(neat); nmr ($CDCl_3$) doublets centered at τ 2.73 and 2.96 (J = 5 cps) (aromatic), singlets at 5.36 and 5.45 (CH_2), and singlets at 6.61 and 6.65 (CH_3), area ratio 1:1:2:2:3:3.

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.78; H, 7.02; S, 18.62. Found: C, 55.65; H, 6.93; S, 18.49.

2,3-Bis[(ethylthio)methyl]thiophene (IX).—In a 100-ml, one-necked flask fitted with a condenser and magnetic stirring apparatus was introduced 30 ml of anhydrous tetrahydrofuran and 1.1 g (0.018 mole) of ethyl mercaptan. One gram (0.02 mole) of 50% suspension of sodium hydride in mineral oil was washed free of mineral oil with anhydrous ether and added to the reaction mixture and stirred for 10 min. A solution of 2 g (0.0074 mole) of 2,3-bis(bromomethyl)thiophene in 30 ml of anhydrous tetrahydrofuran was added all at once and the contents were heated under reflux for 16 hr. After cooling, the reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was vacuum distilled and the product was collected at 115–118° (0.45 mm) as a clear, colorless liquid weighing 1.1 g (69%). For analysis a solution of the sample in hexane was passed over alumina and the product redistilled at 135–136° (0.7 mm), $n^{24}\text{D}$ 1.5709. Infrared spectrum showed strongest absorptions at 2900, 1440, and 705 cm^{-1} (neat); $\lambda_{\max}^{95\%\ \text{EtOH}}$ 242.5 mμ (ϵ 8200); nmr (a, deuterioacetone) two doublets at τ 2.69 and 2.78, 2.96 and 3.04 (J = 5 cps) (aromatic), two singlets at 6.00 and 6.22 (methylene), two superimposed quadruplets at 7.3–7.7 (methylene), and two superimposed triplets at 8.65–8.9 (methyl) (J = 7 cps), area ratio 1:1:2:2:4:6; (b, carbon tetrachloride) τ 2.93 and 3.00, 3.09 and 3.17, singlets at 6.16 and 6.34, quadruplets at 7.33–7.75, and triplets at 8.65–8.9, area ratio 1:1:2:2:4:6.

Anal. Calcd for $C_{10}H_{16}S_3$: C, 51.67; H, 6.94; S, 41.39. Found: C, 51.83; H, 6.82; S, 41.30.

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The Alkylation of Benzene with 1,2-Dichloroalkanes

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Benzene has been alkylated with 1,2-dichloro-4-methylpentane, 1,2-dichlorohexane, 1,2-dichlorobutane, and 1,2-dichloropropane with either aluminum chloride or liquid hydrogen fluoride catalysts. The products obtained are consistent with a mechanism in which the secondary chloride reacts initially to give preferentially the 1-chlorophenylalkane in which the phenyl group is in the penultimate position. Subsequent products are determined largely by the influence of the phenyl group in assisting ionization of the primary chloride which, in turn, is dependent on the relative positions of the phenyl and chloro groups. Other features which affect the product distribution are also discussed.

A study has been made of the products found in the alkylation of benzene with several 1,2-dichloroalkanes. The reactions were performed using liquid hydrogen fluoride and also aluminum chloride catalysts.

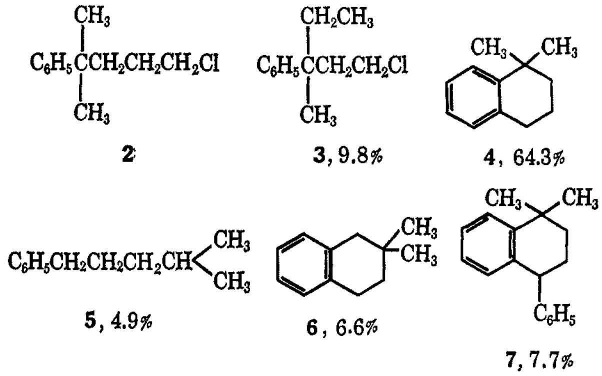
The hydrogen fluoride reactions were carried out under a pressure of dry hydrogen chloride at temperatures greater than 80°. The aluminum chloride reactions were performed by adding the catalyst to a 1 *M* solution of the dichloride in benzene at 25°. In the latter reactions almost complete dichloride conversion was obtained.

The products were isolated by distillation or by preparative gas chromatography and identified by nuclear magnetic resonance (nmr), infrared, and mass spectroscopy. All of the spectral evidence was consistent with the structures assigned and is presented in Table I.

Results

1,2-Dichloro-4-methylpentane (**1**).—After 6 hr at 90° with liquid hydrogen fluoride **1** yielded 1-chloro-4-methyl-4-phenylpentane (**2**, Chart I) as the major product (~80%). The conversion was too low (~15%) to permit identification of other products on the scale employed. From the addition of 9.3 mole % aluminum chloride to **1**, the products **3**–**7** (weight per cent) were identified after 3 hr.

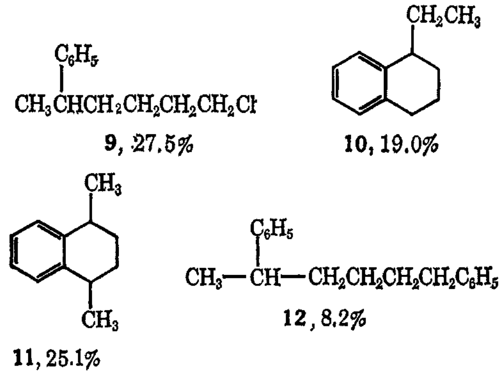
Chart I



Two further reactions were run on a 0.01-mole scale in which it was demonstrated that the addition of aluminum chloride, in the absence of benzene, caused the transformation of **2** to **4** and **4** to **5**.

1,2-Dichlorohexane (**8**).—The hydrogen fluoride catalyzed reaction of benzene with **8** gave a low conversion, but an almost quantitative yield, of 1-chloro-5-phenylhexane (**9**, Chart II). The conversion at 80° was only 5% after 5 hr.

Chart II



Treatment of **8** with 8.8 mole % aluminum chloride for 6 hr gave products **9**–**12** (weight per cent shown),

TABLE I

SPECTROSCOPIC EVIDENCE USED IN STRUCTURE DETERMINATIONS

Compd	Mass spectrum		Nmr spectrum, ppm[a-c]	Infrared spectrum, cm^{-1}	
	Parent	Other		Aromatic substitution	Other
2	196	119	1.31 (s), 3.31 (t), 1.65 (m)	761, 699	741, 649[d]
3	196	167, 133	1.2 (s), 3.2 (t), 0.65 (t), 1.6 (m), 2.1 (m)	760, 700	739, 650[d]
4	160	145	1.18 (s), 2.6 (t), 1.57 (m)	758, 727	1382, 1361[e]
5	162	92	0.85 (d), 2.50 (t), 1.3 (m)	747, 699	1385, 1366[e]
6	160	145	0.95 (s), 1.50 (t), 2.46 (s), 2.73 (t)	757, 739	1386, 1377[e]
7	236	221	1.3 (d), 1.8 (m), 4.0 (t)	760, 740	
				700	1389, 1365[e]
9	196	105	1.15 (d), 2.53 (t), 2.62 (m), 3.19 (t), 1.45 (m)	762, 701	732, 659[d]
10	160	131	0.94 (t), 2.62 (m), 1.75 (m)	750, 730	1380[f]
11	160	145	1.17 (d), 1.20 (d), 2.77 (m), 1.55 (m)	755	1372[f]
12	238	105	1.21 (d), 1.37 (m), 1.67 (m), 2.55 (m)		
14	168	105, 143	1.1 (d), 1.83 (q), 2.85 (h), 3.19 (t)	755, 699	716, 652[d]
15[g]	210	167	0.92 (t), 1.25 (m), 2.0 (q), 3.81 (t)		
16[g]	210	195	1.23 (d), 1.9 (m), 2.5 (m)		
17[g]	210	181	1.53 (s), 1.99 (q), 0.7 (t)		
18[g,h]	210	195	1.03 (d), 2.76 (m)		
19	208	193, 130	1.25 (d), 1.35 (d), 2.3 (m), 4.3 (m)	700, 750	
				760	1376[f]
21	196	181	1.2 (d), 2.7 (m)		
22	196	167	0.82 (t), 1.99 (q), 3.69 (t)		

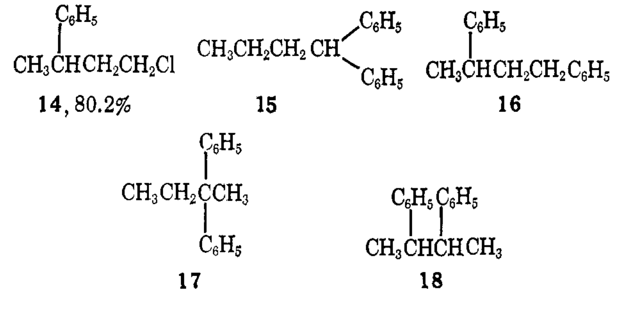
[a] Integrals were correct within experimental error for assigned structure. [b] Down field from internal tetramethylsilane: s = singlet, d = doublet, t = triplet, q = quartet, h = hextet, m = multiplet. [c] Aromatic band omitted. [d] Primary chloride. [e] *gem*-Dimethyl. [f] *n*-Methyl. [g] In good agreement with the nmr data of T. Inukai, *J. Org. Chem.*, **31,** 1124 (1966). [h] *meso* isomer, *dl* isomer has doublet at 1.17 ppm.

the balance being other diphenylhexanes or higher boiling materials.

This reaction was followed as a function of time by vapor phase chromatography (vpc). It was observed that **10** was formed early in the reaction (14.3% after 35 min and did not increase greatly. However, **11** gradually built up (8.0% after 35 min throughout the reaction at the expense of **9** which decreased after reaching a maximum of 53%).

1,2-Dichlorobutane (**13**).—The addition of 6.6 mole % aluminum chloride to **13** gave the products **14**–**18** (Chart III, weight per cent shown) after 3 hr.

CHART III



We were not able, on our Carbowax column, to separate all the isomers of diphenylbutane which constituted 14.3% of the product. Compound **16** was obtained pure by preparative vpc and the *meso* isomer of **18** was obtained crystalline (mp 125°). The nmr of **15** and **17** were both distinctive and the mass spectral cracking patterns of the mixture showed the gross features to be expected. There was also some spectral evidence for the 1,2 isomer, but this was not conclusive.

Under much more vigorous conditions, *i.e.*, 50% aluminum chloride at 40–80° for 3 hr, the products were isobutylbenzene (19.4%), *sec*-butylbenzene (19.4%), diphenylbutanes (7.3%), 1-phenyl-3-methylindan (**19**, 13.0%), and higher boiling materials (36.9%).

1,2-Dichloropropane (**20**).—In a previous study[1,2] 1,2-diphenylpropane[3] (**21**), was formed when benzene was alkylated with **20**. Under our conditions **21** was also the major product; however, 1,1-diphenylpropane (**22**) and cumene were also detected. In this experiment 5 mole % aluminum chloride was added to the benzene solution of **20**. Samples were taken at various times and analyzed. Even after 7 min an appreciable amount of the 1,1-diphenyl isomer was formed. Each sample was distilled to obtain the diphenylpropane fraction which was then analyzed by nmr. Table II shows the product distribution.

TABLE II

PRODUCT DISTRIBUTION DURING ALKYLATION OF 1,2-DICHLOROPROPANE

Time, min	Approx convn, %	Product distribution, wt %			
		Cumene	21	22	Higher boilers
7	30		83	17	
14	81	7	64	15	14
60	90	7	68	12	15
285	100	8	68	8	16

The diphenylpropane fraction (89% **21**, 11% **22**) was subjected to treatment with 10 mole % aluminum chloride activated with a trace of water at 25° for 5 hr. At the end of the reaction benzene (11.7%) and cumene (1.7%) were detected. The diphenylpropane fraction (70.9%) was collected by distillation and shown to be comprised solely of 1,2-diphenylpropane (**21**). The balance was higher boiling products.

1,3-Dichlorobutane (**23**).—It was shown that the major product of reaction of **23** with benzene catalyzed

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(1) R. D. Silva, *Compt. Rend.*, **89**, 606 (1879).

(2) R. D. Silva, *Jahresber. Fortscht. Chem.*, 379 (1879).

(3) Olah and Kuhn[4] have misquoted Silva's work.

by aluminum chloride was 1-chloro-3-phenylbutane (**14**). After 5 hr with 33% catalyst **14** constituted 70% of the product. No attempt was made to identify the other products.

Discussion

The formation of most of the products is best explained by assuming that the initial reaction is ionization of the secondary chloride. The destabilizing inductive effect of the adjacent primary chloride provides a strong driving force for rearrangement of the ion so formed.[4] The most stable carbonium ion in the systems studied is on the penultimate carbon, largely owing to the decrease in the inductive effect with distance and possibly to the greater hyperconjugative stabilization of methyl over methylene. Hence, the major initial product is the phenylalkyl chloride in which the phenyl group is on the penultimate carbon atom.

It has been pointed out[5] that Friedel–Crafts alkylation of most dihaloalkanes does not stop at the primary haloalkylated product owing to the greater reactivity of product over the reactant. In fact, secondary products are determined largely by the role of the phenyl group in assisting ionization of the primary chloride.[6,7]

The parallel behavior of anchimeric assistance in these systems and in the solvolysis studies of Heck and Winstein[8] is most striking. These workers showed that

$$\mathrm{Ar}_1\,3 \gg \mathrm{Ar}_1\,4 \ll \mathrm{Ar}_1\,5 \gg \mathrm{Ar}_1\,6 \text{ and } \mathrm{Ar}_2\,5 \ll \mathrm{Ar}_2\,6 \gg \mathrm{Ar}_2\,7$$

Our observations are perfectly consistent with this order. Furthermore, our observations are also consistent with the work of Khalaf and Roberts,[9] on closures of chlorophenylalkanes, which were published after the completion of this work.

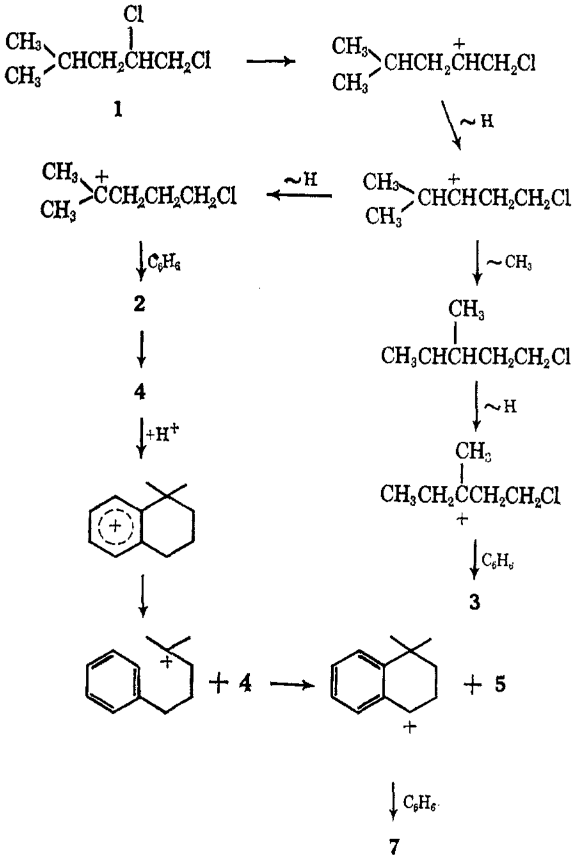
Other factors have influence in determining the products. In the 1,2-dichloro-4-methylpentane system there is a stage reached when either a hydride or a methyl shift may occur. The methyl shift leads ultimately to the formation of **3**. The alternative path leads to the formation of **2**.

Cyclialkylation of **2** to give **4** is a well-documented type of reaction.[9-11] However, the product has additional features which lead to a more complicated product distribution. Compound **4** appears to act quite readily both as a proton acceptor and as a hydride donor. This behavior is evidenced by the formation of **5** and **7**. Protonation of **4** and dealkylation to the tertiary ion occurs and in the presence of a hydride source this ion is reduced to **5**.[9] Abstraction of a benzylic hydride from **4** followed by alkylation on benzene leads to **7**. Schmerling and his co-workers[12] have discussed similar examples.

The reaction of 2-chloro-2-methyl-5-phenylpentane with aluminum chloride, recently studied by Khalaf and Roberts, is of much interest in the light of our work with **1**. 1,1-Dimethyltetralin (**4**) is the major product from both systems. These workers also agree, in qualitative fashion, that **4** is the major source of isohexylbenzene. Compound **4** is probably the only source of isohexylbenzene in our studies.

Products from ring contraction of **4** were not formed.[13] We offer no explanation for the formation of 2,2-dimethyltetralin (**6**). However, once formed, **6** would be stable under the reaction conditions. The over-all reaction scheme is depicted in Scheme I.

SCHEME I



~H = hydride ion migration

There are two 1-chlorophenylhexanes formed in the initial stages of the reaction of 1,2-dichlorohexane: the 4 and 5 isomers. The former reacts rapidly with Ar_1 6 or Ar_2 5 assisted ionization of the primary chloride to give **10**. The latter reacts more slowly with concurrent hydride transfer to yield **11**. Similar closures, with hydride transfers, of 2-chloro-6-methyl-6-phenylheptane and 1-chloro-5-phenylpentane were observed by Barclay, *et al.*[13] In the present study there was no evidence for benzsuberane structures.[14] The over-all scheme is shown in Scheme II.

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[4] E. Grunwald, *J. Am. Chem. Soc.*, **73**, 5458 (1951).

[5] G. E. Olah and S. J. Kuhn, *J. Org. Chem.*, **29**, 2317 (1964).

[6] F. A. Drahowzal, "Friedel–Crafts and Related Reactions," Vol. II, Part I, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 453.

[7] L. Schmerling, R. W. Welch, and J. P. Luvisi, *J. Am. Chem. Soc.*, **78**, 5406 (1956).

[8] R. Heck and S. Winstein, *ibid.*, **79**, 3105 (1957). $\mathrm{Ar}_x Y$ signifies aryl (Ar) participation, the aromatic ring position (*x*) involved, and the size (*Y*) of the ring formed in the transition state.

[9] A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 89 (1966).

[10] J. Von Braun and H. Deutsch, *Ber.*, **45**, 1267 (1912).

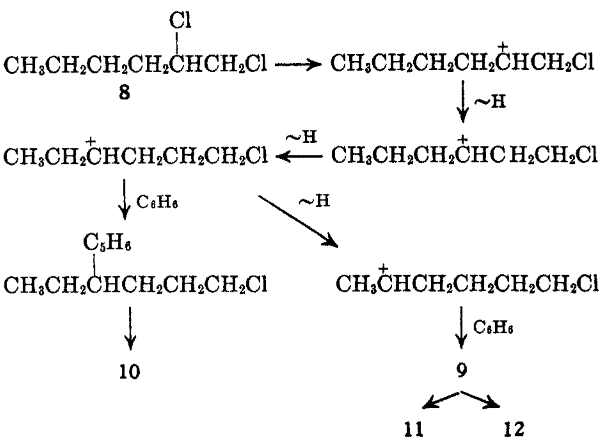
[11] G. Baddeley and R. Williamson, *J. Chem. Soc.*, 4647 (1956).

[12] L. Schmerling, R. W. Welch, and J. P. Luvisi, *J. Am. Chem. Soc.*, **79**, 2636 (1957).

[13] Unlike Barclay's rearrangement of octamethyloctahydroanthracene: L. R. C. Barclay, B. A. Ginn, and C. E. Milligan, *Can. J. Chem.*, **42**, 579 (1964).

[14] Baddeley and Williamson[11] have assigned a benzsuberane structure to the reaction product from 1-chloro-7-phenylheptane with aluminum chloride, but this could not be repeated.[13] Similarly, Cologne and Lazier [J. Cologne and A. Lagier, *Bull. Soc. Chim. France*, **16**, 27 (1949)] claimed a benzsuberane from 2,6-dichloro-2,6-dimethylheptane, but this was found to be in error.

SCHEME II



The study of the 1,2-dichlorobutane system represents a reinvestigation of the work of Schmerling and his co-workers[12] and of Dreisbach.[15] Schmerling incorrectly identified the major product as 1-chloro-2-phenylbutane.

The 1-chloro-3-phenylbutane (**14**) may undergo only the unfavored Ar_1 4 or Ar_2 5 participation in ionization of the primary chloride. Hence, **14** is quite stable under the reaction conditions. Similarly, the lack of phenyl participation explains why **3** builds up during benzene alkylation with 1,2-dichloro-4-methylpentane: 1-bromo-3-phenylpropane is a major initial product from benzene alkylation with 1-chloro-3-bromopropane[16] and 1-chloro-3-methyl-3-phenylbutane is formed in high yield from 1,3-dichloro-3-methylbutane.[7] This is also the reason for the relatively small proportion of diphenylbutanes observed by Schmerling[7] and by ourselves.

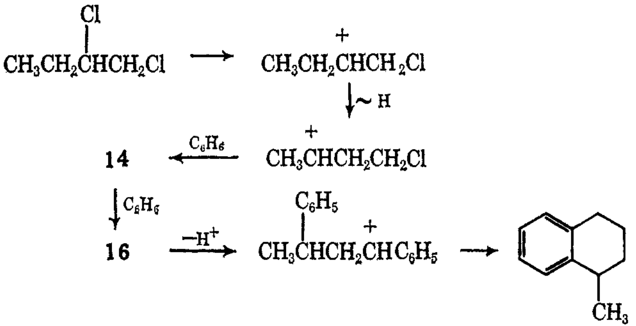
The same product (**14**) was observed to be the major initial product in the alkylation with 1,3-dichlorobutane. This was not detected by Sisido and Nozaki who previously studied this system.[17]

Under the more vigorous conditions[18] to which 1,2-dichlorobutane was subjected one would expect, in view of the work of Roberts, *et al.*,[19] that isobutylbenzene is formed by isomerization of *sec*-butylbenzene.

It was of interest that we detected 1-phenyl-3-methylindan and no 1-methylindan.[20] This would suggest that the former indan is not derived from the latter (by hydride abstraction followed by alkylation on benzene as observed for the previously described 1,1-dimethyltetralin). It seems that hydride abstraction from 1,3-diphenylbutane followed by cyclialkylation to give **19** directly is a more likely course.[21]

Speculation as to the mechanism of formation of the various diphenylbutanes is complicated by the recent observations that isomerization of diphenylbutanes occurs under quite mild conditions with aluminum chloride.[22,23] The over-all mechanism is shown in Scheme III.

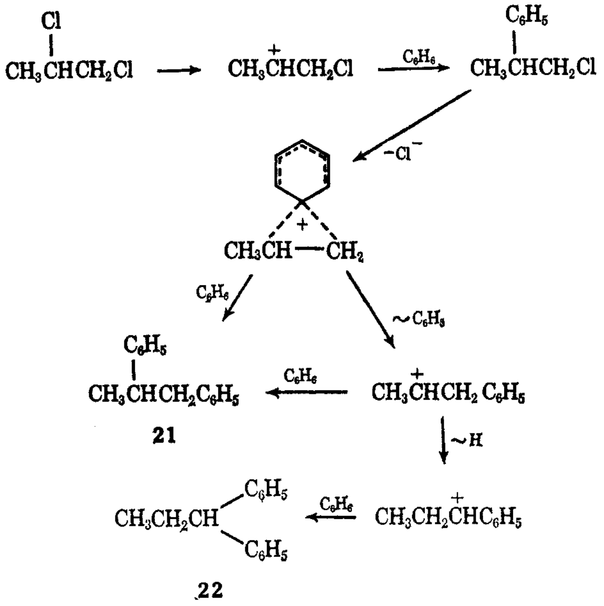
SCHEME III



19

The initially formed ion from 1,2-dichloropropane cannot rearrange readily. Alkylation on benzene would yield 1-chloro-2-phenylpropane. Under the reaction conditions this compound would be expected to react very rapidly with Ar_1 3 participation. Simple assisted ionization of the primary chloride followed by alkylation on benzene would give the 1,2-diphenylpropane (21).[24] However, rearrangement may accompany ionization as in the solvolysis of 2-phenylpropyl brosylate.[25] The resulting ion may then give the 1,2-diphenyl isomer or, after a favorable hydride shift,

SCHEME IV



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[15] R. R. Dreisbach, U. S. Patent 2,355,850 (1944).

[16] I. Tsukervanik and K. Y. Yatsimirskii, *J. Gen. Chem. USSR*, **10**, 1075 (1940).

[17] K. Sisido and H. Nozaki, *J. Am. Chem. Soc.*, **69**, 961 (1947).

[18] These conditions are those used by Sisido and Nozaki[17] on 1,3-dichlorobutane. Since the initial product in this system and the 1,2-dichlorobutane system is the same, one might suspect that isobutylbenzene and the indan, **19**, might also be found in the reaction of the 1,3-dichlorobutane system.

[19] R. M. Roberts, Y. W. Han, C. H. Schmid, and D. A. Davis, *J. Am. Chem. Soc.*, **81**, 640 (1959).

[20] Since no 1-methylindan was observed in this reaction our results tend to support Von Braun[6] and Khalaf and Roberts[9] who found that only traces of methylindan were formed from 1-chloro-3-phenylpropane rather than Baddeley and Williamson who claimed a 50% yield of indan.

[21] Abstraction of the tertiary benzylic hydrogen from 1,3-diphenylbutane probably occurs rapidly and reversibly. However, cyclialkylation to 1-phenyl-1-methylindan is probably readily reversed.

[22] A. A. Mohamed Khalaf, *Dissertation Abstr. XXVI.*, **No. 2**, 699 (1965).

[23] C. D. Nenitzescu and A. Glatz, *Acad. Rep. Popular Romine Studii Cercetari Chim.*, **7**, 505 (1959); *Chem. Abstr.*, **54**, 1954*bc* (1960).

[24] A similar example is the formation of 1,2-diphenyl-2-methylpropane from 1-chloro-2-methyl-3-phenylpropane: W. T. Somerville and P. E. Spoerin, *J. Am. Chem. Soc.*, **74**, 3803 (1952).

[25] S. Winstein and K. G. Schreiber, *ibid.*, **74**, 2171 (1952).

lead to the 1,1 isomer. Isomerization of **21** to **22** is probably not important. (See Scheme IV.)

Experimental Section

Hydrogen Fluoride Alkylations.—These reactions were run in an all-copper vessel with a water-cooled copper tube as condenser. The bomb was charged with the dichloride, 100–200 *M* excess of liquid hydrogen fluoride, and an 11.3 *M* excess of benzene. The vessel was pressured to 75 psig with dry HCl. The magnetically stirred vessel was heated. A Grove loader at the top of the condenser maintained the pressure at 100 psig.

At the end of the reaction the contents were cooled. The benzene layer was separated from the catalyst layer and washed and neutralized.

Aluminum Chloride Reactions.—Aluminum chloride was added in small portions to 1 *M* solutions of the dichlorides in benzene. At the end of the reaction the catalyst was decomposed by cold, dilute hydrochloric acid. Water, dilute sodium bicarbonate, and water were used to wash the benzene solution. The solvent was dried over magnesium sulfate and removed under reduced pressure. Vapor phase chromatographic analysis was performed on a 10 ft × 0.25 in. Carbowax on Chromosorb W column, temperature programmed from 100 to 230° at 6°/min.

Preparation and Thermal Rearrangement of 5,5-Dichloro-5H-dibenzo[*a,d*]cycloheptene

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Received May 20, 1966

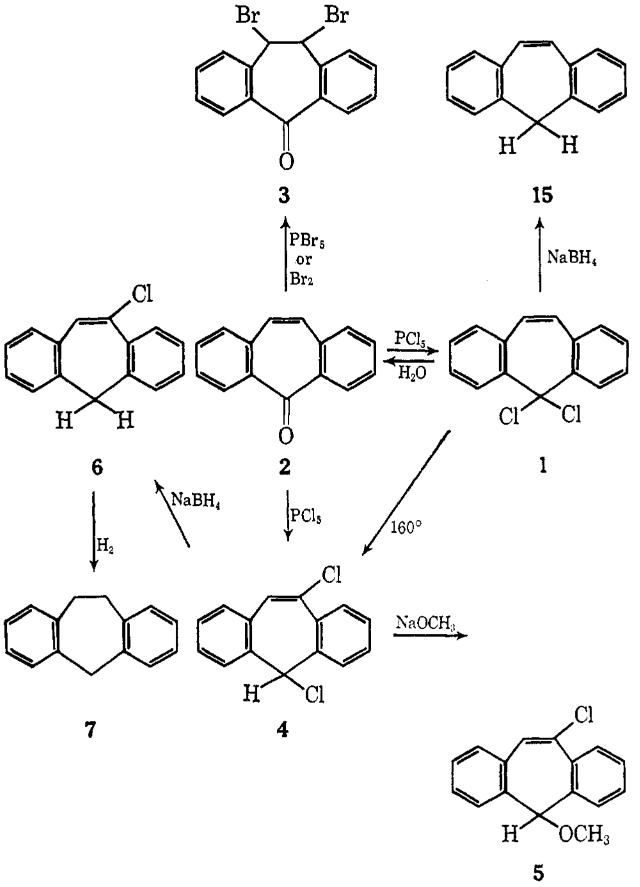
Reexamination of the method of preparation of the title compound has uncovered a thermal rearrangement which converted it into the 5,10-dichloro isomer. The structure of the isomer was established and a mechanism for the transformation is proposed. A convenient synthesis of the title compound has been found.

In connection with another problem, it was necessary to prepare 5,5-dichloro-5H-dibenzo[*a,d*]cycloheptene (**1**) or the dibromide. The route envisioned to the dihalide (Scheme I) was to treat ketone **2** with a phosphorus pentahalide. The only product obtained using phosphorus pentabromide was the bromine addition product (**3**) which was identical with material obtained by the use of bromine. Its formation is best explained by thermal dissociation of phosphorus pentabromide into bromine and phosphorus tribromide followed by addition of bromine to ketone **2**.

Treatment of ketone **2** with phosphorus pentachloride has been reported[1] to give dichloro compound **1**, but the product was used without characterization. The procedure was repeated, with molar equivalents of each reactant at 160°, instead of 2 molar equiv of halide per mole of ketone, and a dichloride was obtained. The product had only one reactive halogen atom, as demonstrated by its reaction with sodium methoxide and sodium borohydride; both products still contained one chlorine atom. The nmr spectrum of this dichloride showed one benzylic hydrogen atom (τ 3.91) with the remaining protons in the aromatic region. Structure **4** can be suggested as the most reasonable possibility from this information. The products from the reaction with sodium methoxide and sodium borohydride would be compounds **5** and **6**, respectively.

One of the chlorine atoms was most certainly at position 5, as indicated by its reactivity. The position of the other atom could be a vinyl or aromatic position. The nmr spectrum was not helpful because the olefinic proton(s) is(are) shifted into the aromatic region. This indicates that the olefinic proton is deshielded, and the presence of a vinyl chlorine atom would explain this effect. Since nuclear chlorination can occur,[2] it was necessary to establish the position of the second halogen atom.

Scheme I



Catalytic hydrogenation of chloride **6** provided evidence for the position of the second halogen atom (Scheme I). If the inert chlorine atom were on an aromatic carbon atom, it would not be affected by reduction of the double bond. If it were on an olefinic carbon atom, it would become a benzyl halide, upon

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[1] E. D. Bergmann, D. Ginsburg, Y. Hirshberg, M. Mayot, A. Pullman, and B. Pullman, *Bull. Soc. Chim. France*, **18**, 697 (1951).

[2] E. D. Bergmann and J. Szmuszkovicz, *Bull. Res. Council Israel*, **1**, 90 (1952).