After removal of the solvent *in vacuo*, a solid residue remained which was dried under vacuum over both potassium hydroxide and sulfuric acid to yield 4.4 g. of hygroscopic material, m.p. 45–50°. This product was then sublimed at 130° using a mercury-vapor vacuum pump to yield an analytical sample, m.p. 53°.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.60; H, 7.55.

A 2,4-dinitrophenylhydrazone derivative was prepared in the usual manner, and after recrystallization from chloroform–Skellysolve B, yielded fine yellow needles, m.p. 215–216°.[17]

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[17] D. D. E. Newman and L. N. Owen, *J. Chem. Soc.*, 4713 (1952), report a m.p. of 211–212° for this derivative.

AUSTIN 12, TEXAS

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

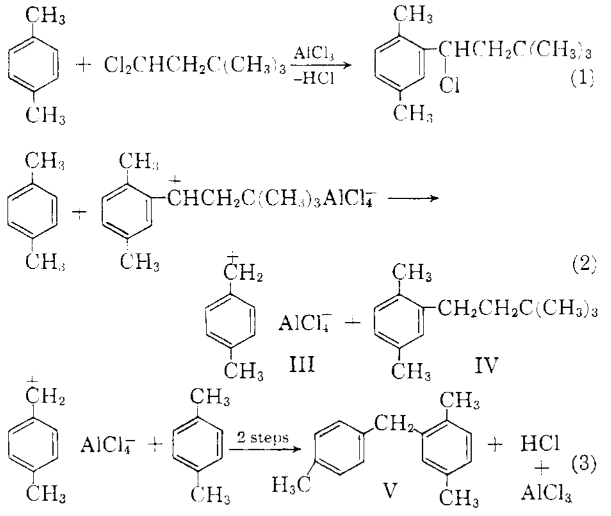
Hydrogen Transfer during the Alkylation of *p*-Xylene and of *p*-Chlorotoluene[1]

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

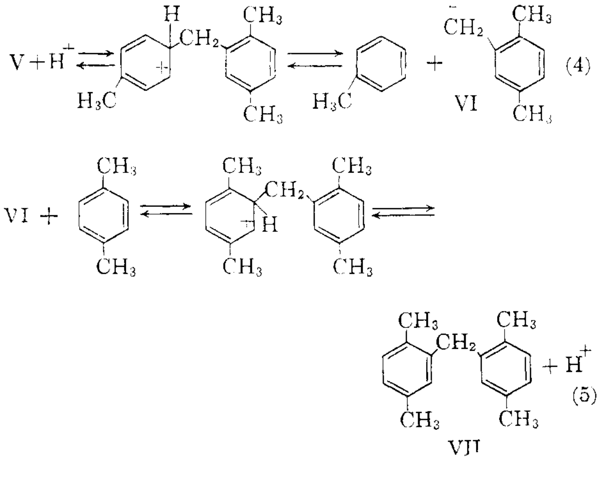
RECEIVED NOVEMBER 26, 1958

Hydrogen transfer involving benzylic hydrogen occurs when *p*-xylene or *p*-chlorotoluene is alkylated with a 1,1-dichloroalkane or a *t*-alkyl chloride in the presence of aluminum chloride. For example, the reaction of *p*-xylene with 1,1-dichloro-3,3-dimethylbutane yields (3,3-dimethylbutyl)-*p*-xylene (IV) and di-(*p*-xylyl)-methane (VII), production of the latter involving the intermediate formation of (*p*-methylbenzyl)-*p*-xylene (V), which then undergoes transaralkylation with excess *p*-xylene present. When the reaction is carried out in the presence of methylcyclohexane, the product consists chiefly of the hexyl-*p*-xylene (IV) and (methylcyclohexyl)-*p*-xylene, together with only a very minor amount of the dixylylmethane (VII), indicating that the saturated hydrocarbon containing a tertiary carbon atom furnishes the hydrogen necessary for the formation of the hexylxylene more readily than does the *p*-xylene. Aluminum chloride and zirconium chloride, but not ferric chloride, yield hydrogen transfer products in the reaction of *p*-xylene and *t*-butyl chloride.

It was previously shown that saturated hydrocarbons containing tertiary carbon atoms are involved in a hydrogen transfer reaction during the alkylation of benzene with polyhalides in the presence of aluminum chloride.[2] For example, excellent yields of a primary mono-alkylbenzene, 1-phenyl-3,3-dimethylbutane (I, 60%), and of a secondary cycloalkylbenzene, (x-methylcyclopentyl)-benzene (48%), together with only a minor amount (6%) of the expected disubstitution product, 1,1-diphenyl-3,3-dimethylbutane (II), are obtained by the reaction of benzene with 1,1-dichloro-3,3-dimethylbutane and methylcyclopentane at about 0°.[2a] In the absence of the saturated hydrocarbon, I and II are formed in approximately equal yields (26–28% and 19–20%, respectively).



Reaction of *p*-Xylene with 1,1-Dichloroalkanes.—It has now been found that hydrogen transfer is the principal reaction even in the absence of saturated hydrocarbon when *p*-xylene is alkylated with 1,1-dichloroalkanes, the source of the hydrogen being the benzylic hydrogens in the *p*-xylene (Table I). The reaction of 0.5 mole of 1,1-dichloro-3,3-dimethylbutane with 2.5 moles of the hydrocarbon in the presence of 0.04 mole of aluminum chloride at 1–20° yielded 0.14 mole of (3,3-dimethylbutyl)-*p*-xylene (IV, "neohexyl-*p*-xylene") and 0.095 mole of crystalline hydrogen transfer product, di-(*p*-xylyl)-methane (VII). There was no evidence of the formation of the disubstitution product, 1,1-di-(*p*-xylyl)-3,3-dimethylbutane; hydrogen transfer apparently occurred too readily.



The (*p*-methylbenzyl)-*p*-xylene (V) undergoes transaralkylation in the presence of excess *p*-xylene to yield the di-(*p*-xylyl)-methane (VII).[3]

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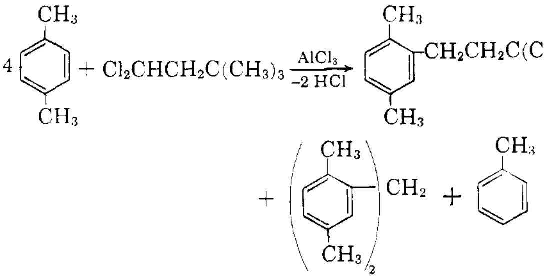
[1] Presented before the Division of Organic Chemistry of the American Chemical Society at the Chicago Meeting, September, 1958.

[2] (a) L. Schmerling, J. P. Luvisi and R. W. Welch, THIS JOURNAL, **77**, 1774 (1955); (b) L. Schmerling, R. W. Welch and J. P. West, *ibid.*, **78**, 5406 (1956); L. Schmerling, R. W. Welch and J. P. Luvisi, *ibid.*, **79**, 2636 (1957).

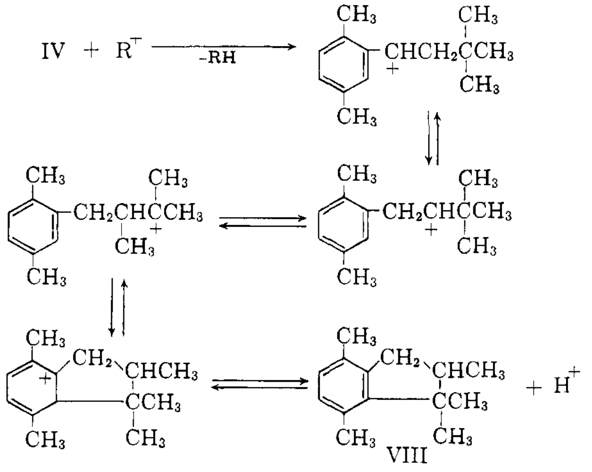
[3] Alternatively, the transaralkylation may be formulated analogously to the transalkylation scheme of D. A. McCauley and A. P. Lien *ibid.*, **75**, 2411 (1953).

The over-all reaction is



(6)

There was also obtained about 0.045 mole of a hydrocarbon, $C_{14}H_{20}$ (VIII), the infrared spectrum of which showed that it was a 1,2,3,4-tetrasubstituted benzene. This, together with its refractive index and density, indicated that it was probably a pentamethylindan formed by dehydroalkylation of the "neohexylxylene" (IV) or from the intermediate monochloride produced by the reaction of the xylene with the dichloride (equation 1).



When the reaction of excess p-xylene with 0.5 mole of 1,1-dichloro-3,3-dimethylbutane was carried out in the added presence of 1.5 moles of methylcyclohexane at 3°, there was obtained 0.24 mole of the hexyl-p-xylene (IV) and 0.18 mole of what was presumably a (methylcyclohexyl)-p-xylene, very probably secondary[4] cycloalkyl derivative. Only about 0.01 mole of the dixylylmethane (VII) was also isolated. It may be concluded that the saturated hydrocarbon containing a tertiary carbon atom furnishes the hydrogen necessary for the formation of the hexylxylene more readily than does the p-xylene.

Other 1,1-dichloroalkanes reacted similarly with p-xylene. The reaction with ethylidene chloride at room temperature gave ethyl-p-xylene (X, 22%), 2,5-diethyl-p-xylene (XI, 6%) and the dixylylmethane (VII, 14%). The chief products obtained with methylene chloride at 28–63° were 1,2,4-trimethylbenzene (XII, 20%), 1,2,4,5-tetramethylbenzene (XIII, 10%) and VII (8%). Toluene formed chiefly by transaralkylation (equation 6) was obtained in 15% yield; in the other experiments it probably underwent further reaction readily (compared to the p-xylene) and was converted to alkylation products present in intermediate fractions and the higher boiling residues but not isolated.

TABLE I

REACTION OF p-XYLENE WITH 1,1-DICHLOROALKANES

Expt.	Reactants, moles p-X	Reactants, moles RCl_2	$AlCl_3$, mole	Temp., °C.	Time, hr.	Chief products Compound	Chief products G.	Chief products %[a]
			With 1,1-dichloro-3,3-dimethylbutane					
1	2.5	0.5	0.04	1- 5[b]	1.1[b]	IV	26	27
				5–20[c]	2.8[c]	VIII	8	9
						VII	21	19
						Higher	12	..
2	2.5[d]	0.5	0.04	3[b]	0.7[b]	IV	46	48
				3[c]	1.5[c]	IX	36	36
						VII	2	2
						Higher	10	..
			With 1,1-dichloroethane					
3	3.0	1.0	0.14	22–26[b]	1.7[b]	X	30	22
				20–26[c]	1.7[c]	XI	4	6
						VII	32	14
						Higher	12	..
			With methylene chloride					
4	3.0	1.0	0.08	28–31[b]	0.9[b]	PhMe	14	15
				31–63[c]	1.9[c]	XII	24	20
						XIII	6	10
						VII	18	8
						Higher	11	..

[a] Based on the chloroalkane (*cf.* equation 6). [b] Temperature and time for addition of solution of chloroalkane in aromatic compound to stirred mixture of aromatic compound and catalyst. [c] Temperature and time for additional stirring. [d] Also 1.5 moles of methylcyclohexane.

Reaction of p-Xylene with t-Alkyl Chlorides.—p-Xylene also undergoes the hydrogen transfer reaction when treated with a tertiary alkyl halide in the presence of aluminum chloride (Table II).[5] Because of steric hindrance the intermediate t-alkyl cation has difficulty in adding to the aromatic nucleus. Instead, it abstracts a benzylic hydride ion to yield isoalkane and p-methylbenzyl cation, which, being a primary ion, is not hindered by steric factors from condensing with p-xylene to yield the dixylylmethane (VII) as ultimate product. Thus, the reaction of 0.5 mole of t-butyl chloride with 2.5 moles of p-xylene at 0–22° resulted in 0.18 mole (36% yield) of VII. There was also isolated 0.065 mole (13%) of toluene (formed by reactions analogous to those involved in equation 6) and 0.04 mole (8%) of its butylation product, m- and p-t-butyltoluene (XIV).

There were indications that some p-methylbenzyl chloride (corresponding to III) and p-methylbenzyl-p-xylene (V), the forerunner of the di-xylylmethane (VII), were present in intermediate fractions. However, none was isolated in pure form. On the other hand, from a similar experiment, Friedman, Morritz, Morrissey and Koncos,[5] obtained 7% of V, 6% of p-butyltoluenes (XIV), 18% of 3,5-di-t-butyltoluene (XV) and 15% of the

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

(5) Subsequent to our investigation of this reaction, it was described by B. S. Friedman, F. L. Morritz, C. J. Morrisey and R. Koncos (one day meeting of the Catalysis Club of Chicago, March, 1957; 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957). See THIS JOURNAL, **80**, 5867 (1958). The present discussion is therefore limited chiefly to significant differences in mechanism or catalysts.

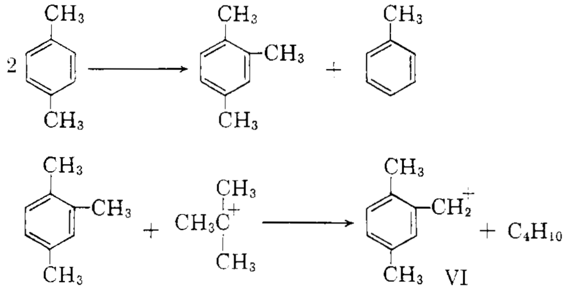
TABLE II

REACTION OF *p*-XYLENE WITH ALKYL CHLORIDES

Expt.	Reactants, moles *p*-X	RCl	Catalyst Kind	Mole	Temp., °C.	Time, hr.	Chief products Compound	G.	%^{a}
				With *t*-butyl chloride					
5	2.5	0.50	$AlCl_3$	0.04	0–10^b	1.5^b	PhMe^d	6	13
					10–22^c	1.3^c	XIV	6	8
							VII	40	38
							Higher	14	..
6	1.25	0.32	$FeCl_3$	0.04	27–25^b	0.5^b	XV	5	10
					25–44^c	3.8^c	Higher	8	..
7^e	1.25	0.32	$FeCl_3$	0.04	78–82^e	2.0^e	XV	8	16
							Higher	7	..
8	1.25	0.32	$ZrCl_4$	0.02	24–24^b	0.4^b	Me_3CH	4	22
					24–44^c	2.3^c	XVI	9	25
					44–80^c	2.1^c	VII	12	17
							Higher	6	..
				With *t*-pentyl chloride					
9	5.0	1.0	$AlCl_3$	0.04	6– 2^b	1.5^b	XVII	95	54
					5–24^c	2.0^c	VII	22	10
							Higher	6	..
10	3.0	0.75	$FeCl_3$	0.04	24–28^b	1.0^b	XVII	40	30
					28–28^c	2.0^c	XVIII	11	12
							Higher	8	..
				With isopropyl chloride					
11	1.25	0.25	$AlCl_3$	0.02	5– 1^b	0.5^b	XIX	28	76
					1–23^c	1.5^c	Higher	2	..

^{a} Based on the chloroalkane (*cf.* equation 6). ^{b} Temperature and time for addition of solution of chloroalkane in aromatic compound to stirred mixture of aromatic compound and catalyst. ^{c} Temperature and time for additional stirring. ^{d} Isobutane was also formed but was not collected. ^{e} Mixture of reactants and catalysts heated under reflux.

di-(*p*-xylyl)-methane (VII). They explain the formation of VII by postulating that transalkylation (methyl disproportionation) of *p*-xylene yields pseudocumene (1,2,4-trimethylbenzene) which undergoes hydrogen transfer to yield the ion VI which on condensation with *p*-xylene yields the dixylylmethane (VII). However, it does not seem plausible to propose that the 2,5-dimethylbenzyl cation (VI) will be formed exclusively in preference to the 2,4-dimethylbenzyl ion by the transfer reaction with pseudocumene. Furthermore, formation of ion VI by the reactions of equations 2, 3 and 4 explains the presence of V in the product.



Zirconium chloride also catalyzed the hydrogen transfer reaction with *p*-xylene. Approximately equal yields of di-*t*-butyltoluene (XVI), the dixylylmethane (VII) and isobutane (25, 17 and 22%, respectively) were isolated.

On the other hand, little or no hydrogen transfer occurred with ferric chloride at 25–44° or at 78–86°, the chief product being butylxylene obtained in about 10 and 16% yields, respectively.

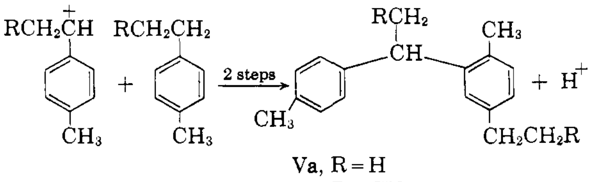
The dixylylmethane (VII) was also produced, but in smaller yield (9%) than with *t*-butyl chloride, when *t*-pentyl chloride was used as alkylating agent in the presence of aluminum chloride at 2–24°; pentylxylene (XVII) was obtained in 54% yield. Use of ferric chloride as catalyst resulted in a 30% yield of the same pentylxylene, as well as 12% of dipentylxylene (XVIII), but there was no evidence of the hydrogen transfer product VII. The formation of the same pentylxylene with both catalysts (as well as with aluminum chloride dissolved in nitromethane[4]) was very surprising since alkylation of benzene with *t*-pentyl chloride yields a mixture consisting chiefly of the secondary pentylbenzene, 2-methyl-3-phenylbutane, when aluminum chloride is used 'as catalyst, but pure *t*-pentylbenzene when ferric chloride or nitromethane solutions of aluminum chloride are used.[6] That the pentylxylene was (1,2-dimethylpropyl)-*p*-xylene (or as it may also be named, 2-methyl-3-*p*-xylylbutane) was proved, as was also subsequently reported by Friedman and co-workers,[5] by synthesis. It may be concluded that the *t*-pentyl ion formed from the *t*-pentyl chloride isomerizes to the secondary isopentyl ion which is not sterically hindered from condensing with the *p*-xylene; the *t*-butyl ion, on the other hand, cannot readily isomerize to a secondary ion and hence yields chiefly hydrogen transfer product rather than alkylate with *p*-xylene as such.

When a secondary alkyl chloride, isopropyl chloride, was used as alkylating agent in the presence of aluminum chloride at 0–23°, a high yield (76%) of alkylation product, apparently

(6) (a) M. Inatome, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **74**, 292 (1952); (b) L. Schmerling and J. P. West, *ibid.*, **76**, 1917 (1954).

isopropyl-*p*-xylene, was obtained unaccompanied by any hydrogen transfer product VII.

It is significant to note that only a very minor amount of hydrogen transfer product was obtained in the alkylation of *p*-xylene with hydrogen fluoride as catalyst and none at all with sulfuric acid.[5] It is further significant that these catalysts did yield major amounts of hydrogen transfer product by reaction of methylcyclohexene with *p*-dialkylbenzenes which contain at least one alkyl group attached to the benzene ring by a secondary[7] or tertiary[8] carbon atom. With the former (*e.g.*, with *p*-ethyltoluene and *p*-propyltoluene) the products were diarylalkanes [1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane (Va) and 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane (Vb), respectively] formed by reactions analogous to those leading to V (equation 3). The transaralkylation reaction analogous to that of equations 4 and 5 presumably does not occur; no bis-(*p*-ethyltolyl)-ethane or bis-(*p*-propyltolyl)-propane was obtained.



Va, R = H
Vb, R = CH$_3$

When the protonic acids catalyze hydrogen transfer during the alkylation of a *p*-dialkylbenzene containing a tertiary carbon atom (*e.g.*, *p*-cymene), the product is an arylindane (*e.g.*, 1,3,5-tetramethyl-3-*p*-tolylindan).[8]

Reaction of *p*-Chlorotoluene with *t*-Butyl Chloride.—Steric hindrance also resulted in hydrogen transfer with *p*-chlorotoluene was treated with *t*-butyl chloride in the presence of aluminum chloride at room temperature. Isobutane and bis-(*p*-chlorotolyl)-methane (XXII) were isolated in 24 and 14% yields, respectively. There were also obtained 10% *t*-butylchlorobenzene (XX, largely the *p*-isomer) and 2% di-*t*-butylchlorobenzene (XXI), produced by alkylation of chlorobenzene formed by the reaction analogous to that of equation 6.

The orientation of the methylene group in the diarylmethane XXII was not established. Substitution in *o*-position to the chlorine atom is said to be favored in the reaction of acyl halides with *p*-chlorotoluene in the presence of aluminum chloride.[9] It seems probable that XXII was chiefly bis-(3-*p*-chlorotolyl)-methane mixed with minor amounts of the isomers, bis-(2-*p*-chlorotolyl)-methane and (2-*p*-chlorotolyl)-(3-*p*-chlorotolyl)-methane.

The bis-(*p*-chlorotolyl)-methane was shown by both its infrared spectrum and its nitro derivative to be essentially the same as the product synthesized by condensing 3-chloromethyl-*p*-chlorotoluene with *p*-chlorotoluene in the presence of ferric chloride.

Reaction of *p*-Chlorotoluene with 1,1-Dichloroalkanes.—*p*-Chlorotoluene also underwent hydrogen transfer when alkylated with 1,1-dichloroalkanes. Methylene chloride yielded methylated products, chloroxylene (XXVI, 13%) and trimethylchlorobenzene (XXVII, 3%), and bis-(chlorotolyl)-methanes (XXII, 19%). Chlorobenzene was isolated in 11% yield. Part of XXII may have been formed by the direct condensation of the methylene chloride with two moles of the *p*-chlorotoluene.

Infrared analysis indicated that the bis-(*p*-chlorotolyl)-methane (XXII) obtained by alkylation with methylene chloride was very similar but not identical to that obtained with *t*-butyl chloride, probably because of the presence of different amounts of the different isomers.

Reaction of *p*-chlorotoluene with ethylidene chloride produced ethyl-*p*-chlorotoluene (XXIII) and XXII in about 25–26% yield each. There was also obtained crystalline 1,1-bis-(*p*-chlorotolyl)-ethane (XXIV, about 4% although more may have been present in solution in XXII, an oil) formed by the direct condensation of the chlorotoluene with ethylidene chloride. The relative yields of XXII and XXIV indicate that hydrogen transfer occurs more readily than does condensation when the intermediate 2- or 3-(1-chloroethyl)-*p*-chlorotoluene (or its ionic equivalent) contacts a *p*-chlorotoluene molecule.

Experimental

Procedure.—A solution of the alkyl chloride or dichloroalkane in about 20–35% of the total amount of the aromatic compound used was added dropwise to a stirred mixture of the remainder of the aromatic compound and the catalyst. Stirring was continued for approximately 1 to 4 hours 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 potassium carbonate and distilled. The experiments are summarized in Tables I, II and III. The physical properties of the products are given in Table IV.

Materials.—The 1,1-dichloro-3,3-dimethylbutane was prepared by condensing *t*-butyl chloride with vinyl chloride in the presence of aluminum chloride.[10] The other dichlorides, alkyl chlorides and aromatic compounds were commercially available products.

Identification of Products.—The previously reported alkylbenzenes and alkylchlorobenzenes were identified by their physical properties and infrared spectra. The identity of the hexyl-*p*-xylene (IV), the dipentyl-*p*-xylene (XVIII), the methylcyclohexyl-*p*-xylene (IX), the isopropyl-*p*-xylene (XIX), the ethyl-*p*-chlorotoluene (XXIII) and the bis-(*p*-chlorotolyl)-ethane (XXIV) was assumed from the method of formation, the analytical data and the infrared spectra. The pentyl-*p*-xylene (XVII) was compared with an authentic sample synthesized as described below. The butylchlorobenzenes (XX and XXI) obtained by the reaction of *t*-butyl chloride with *p*-chlorotoluene (experiment 12) were compared by infrared with the compounds prepared by the reaction of *t*-butyl chloride with chlorobenzene (experiment 13). The bis-(*p*-chlorotolyl)-methane (XXII) was compared with a synthetic sample (see below).

Synthesis of (1,2-Dimethylpropyl)-*p*-xylene (XVII).—To the Grignard reagent prepared from 31 g. (0.17 mole) of 2-bromo-*p*-xylene and 4 g. (0.17 mole) of magnesium turnings in 120 cc. of anhydrous ether there was added slowly 15 g. (0.17 mole) of 3-methyl-2-butanone. The product was hydrolyzed with cold water, added dropwise and the ether solution was washed, dried and distilled under reduced pressure to recover 11 g. (34%) of (1-hydroxy-1,2-dimethylpro-

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[7] H. Pines, D. R. Strehlau and V. N. Ipatieff, THIS JOURNAL, **71**, 3534 (1949).

[8] V. N Ipatieff, H. Pines and R. C. Olberg, *ibid.*, **70**, 2123 (1948).

[9] A. Claus, *J. prakt. Chem.*, [2] **43**, 355 (1891).

[10] L. Schmerling, THIS JOURNAL, **68**, 1650 (1946).

TABLE III

REACTION OF p-CHLOROTOLUENE WITH CHLOROALKANES

Expt.	Reactants ClPhMe	Chloride Kind	Mole	$AlCl_3$, mole	Temp., °C.	Time, hr.	Chief products Compound	G.	%[a]
12	1.34	Me_3CCl	0.49	0.08	24–26[b]	1.1[b]	$i\text{-}C_4H_{10}$	7	24
					24–24[c]	0.3[c]	XX	8	10
							XXI	2	4
							XXII	18	14
							Higher	16	..
14	1.34	$MeCHCl_2$	0.49	0.08	26–30[b]	1.3[b]	XXIII	20	26
					26–27[c]	0.5[c]	XXII	32[e]	25
							XXIV	5[e]	4
							XXV	7	7
							Higher	30	..
15	1.34	CH_2Cl_2	0.50	0.09	26–63[b]	1.3[b]	PhCl	6	11
					56–62[c]	1.1[c]	XXVI	9	13
							XXVII	1	3
							XXII	25	19
							Higher	45	..
13	1.00[d]	Me_3CCl	0.50	0.04	26–27[b]	1.1[b]	XX	54	64
					27–27[c]	0.5[c]	XXI	5	9

[a] Based on the chloroalkane (*cf.* equation 6). [b] Temperature and time for addition of solution of chloroalkane in aromatic compound to stirred mixture of aromatic compound and catalyst. [c] Temperature and time for additional stirring. [d] Chlorobenzene. [e] XXII, an oil, may have contained some crystalline XXIV in solution.

TABLE IV

PROPERTIES OF THE ALKYLATION PRODUCTS

Compd.	Formula	B.p., °C.	Mm.	B.p. at 760 mm., °C.[a]	$n^{20}D$	Analyses, % Calculated C	H	Cl	Found C	H	Cl
IV	$2\text{-}Me_3CCH_2CH_2C_6H_3Me_2\text{-}1,4$	115–115	9.5	250–250	1.4910	88.34	11.66		88.23	11.81	
VII	$(p\text{-}Me_2C_6H_3)_2CH_2$[b]	154–155	5.3	320–321	....[c]	91.01	8.99		90.98	9.07	
VIII	$C_{14}H_{20}$[d]	89– 89	1.6	261–261[e]	1.5169[f]	89.29	10.71		88.78	10.84	
IX	$2\text{-}(MeC_6H_{10})C_6H_3Me_2\text{-}1,4$	152–155	21	276–280	1.5200	89.04	10.96		89.10	11.00	
X	$2\text{-}EtC_6H_3Me_2\text{-}1,4$[g]	184–184	753		1.5035						
XI	$2,5\text{-}Et_2C_6H_2Me_2\text{-}1,4$[g]	38– 39	0.4	216–218	1.5039						
XII	$C_6H_3Me_3\text{-}1,2,4$[g]	167–168	745		1.5040						
XIII	$C_6H_2Me_4\text{-}1,2,4,5$[g]	84– 87	19	195–197	....[h]						
XIV	$MeC_6H_4Bu\text{-}t$[g]	83– 92	25	190–196	1.4919						
XV	$Me_2C_6H_3Bu\text{-}t$[g]	46– 48	0.8	217–220	1.4947						
XVI	$t\text{-}Bu_2C_6H_3Me$[g]	92– 93	4.5	241–242[i]	1.4945	88.16	11.84		88.39	11.88	
XVII	$2\text{-}(Me_2CHCHMe)C_6H_3Me_2\text{-}1,4$[j]	92– 93	8.5	225–226	1.4975	88.56	11.44		88.26	11.85	
XVIII	$2,5\text{-}(Me_2CHCHMe)_2C_6H_2Me_2\text{-}1,4$	126–127	5.0	285–286	....[k]	87.73	12.27		87.70	12.32	
XIX	$Me_2CHC_6H_3Me_2\text{-}1,4$	61– 62	4.6	201–202	1.5006	89.12	10.88		89.28	10.90	
XX	$t\text{-}BuC_6H_4Cl$[l]	96– 76	5.3	212–212	1.5120	71.21	7.77	21.02	71.43	7.86	20.73
XXI	$t\text{-}Bu_2C_6H_3Cl$	89– 96	1.5	265–276	1.5199[m]	74.81	9.42	15.77	74.52	9.42	15.95
XXII	$(p\text{-}MeC_6H_3Cl)_2CH_2$	156–156	1.8	351–351[n]	1.5895	67.94	5.32	26.74	68.13	5.43	26.65
XXIII	$Et(p\text{-}MeC_6H_3Cl)$	49– 51	1.5	212–214	1.5210						
XXIV	$(p\text{-}MeC_6H_3Cl)_2CHMe$	.....[o]		.....[o]	....[o]	69.07	5.80	25.49	68.95	5.80	25.46
XXV	$C_{25}H_{25}Cl_3$[p]	236–239	3.0	450–454	1.6298	69.53	5.84	24.63	69.35	5.48	25.16
XXVI	$Me_2C_6H_3Cl$[l]	185–192	749		1.5242						
XXVII	$Me_3C_6H_2Cl$[l]	47– 47	0.5	222–222	1.5305[q]						

[a] Calculated from boiling point using group 2 of Lippincott nomograph, *Ind. Eng. Chem.*, **38**, 320 (1946); this gives high values in some cases, but is, nevertheless, useful for purposes of comparison. [b] R. C. Huston and D. T. Ewing, THIS JOURNAL, **37**, 2394 (1915); see also reference of footnote 5. [c] M.p. 64–64.8° (from ethanol). [d] Infrared analysis indicates 1,2,3,4-tetrasubstituted benzene. [e] B.p. in test-tube, 148–151°. [f] d^{20}_4 0.9213; mol. ref. calcd. 61.16, obsd. 61.80. [g] For previously described properties, see G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1946, Vol. III. [h] M.p. 78–79°. [i] B.p. in test tube, 230–232°. [j] See reference of footnote 5. [k] M.p. 64–66°; "mixed m.p." with VII, below 48°. [l] Beilstein's "Handbuch," Vol. V. [m] Refractive index of liquid portion (about one-half) of fraction, filtration of which yielded crystals, m.p. 54–55° (recrystallized from ethanol). [n] B.p. in test-tube, 327–328°. [o] A fraction (b.p. 151–151° at 1.7 mm., 351–351° at 760 mm.; $n^{20}D$ 1.5859) deposited crystals on standing. Filtration followed by recrystallization from absolute ethanol gave white platelets, m.p. 112–113°. [p] Bis-[1-(p-chlorotolyl)-ethyl]-p-chlorotoluenes. [q] Refractive index of liquid portion of fraction, filtration of which yielded crystals which on recrystallization from dilute alcohol were obtained as nacreous flakes, m.p. 72°. 5-Chloro-1,2,4-trimethylbenzene is reported to melt at 70–71° (Beilstein's "Handbuch," Vol. V).

pyl)-p-xylene (*i.e.*, 3-methyl-2-p-xylyl-2-butanol), b.p. 99–101 at 1 mm., $n^{20}D$ 1.5140.

To 5.4 g. (0.028 mole) of the butanol dissolved in 3.5 g. of absolute ethanol there was added about 150 cc. of liquid ammonia. Sodium (1.7 g., 0.074 mole) was added in small portions to the stirred solution. The temperature was then permitted to rise to room temperature in order to evaporate most of the ammonia, after which water was added dropwise and the product was extracted with pentane. The extract was washed, dried and distilled yielding 2.9 g. (64%) of XVII, boiling chiefly at 78–79° at 4.25 to 4.0 mm. (about 223–227° at 760 mm.), $n^{20}D$ 1.4955. The infrared spectrum of this compound was identical with those of the pentylxylenes obtained by the reaction of t-pentyl chloride with p-xylene in the presence of aluminum chloride or ferric chloride (experiments 9 and 10).

Synthesis of Bis-(3-p-chlorotolyl)-methane (XXII).—p-Chlorotoluene was chloromethylated by bubbling hydrogen chloride through a stirred mixture of 127 g. (1.0 mole) of p-chlorotoluene and a solution of 100 g. of zinc chloride and 38

g. of 40% formaldehyde (0.5 mole) in 50 cc. of concentrated hydrochloric acid at 55–70° during 12 hours.[11] The upper layer was taken up in pentane, washed with water, dried and distilled over anhydrous potassium carbonate. There was obtained 51 g. (58%) of chloromethyl-*p*-chlorotoluene, b.p. 75–75° at 1.5 mm., $n^{20}D$ 1.5560; and 8 g. (14%) of bis-(chloromethyl)-*p*-xylene, as crystalline residue which gave short white needles, m.p. 108–109°, on recrystallization from heptane.

Anal. Found: C, 48.45; H, 4.35; Cl, 47.38. Calcd. for $CH_3C_6H_2Cl(CH_2Cl)_2$ or $C_9H_9Cl_3$: C, 48.36; H, 4.06; Cl, 47.59.

Tschunker and Eichler[11] state that oxidation of the monochloromethylated compound yielded 2-chloro-5-methylbenzoic acid while reduction yielded 4-chloro-*m*-xylene, indicating that the compound (no physical properties of which are given in the patent) was 3-chloromethyl-4-chlorotoluene.

A solution of 15 g. (0.086 mole) of the chloromethylchlorotoluene in 29 g. of *p*-chlorotoluene was added during 1.5 hours to a stirred mixture of 58 g. (0.69 mole total) of *p*-chlorotoluene and 3 g. of ferric chloride at 28–29°. The product was stirred for an additional 50 minutes, after which the upper layer was separated from 5.5 g. of solid catalyst layer, treated in the usual manner and distilled, yielding 10.5 g. (60%) of XXII, b.p. 147–149° at 0.9 to 1.0 mm. (converts to 358–359° at 760 mm., 328–331° in a test-tube), $n^{20}D$ 1.5876 to 1.5891.

Infrared analysis of various fractions indicated that the product consisted essentially of one compound and that this was a component of the product obtained by the reaction of *p*-chlorotoluene with *t*-butyl chloride.

Nitration of various samples of XXII with 2:1 sulfuric acid–nitric acid yielded a dinitro derivative, m.p. 144° (recrystallized from Formula 30 alcohol).

Anal. Found: C, 50.68; H, 3.71; N, 8.17; Cl, 20.20. Calcd. for $C_{15}H_{12}Cl_2N_2O_4$: C, 50.72; H, 3.41; N, 7.88; Cl, 19.97.

Tetranitrodi-*p*-xylylmethane.—Nitration of VII with 2:1 nitrating mixture yielded a tetranitro derivative, m.p. 190°.

Anal. Found: C, 50.36; H, 4.03; N, 13.85. Calcd. for $C_{17}H_{16}N_4O_8$: C, 50.50; H, 3.98; N, 13.85.

DES PLAINES, ILL.

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[11] E. Tschunker and F. Eichler, German Patent 509,149 (1930).

[CONTRIBUTION NO. 509 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Chemistry of Cyclobutanes. I. Synthesis of Methylenecyclobutanes

BY H. N. CRIPPS, J. K. WILLIAMS AND W. H. SHARKEY

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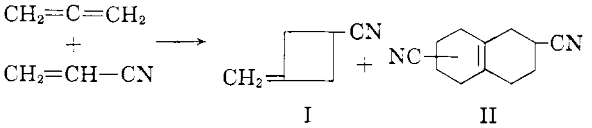
A new route to substituted methylenecyclobutanes has been discovered that involves cycloaddition of allenes to appropriately substituted olefins. This reaction has been used to prepare 3-methylenecyclobutanes substituted in the 1-position with nitrile, carboxyl, carboalkoxy, aldehyde and aryl groups. 2,6(and/or 2,7)-Disubstituted -1,2,3,4,5,6,7,8-octahydronaphthalenes were also obtained as secondary products. When substituted allenes were employed, products corresponding to cycloaddition to each double bond were usually obtained. In these cases reaction of the less substituted allenic double bond appeared to be favored.

The cycloaddition of tetrafluoroethylene, chlorotrifluoroethylene and 1,1-dichloro-2,2-difluoroethylene to olefins[1] has made a variety of fluorinated cyclobutanes readily available for study. However, the direct syntheses of simple non-fluorinated cyclobutanes has been limited to the dimerization of acrylonitrile,[2] methacrylonitrile,[3] allenes[4] and alkylketenes[5] and the addition of ketene to cyclopentadiene[6,7] and cyclohexadiene.[7]

Recently, a synthesis of non-fluorinated cyclobutanes[8] of breadth and simplicity comparable to the direct cycloaddition of fluoroölefins has been discovered. Allenes have been found to react with suitably substituted olefins at elevated temperatures to give alkylidenecyclobutanes. Alder and Ackermann[9] reported that allenes and maleic anhydride react to form 3-alkylidenecyclobutane-1,2-dicarboxylic anhydrides. Prior to Alder and Ackermann's report we had independently discovered the thermal cycloaddition of allenes to olefins and had found the reaction to be generally applicable to the preparation of a wide variety of substituted alkylidenecyclobutanes.

The thermal cycloaddition of allenes to substituted olefins is best exemplified by allene and acrylonitrile, which react smoothly to give a cyclobutane, I, and an octahydronaphthalene, II.



I II

Reaction conditions are 150–250° at autogenous pressure. The maximum pressure during reaction is in the range of 4–4.5 atm. When a large excess of acrylonitrile is used 3-methylenecyclobutanecarbonitrile (I) is formed in yields as high as 60%. The formation of the second product, 2,6(and/or 2,7)-dicyano-1,2,3,4,5,6,7,8-octahydronaphthalene (II), which is obtained in 15–25% yields under these conditions, will be discussed later.

The identity of the 1:1 adduct as 3-methylenecyclobutanecarbonitrile (I) was established by its conversion to known compounds. Catalytic hydrogenation of I gave a saturated nitrile that was hydrolyzed to 3-methylcyclobutanecarboxylic acid. The anilide of this acid, III, melted at 127–128°, which is in agreement with the melting point of 3-

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[1] (a) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, THIS JOURNAL, **71**, 490 (1949); (b) P. L. Barrick and R. D. Cramer, U. S. Patent 2,427,128 (1947); (c) P. L. Barrick, U. S. Patent 2,427,116 (1947); (d) J. Harmon, U. S. Patent 2,404,374 (1946).

[2] E. C. Coyner and W. S. Hillman, THIS JOURNAL, **71**, 324 (1949).

[3] C. J. Albisetti, D. C. England, M. J. Hogsed and R. M. Joyce, *ibid.*, **78**, 472 (1956).

[4] S. V. Lebedeff and B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913); S. V. Lebedeff, *ibid.*, **43**, 820 (1911).

[5] W. E. Hanford and J. C. Sauer, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 108–140.

[6] B. T. Brooks and G. Wilbert, THIS JOURNAL, **63**, 879 (1941).

[7] A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

[8] H. N. Cripps, J. K. Williams and W. H. Sharkey, *ibid.*, **80**, 751 (1958).

[9] K. Alder and O. Ackermann, *Chem. Ber.*, **90**, 1697 (1957).