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

Condensation of Benzene with Unsaturated Chlorides¹

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RECEIVED JULY 18, 1957

Vinylic chlorides (such as 2-chloropropene, 1-chlorocyclohexene, 2,3-dichloropropene, 1,3-dichloropropene and 1,3-dichloro-2-methylpropene) unlike allylic chlorides (such as allyl chloride and methallyl chloride) and a tricyclic chloride (3chloronortricyclene) are not condensed with benzene when sulfuric acid is used as catalyst. The dichloroölefins do undergo condensation with benzene in the presence of aluminum chloride catalysts. The reaction may take place at either the double bond or the allylic carbon atom, depending on the conditions; 1,3-dichloro-2-methylpropene produces 1,3-dichloro-2-phenyl-2-methylpropane (III) in the presence of aluminum chloride dissolved in nitromethane, and (3-chloro-2-methylallyl)-benzene (IV) in the presence of granular aluminum chloride. 1,3-Dichloroppene yields (3-chloroallyl)-benzene (II) even in the presence of sturated hydrocarbons containing tertiary carbon atoms, hydrogen transfer occurs. Thus, the reaction with allyl chloride and methylcyclopentane yields *n*-propylbenzene and (methylcyclopentyl)-benzene rather than (2-chloropropyl)-benzene which is obtained in the absence of the cycloparaffin. Similar hydrogen transfers occur with methallyl chloride, isocrotyl chloride, *trans*-dichloroethylene and trichloroethylene.

Comparatively few examples of the chloroalkylation of benzene with a chloroalkene have been described. The reaction with allyl chloride in the presence of sulfuric acid yields 1-chloro-2phenylpropane, condensation occurring at the secondary doubly-bonded carbon atom of the chloride.² Similarly, the reaction of methallyl chloride in the presence of sulfuric acid³ or of hydrogen fluoride⁴ yields 1-chloro-2-phenyl-2-methylpropane, condensation occurring at the tertiary carbon atom.

On the other hand, when aluminum chloride is used as catalyst, the reaction of allyl chloride involves the elimination of hydrogen chloride, the products (which include allylbenzene, propylbenzene, indan and 2-chloropropylbenzene) being formed via the intermediate condensation at the primary allylic carbon atom.⁵ Similarly, the reactions of 1,3-dichloropropene in the presence of aluminum chloride produces (3-chloroallyl)-benzene.⁶

The present paper describes an investigation of the scope of such benzene alkylations. Table I summarizes the results of experiments with monoand dichloroölefins in the presence of sulfuric acid or of aluminum chloride as such or in nitromethane solution. The reaction of 3-chloronortricyclene is included for purposes of comparison. Table II shows the effect of carrying out aluminum chloridecatalyzed reactions in the presence of saturated hydrocarbons containing a tertiary carbon atom.

Unlike allyl chloride, 2-chloropropene could not be condensed with benzene in the presence of 96%sulfuric acid at 0°. Similarly, no chlorocyclohexylbenzene was obtained by the reaction of 1chlorocyclohexene with benzene under the same conditions; the only reaction product obtained was

(1) Presented before the Division of Organic Chemistry of the American Chemical Society at the Miami Meeting, April, 1957.

(2) R. Truffault, Compt. rend., 202, 1286 (1936).

(3) (a) F. C. Whitmore, C. A. Weisberger and A. C. Shabica, THIS JOURNAL, 65, 1469 (1943); (b) L. Schmerling and V. N. Ipatieff, *ibid.*, 67, 1862 (1945).

(4) W. S. Calcott, J. M. Tinker and V. Weinmayr, *ibid.*, **61**, 1010 (1939).

(5) (a) R. B. Silva, Compt. rend., 89, 606 (1879); (b) P. Wispek and R. Zuber, Ann., 218, 374 (1883); (c) M. Konowalov and S. Dobrovolsky, J. Russ. Phys.-Chem. Scc., 37, 548 (1905); (d) C. D. Nenitzescu and D. A. Isacescu, Ber., 66, 1100 (1933); (e) I. P. Losev, O. V. Smirnova and T. A. Pfeifer, J. Gen. Chem. U.S.S.R., 21, 668 (1051).

(6) P. Bert. Compt. rend., 213, 619 (1941).

cyclohexanone which was isolated in 32% yield by hydrolysis of the catalyst layer followed by steam distillation. These results suggest that the chlorine substituent markedly decreases the reactivity of the double bond, presumably because of its effect on the conversion of the olefin into the intermediate carbonium ion.

Sulfuric acid was also not a catalyst for the condensation of benzene with 2,3-dichloropropene, 1,3-dichloropropene and 1,3-dichloro-2-methylpropene. The unreactivity of the dichloromethylpropene was unexpected in view of the fact that sulfuric acid catalyzes the condensation of both methallyl chloride and isocrotyl chloride with benzene to form 1-chloro-2-phenyl-2-methylpropane. It seems plausible to conclude that the isocrotyl chloride undergoes intermediate isomerization to methallyl chloride.

The reaction of 1-chloro-2,4,4-trimethyl-1-pentene with benzene in the presence of sulfuric acid at ice temperature resulted in a small yield (10%)of 1-chloro-2-phenyl-2-methylpropane. "Depolymerization" of the chloroölefin to isobutylene and methallyl chloride apparently occurred. The isobutylene reacted to form *t*-butylbenzene and catalyst sludge.

Condensation did occur when benzene was treated with 3-chloronortricyclene in the presence of sulfuric acid at about 0° . (Chlorobicycloheptyl)-benzene was obtained in 67% yield. The chlorine atom had little effect on the opening of the strained three-membered ring and the resultant formation of a carbonium ion.

Aluminum chloride dissolved in nitromethane was a somewhat more effective catalyst. It caused little reaction between benzene and 2,3-dichloropropene but did catalyze the condensation of benzene and 1,3-dichloropropene. However, the reaction did not directly involve the double bond; instead, the allylic chlorine atom was eliminated and (3-chloroallyl)-benzene was obtained in 47% yield. The reaction was the same as that which occurs in the presence of aluminum chloride as such.⁶

Condensation at the allylic carbon atom also occurred with a dichloride containing a tertiary carbon atom (1,3-dichloro-2-methylpropene) in the presence of unmodified aluminum chloride. A 23% yield of (3-chloro-2-methylallyl)-benzene was

				Catalyst-		Chief product		
Expt.ª	C ₆ H ₆	Haloölefin	Mole	Kind	g.	Formula	Vield, %	
1	1.3	CH2:CClMe	0.40	H_2SO_4	30	Little reaction	••	
2	1.2	Me ₃ CCH ₂ CMe:CHCl	.20	H_2SO_4	40	PhCMe ₂ CH ₂ Cl ^b	10	
3	1.3	cyclo-C ₆ H ₉ Cl-1	.16	H_2SO_4	30	Little reaction ^e	••	
4	1.5	C7H2Cl ^d	.20	H_2SO_4	30	$PhC_7H_{10}C1$ (I)	67	
5	3.1	CH2: CClCH2Cl	.50	H_2SO_4	5 0	Little reaction		
6	2.1	CH2:CClCH2Cl	.45	AlCl ₃ ·NM ^e	1 1ª	Little reaction	••	
7	3.1	CHCl:CHCH₂Cl	.45	H_2SO_4	50	Little reaction	• ·	
8	2.1	CHC1:CHCH2C1	.45	AlCl3·NM ^e	10°	$PhCH_{2}CH:CHCl$ (II)	47	
9	2.1	CHCl:CMeCH ₂ Cl	.38	H_2SO_4	50	Little reaction	••	
10	2.1	CHCl:CMeCH ₂ Cl	.44	AlCl ₃ ·NM ^e	1 1°	$PhC(CH_2Cl)_2Me$ (III)	51'	
11	2.1	CHCl:CMeCH ₂ Cl	.44	A1C1	5	PhCH ₂ CMe:CHCl (IV)	23°	

11 2.1 CHCl: CMeCH₂Cl .44 AlCl₂ 5 PhCH₂CMe: CHCl (IV) 23^{*a*} ^{*a*} Experiments carried out at ice-bath temperature. ^{*b*} 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). ^{*c*} Cyclohexanone was obtained in 32% yield by hydrolysis of the lower, catalyst, layer. ^{*a*} 3-Chloronortricyclene (b.p. 60-60.5° at 19 mm., *n*²⁰p 1.4971) prepared by the chlorination of bicycloheptene; J. D. Roberts, F. O. Johnson and R. A. Carboni, *ibid.*, 76, 5692 (1954). ^{*e*} Five g. of aluminum chloride dissolved in 5 or 6 g. of nitromethane. ^{*f*} Also 13 g. of higher-boiling product. ^{*a*} Also 40 g. of higher-

TABLE II

		React Halo-	ants, moles Satd. h	chn	AICI,	Average	Chief products-	Yield
Expt.	C6H6	olefins	Kind	Moles	g.	°C,	Formula	%
				With a	allyl chlori	de		
12	4.1	1.0	None	••	5 ⁶	3–6	PhCH ₂ CHClMe (V) 1,2-Ph ₂ Pr (VI) Higher (60 g.)	28 8
13	2.6	0.5	MCP ^a	1.5	5	3- 6	PhPr ^e PhC ₆ H ₈ Me 1,2-Ph ₂ Pr Higher (26 g.)	10 19 14
				With me	thallyl chl	oride		
14	2.6	0.5	MCH ^a	1.5	5	2-4	i-BuPh ^d PhC₀H₁₀Me i-BuPhC₀H₁₀Me Higher (12 g.)	39 52 19
				With iso	erotyl chlo	oride		
15	2.6	0.5	None	••	5	5-7	Me ₂ CPhCH ₂ Ph [•] Higher (23 g.)	52
16	2.6	0.5	MCH ^ª		5	2-4	<i>i</i> -BuPh ^a PhC ₆ H ₁₀ Me <i>i</i> -BuPhC ₆ H ₁₀ Me Higher (10 g.)	42 58 16
				With trans	-dichloroet	hylene		
17	2.6	1.0	None	••	5	40-50	(PhCH ₂) ₂ (VII) Higher (7 g.)	3
18	2.6	1.0	<i>i</i> -C ₅ H ₁₂	2.0	5	38-43	(PhCH ₂) ₂ (VII) PhAm ^f Higher (7 g.)	12 10
				With tri	chloroethy	vlene		
19 20	3.1 2.6	0.5 .5	None None	•••	5 7	3 9-41 40 - 45	(Ph ₂ CH) ₂ (VIII) (Ph ₂ CH) ₂ (VIII) Ph ₂ CHCH ₂ Ph (IX)	4 3 2
21	3.1	.5	<i>i</i> -C ₅ H ₁₂	2.9	5	35-42	(PhCH ₂) ₂ (VII) PhAm ^f	22 20 °

MCP = methylcyclopentane; MCH = methylcyclohexane.
Five g. of aluminum chloride dissolved in 10 g. nitromethane.
Infrared spectrum indicates 100% n-propylbenzene.
Infrared spectra indicate 98-99% isobutylbenzene.
F. Bodroux, Compt. rend., 132, 1333 (1901); L. Schmerling, R. W. Welch and J. P. West, THIS JOURNAL, 78, 5406 (1956).
80-85% 2-phenyl-3-methylbutane and 15-20% t-pentylbenzene.
Based on a theoretical yield of 2.0 moles of pentylbenzene.

obtained together with a small amount of diphenyland triphenylbutanes and a large amount of higher boiling material which was apparently polyconden-

sation product. On the other hand, condensation at the tertiary carbon atom apparently occurred when the catalyst consisted of a nitromethane solu-

TABLE I Reaction of Unsaturated Chlorides with Benzene tion of aluminum chloride. Product which seemed to be $(\beta,\beta'$ -dichloro-*t*-butyl)-benzene (1,3-dichloro-2-phenyl-2-methylpropane) was obtained in 51% yield.

Condensation at the allylic carbon atom is also the primary reaction of benzene with allyl chloride in the presence of aluminum chloride, various products being obtained depending chiefly on the purity of the catalyst and the ratio of allyl chloride to catalyst. Some of the early workers reported only 1,2diphenylpropane as the reaction product.^{5a,5c} Others obtained also *n*-propylbenzene.^{5b} Later, it was shown that in the presence of pure aluminum chloride, the only product is 1,2-diphenylpropane; if, on the other hand, the aluminum chloride is first weakened or "poisoned" by adding water (0.5 mole of water per mole of aluminum chloride),*n*-propylbenzene and 9,10-diethylanthracene are formed as by-products.^{5d} Thus, from the reaction product of 3.5 moles of benzene and 1.0 mole of allyl chloride at 50° in the presence of 66 g. (0.5 mole) of aluminum chloride which had been treated with 4.5 cc. (0.25 mole) of water, there was isolated a 15% yield of *n*-propylbenzene and a 4% yield of the 9,10-diethylanthracene. Nenitzescu and Isacescu^{5d} state that the propylbenzene was obtained only when the diethylanthracene also was formed; it was produced by the hydrogen transfer involving the chloropropylbenzene and 9,10-dihydro-9,10diethylanthracene formed by the self-condensation of the chloropropylbenzene. They indicate that only moistened ("poisoned") aluminum chloride is able to yield this side reaction. They point out further that the hydrogenation activity of aluminum chloride was not generally realized (as of 1933).

In a more recent paper, it is claimed that the product of the reaction of 1 mole of allyl chloride with 3 moles of benzene in the presence of 0.5 mole of anhydrous aluminum chloride at 50° yields 3chloropropylbenzene, allylbenzene, indan, 1,2-diphenylpropane and 9-methyl-9,10-dihydroanthracene.^{5e} The authors mention the previous work of Wispek and Zuber^{5b} and of Konowalov and Dobrovolsky^{5c} and state that these papers literally exhaust the material in the literature on the reaction of allyl chloride with benzene in the presence of aluminum chloride. It is apparent that they were unaware of the work of Nenitzescu and Isacescu.^{5d} They found that increasing the relative amount of aluminum chloride resulted in an increase in the yield of indan, while decreasing the percentage of aluminum chloride resulted in an increase of the yield of 1,2-diphenylpropane up to 60% of the theoretical. It should be noted that the yields of products obtained in the presence of 0.5 mole of aluminum chloride were low. Fractionation of the product yielded 1.1 g. of a fraction boiling at 150-200°, 0.8 g. of the chloropropylbenzene (b.p. 219°, the reported boiling point of the 3-chloropropyl isomer), 2.0 g. of 1,2-diphenylpropane (b.p. 280-282°) and 5.2 g. of crystalline 9-methyl-9,10-dihydroanthracene (m.p. 79-80°) which was isolated from the material boiling at $282-300^{\circ}$. The 1.1 g. of the fraction boiling at 150-200° was apparently fractionated into allylbenzene (b.p. 155°), p-diallylben-zene (b.p. 81–83° at 12 mm.), o-diallylbenzene (b.p. 94° at 12 mm.) and indan (b.p. 176.5°),

The reaction of benzene with allyl chloride, catalyzed by a nitromethane solution of aluminum chloride, yielded 28% 2-chloropropylbenzene, 8% 1,2-diphenylpropane and a large amount of higher boiling product. In the presence of unmodified aluminum chloride and methylcyclopentane, the reaction yielded 10% n-propylbenzene, 19% (methylcyclopentyl)-benzene, 14% 1,2-diphenylpropane and much higher-boiling material. None of the chloropropylbenzene was isolated; it was apparently reduced to n-propylbenzene by hydrogen transfer with the methylcyclopentane⁷ which was converted to methylcyclopentyl cation and thence to (methylcyclopentyl)-benzene. The latter was chiefly the secondary isomer, (3-methylcyclopentyl)-benzene, rather than the tertiary compound, (1-methylcyclopentyl)-benzene.7

Hydrogen transfer reactions also occurred when benzene was treated with isocrotyl chloride or methallyl chloride in the presence of methylcyclohexane and aluminum chloride. The reactions were analogous to that with isobutylene dichloride (1,2-dichloro-2-methylpropane).8 The chief products in both cases were isobutylbenzene (about 40%), (methylcyclohexyl)-benzene (about 55%) and (isobutylphenyl)-methylcyclohexane (16-19%). On the basis of the available evidence, it is not possible to decide which of two possible mechanisms is involved. Condensation may have taken place at the primary allylic carbon atom (in a manner analogous to that shown above for the reaction of allyl chloride) with the intermediate formation of (2-chloro-2-methylpropyl)-benzene, the isocrotyl chloride undergoing preliminary isomerization to methallyl chloride. Alternatively, condensation may have taken place first at the tertiary carbon atom (as with sulfuric acid as catalyst) to yield the chloro-*t*-butylbenzene which then underwent the hydrogen transfer reaction via the formation of a bridged phenonium ion, formation of which was due to anchimeric assistance⁹ by the phenyl group on a carbon atom adjacent to that holding the chlorine atom. A similar mechanism is involved in the reaction of benzene with 1,2-dichloro-2methylpropane⁸ and with certain other dihalides.¹⁰

The reaction of isocrotyl chloride with benzene in the presence of aluminum chloride alone gave a 52%yield of 1,2-diphenyl-2-methylpropane. Again, it cannot be decided definitely whether it was formed via (2-chloro-2-methylpropyl)-benzene or (2-chloro-1,1-dimethylethyl)-benzene (*i.e.*, β -chloro-*t*-butylbenzene).

The aluminum chloride catalyzed condensation of benzene with polychloroethylenes in the presence of aluminum chloride was accompanied by hydrogen transfer both in the presence and absence of added saturated hydrocarbons. Thus, the reaction of benzene with *trans*-dichloroethylene at about 40° resulted in a 3% yield of crystalline bibenzyl; the chief by-product was higher boiling viscous

(7) L. Schmerling, J. P. Luvisi and R. W. Welch, THIS JOURNAL, **77**, 1775 (1955).

(8) L. Schmerling, R. W. Welch and J. P. West, *ibid.*, **78**, 5406 (1956).

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

(10) L Schmerling, R. W. Welch and J. P. Luvisi, *ibid.*, **79**, 2636 (1957),

	В.р.,				Carbon, %		Hydrogen, %		Chlorine, %	
	Compound	°C.	Mm.	n 20 D	Calcd.	Found	Calcd.	Found	Caled.	Found
I	PhC ₇ H ₁₀ Cl	133-133	3	1.5605	75.51	75.46	7.32	7.25	17.17	17.36
II	$PhCH_2CH: CHCl^a$	50-51	1	1.5389						
III	$PhC(CH_2Cl)_2Me$	103-104	4	1.5359	59.11	59.18	5.96	5.90	34.93	34.78
IV	$PhCH_2CMe:CHCl$	80-81	2	1.5353	72.05	71.55	6.66	6.82	21.29	21.64
V	PhCH₂CHClMe ^b	67-67	3	1.5164					· · · ·	
VI	$1,2$ -Ph $_2$ Pr $^\circ$	115-118	3	1.5563						
VII	$(PhCH_2)_2{}^d$	120-121	5	^g						
VIII	(Ph ₂ CH) ₂ ^e			^h						
IX	$Ph_2CHCH_2Pl1^{f}$	180-186	6	· · · · ⁱ	92.98	93 .04	7.02	7.07		

TABLE III PUNCION PROPERTIES OF THE CONDENSATION PROPHOTS

Bert, Compt. rend., 213, 619 (1941).
 C. D. Nenitzescu and D. A. Isacescu, Ber., 66, 1100 (1933).
 G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946, p. 354.
 Idem., p. 536.
 Idem., p. 487.
 M.p. and "mixed m.p." 50-51°.
 M.p. and "mixed m.p." 200-203°.
 M.p. 42-45°.

residue which was obtained in amount about equal to the weight of the bibenzyl. When the reaction was carried out in the presence of isopentane, bibenzyl was isolated in 12% yield together with a 10% yield of pentylbenzene, chiefly 2-phenyl-3methylbutane, formation of which is consistent with the observation that the alkylation of benzene with *t*-pentyl chloride in the presence of aluminum chloride yields the secondary alkylbenzene rather than the tertiary alkylbenzene as principal product.^{7,11}

The formation of bibenzyl probably involved the condensation of the benzene across the double bond of the dichloroethylene to form (1,2-dichloroethyl)-benzene followed by replacement of the benzylic chlorine atom by hydrogen and of the other by a phenyl group. The source of hydrogen in the absence of added saturated hydrocarbon was probably triphenylethane formed by direct reaction of the (dichloroethyl)-benzene with benzene or polymeric product found in the lower layer complex.

Boeseken and Bastet¹² found that the reaction of benzene with a mixture of *cis*- and *trans*-dichloroethylene at room temperature in the presence of a catalyst prepared *in situ* by boiling a mixture of mercuric chloride and aluminum powder in benzene produced small yields of bibenzyl, 1,1,2-triphenylethane (formed by the direct reaction of (1,2-dichloroethyl)-benzene with benzene) and 1,1,2,2-tetraphenylethane (formed *via* hydrogen transfer with the triphenylethane); at a higher temperature, 80°, there was obtained a 39% yield of a crude fraction consisting chiefly of bibenzyl and a 32% yield of a crude fraction consisting largely of the triphenylethane together with a smaller amount of the tetraphenylethane.

Triphenylethane (a hydrogen transfer product) was isolated in about 2% yield and 1,1,2,2-tetraphenylethane in up to 4% yield by the reaction of benzene with trichloroethylene in the presence of aluminum chloride at 40–45° in the absence of a saturated hydrocarbon. It has been reported¹² that the reaction in the presence of the catalyst formed from aluminum and mercuric chloride resulted in a small amount (no more than 3% yield) of a liquid fraction containing 1,1-diphenylethane (proved by oxidation to benzophenone) and a frac-

(11) M. Inatome, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, 74, 292 (1952).

(12) J. Boeseken and M. C. Bastet, Rec. trav. chim., 32, 199 (1913).

tion boiling over at 60° range from which 1,1,2,2-tetraphenylethane (maximum yield, 20%) was isolated.

When the reaction was carried out in the presence of aluminum chloride and isopentane at about 40° , there was obtained a 22% yield of bibenzyl and a 20% yield of pentylbenzene, the latter yield being based on a theoretical yield of 2.0 moles of pentylbenzene per mole of trichloroethylene charged. The mechanism of the reaction apparently consisted of the addition of the trichloroethylene to the benzene (via the carbonium ion mechanism) to yield (1,2,2-trichloroethyl)-benzene followed by nucleophilic displacement of one of the chlorine atoms attached to the primary carbon atom by phenyl and subsequent replacement of both benzylic chlorine atoms by hydrogen. Evidence that the intermediate trichloroethylbenzene was the 1,2,2trichloroethyl isomer rather than (1,1,2-trichloroethyl)-benzene may be deduced from the fact that the tetraphenylethane obtained in the absence of the saturated hydrocarbon was the symmetrical 1,1,2,2-isomer and not 1,1,1,2-tetraphenylethane.

Experimental

Procedure.—A solution of the unsaturated chloride in about 20–25% of the total amount of benzene was added slowly (usually during about 1 to 3 hours) to a stirred mixture of the remainder of the benzene, the saturated hydrocarbon when used, and the catalyst. Stirring was continued for approximately 1 to 2 hours (3 to 8 hours in the reactions with the polychloroethylenes) 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 experimental details are summarized in Tables I and II.

Identification of the Products.—The physical properties of the less common products are summarized in Table III. Some of these (VII and VIII) were characterized by means of their "mixed melting points" with authentic samples; others (II, V, VI and IX), by comparison of their boiling points and refractive indices with those reported in the literature. A number of the compounds [β -chloro-t-butylbenzene, propylbenzene, isobutylbenzene, the pentylbenzenes, 1,2-diphenyl-2-methylpropane, (methylcyclopentyl) benzene, (methylcyclohexyl)-benzene and 1-(methylcyclohexyl)-4-isobutylbenzene] were identified by comparison of their infrared spectra with those of previously prepared samples. The identity of the new compounds (I, III and IV) was based chiefly on their physical properties, their analysis and comparison of the method of their formation with analogous reactions.

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