxyl. The spectrum of solid α-chloretyl showed a sharp hydroxyl band at 3480 cm.$^{-1}$ and that of β-chloretyl at 3450 cm.$^{-1}$ (Nujol mull). There were also present in the 9–11 μ region absorption bands resembling those exhibited by tetrahydrofuran. The most logical structure for chloretyl, consistent with the precursors in synthesis and the ana-

(1) National Science Foundation Fellow, 1954–1957.

(2) Eli Lilly and Co. Fellow, 1952–1953.

(3) H. Schlenk, *Ber.*, **85**, 901 (1952). We wish to record our appreciation for recent conversations with Dr. Schlenk concerning the structure and chemistry of this product.