was added dropwise (30 min) to a stirred solution of 18.0 g (0.047 mole) of lithium aluminum hydride in 300 ml of ether. The mixture was heated at reflux for 3 hr and cooled. A saturated solution of ammonium chloride was added dropwise, with stirring, until further reaction was no longer evident and then 10 ml excess added. The mixture was stirred for an additional 15 min; the precipitated white solid was filtered and washed with 150 ml of 1:1 methanol-ether. The combined filtrates were washed with four 50-ml portions of 10% hydrochloric acid. The acid washings were saturated with solid potassium hydroxide under a layer of ether and extracted with four 50-ml portions of ether. The combined ether extracts were dried, filtered; solvent was removed *in vacuo*. The residual oil was distilled to give 9.4 g (59%) of **3a**, bp 138–142° (0.7 mm), $n^{25}\text{D}$ 1.5761. Its infrared spectrum (CCl_4) showed a broad band at 2.96 μ (NH) and at least four bands in the 3.20–3.50-μ region (CH). On standing in air, **3a** decomposed to a viscous gum within 48 hr.

Compound **3a** gave a strong positive test for secondary amines with nickel chloride–carbon disulfide–ammonium hydroxide.[11]

Compound **3a**, in hydrochloric acid was treated with a 30% solution of chloroplatinic acid. The amber solid that precipitated was filtered and recrystallized from ethanol–ether acidified with hydrochloric acid to yield the chloroplatinate of **3a** as amber chunks, mp 193–194° dec.

Anal. Calcd for $C_{22}H_{28}N_2 \cdot PtCl_6 \cdot H_2O$: C, 35.40; H, 4.05. Found: C, 35.59; H, 4.33.

The phenylthiourea derivative of **3a** was obtained in the usual manner as a white solid, mp 168.5–169° after two recrystallizations from ethanol–petroleum ether (bp 60–75°).

Anal. Calcd for $C_{18}H_{18}N_2S \cdot H_2O$: C, 69.23; H, 6.45; N, 9.03. Found: C, 69.44; H, 6.50; N, 9.03.

7-Methylbenzo[*d*]-*cis*-7-azabicyclo[4.2.0]octane (3b).—A solution of 9.40 g of **3a**, 25 g of 38% formaldehyde, and 25 g of 90% formic acid was heated on a steam bath for 2 hr. The mixture was saturated with solid sodium hydroxide and extracted with ether. The extracts were dried, filtered, and evaporated. The residue was distilled to give 9.24 g (90%) of **3b**, bp 107–109° (0.6 mm), $n^{25}\text{D}$ 1.5550.

The 2-nitro-1,3-indandione salt of **3b** was obtained in the usual manner,[31] mp 164–166° dec.

Anal. Calcd for $C_{21}H_{20}N_2O_4 \cdot 0.5H_2O$: C, 67.39; H, 5.67. Found: C, 67.39; H, 5.73.

The Reaction of Cyclopropyl Ketones with Phosphorus Pentachloride[1]

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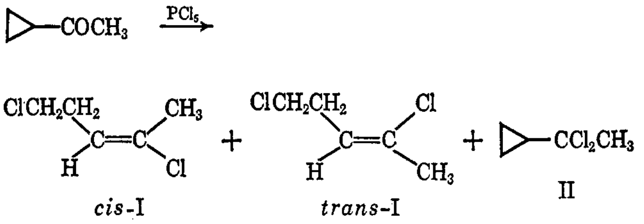
The reactions of a number of cyclopropyl ketones with phosphorus pentachloride have been studied. When run in carbon tetrachloride, the ketonic oxygen of phenyl 1-phenylcyclopropyl ketone is replaced by two chlorines. However, when run in methylene chloride, the cyclopropyl ring of all of the ketones studied is opened and 1,4-dichloro-1-butenes are formed. These facts are explained by nonionic mechanisms utilizing the observation that phosphorus pentachloride is dimeric in carbon tetrachloride and monomeric in methylene chloride.

In an earlier publication[3] the reactions of ketones with phosphorus pentachloride were explained in terms of a chlorocarbonium ion mechanism. The work described herein was undertaken to obtain more information about the reaction mechanism by studies on the reaction of phosphorus pentachloride with ketones containing a cyclopropyl group attached to the ketonic carbonyl group. The result of these studies makes it unlikely that a chlorocarbonium ion is involved for reasons stated below. This conclusion is in agreement with that reached in another study on the reactions of 4-phenyl-2-butanone and 5-phenyl-2-pentanone with phosphorus pentachloride.[4]

The reaction of methyl cyclopropyl ketone with phosphorus pentachloride has been reported to yield 2,5-dichloro-2-pentene[5] (I) and a mixture of I and 1,1-dichloroethyl cyclopropane (II).[6] No mention of the stereochemistry of the 2,5-dichloro-2-pentene produced was made.[5,6] We have found that in methylene chloride at 0° approximately an 80% yield of 70% *cis*- and 30% *trans*-2,5-dichloro-2-pentene is obtained. This ratio was remarkably constant over reaction periods of from 18 to 72 hr. When the reaction was carried out in refluxing carbon tetrachloride for 2 hr, a mixture of unreacted ketone (23%), *cis*-I (26%), *trans*-I (15%), and 36% of a compound believed to be 1,1-dichloroethylcyclopropane (II) (see Experimental Section) was obtained. On standing for 1 week at room temperature, any II had rearranged to a mixture of *cis*-I and *trans*-I. The ratio of *cis*-I to *trans*-I in this mixture was the same as that in reactions run in methylene chloride. The significance of the difference in products obtained depending on whether methylene chloride or carbon tetrachloride was the solvent will be discussed later in this paper.



On reaction of cyclopropyl phenyl ketone with phosphorus pentachloride in methylene chloride at room temperature for 3 days, or in carbon tetrachloride at reflux for 1 day, there was obtained a mixture of the isomers of 1,4-dichloro-1-phenyl-1-butene (III) in 86 and 95% yield, respectively. *trans*-III (90–98%) was formed in preference to *cis*-III (10–2%) in different runs.

The reaction of cyclopropyl *m*-nitrophenyl ketone with phosphorus pentachloride in methylene chloride was much slower, as after 13 days at room temperature

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[1] The material in this paper was taken from the Ph.D. Thesis presented by G. Kaugars to The Ohio State University, 1964. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR-569-64.

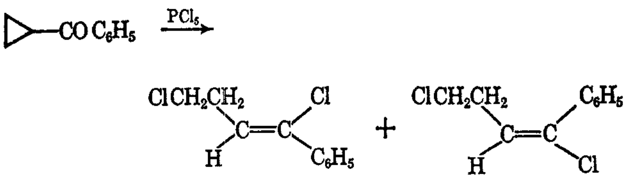
[2] Upjohn Fellow, 1960–1961; Lubrizol Fellow, 1962–1963.

[3] M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 4300 (1959).

[4] M. S. Newman, G. Fraenkel, and W. N. Kirn, *J. Org. Chem.*, **28**, 1851 (1963).

[5] I. A. Diyakonov, *Zh. Obshch. Khim.*, **10**, 414 (1940); *Chem. Abstr.*, **34**, 7861 (1940).

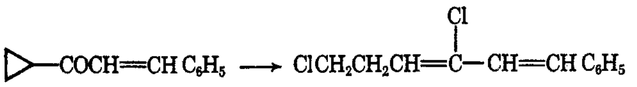
[6] Y. M. Slobodin and I. N. Shokhor [*Zh. Obshch. Khim.*, **22**, 195 (1952); *Chem. Abstr.*, **46**, 10122 (1952)] did not actually isolate II but assumed its presence because of the formation of cyclopropylacetylene on treatment of the reaction mixture with base.



trans-III *cis*-III

15% of unreacted ketone was present. The only isomer of 1,4-dichloro-1-(*m*-nitrophenyl)-1-butene obtained (in 74% yield) was assumed to be the *trans* isomer, but no proof of structure was carried out.

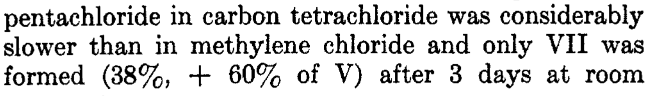
The reaction of cyclopropyl styryl ketone with phosphorus pentachloride in carbon tetrachloride at reflux led to formation of 3,6-dichloro-1-phenyl-1,3-hexadiene (IV), of unknown stereochemical structure, in 63% yield. The structure was determined by examination of the nmr spectrum and that of its Diels–Alder adduct with maleic anhydride (see Experimental Section). The reaction of this ketone in methylene chloride led to such labile products that no study of them was made.



IV

The reaction of only one aldehyde containing a cyclopropyl group was studied. 1-Phenylcyclopropylcarboxaldehyde afforded dichloro-1-phenylcyclopropylmethane in about 75% yield in both carbon tetrachloride and methylene chloride.

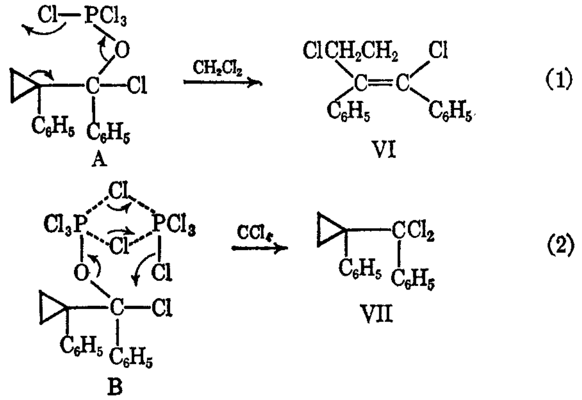
The reactions which afforded the most information about the mechanism of reaction of phosphorus pentachloride with cyclopropyl ketones were those involving phenyl 1-phenylcyclopropyl ketone (V). Two products were obtained, *cis*-1,4-dichloro-1,2-diphenyl-1-butene (VI) and phenyl(1-phenylcyclopropyl)dichloromethane (VII). When the reaction was carried out in methylene chloride solution for from 3 to 5 days at room temperature, the only chlorinated product obtained was VI.[7] When the reaction was carried out in carbon tetrachloride for 1.5 hr at reflux, there was obtained 70% of VII and 26% of VI. At room temperature the rate of reaction of ketone V with phosphorus pentachloride in carbon tetrachloride was considerably slower than in methylene chloride and only VII was formed (38%, + 60% of V) after 3 days at room temperature.



To cast further light on this subject, the stability of VII was studied. When VII was held at reflux in carbon tetrachloride for 2 hr, it was recovered unchanged, *with or without added phosphorus oxychloride.* However, in methylene chloride VII rearranged to VI on standing at room temperature for 4 days in the presence of 0.7 equiv of phosphorus oxychloride but was stable in its absence. Dichloride VII was stable on heating to 80° for 2 days in a sealed tube. In one case, VII rearranged completely to VI on chromatography over alumina in benzene. On standing in methylene chloride containing dry hydrogen chloride, VII rearranged to the extent of about 50% to VI in 3 days at room temperature. Finally, when VII was treated with ethanol, aqueous dioxane, or acetic acid it was readily converted into VI in high yields.

In order to obtain information about the reaction of V in methylene chloride, aliquots of a typical reaction mixture were removed after short reaction times and analyzed for the amount of ketone remaining and the amount of VII that was present. This was done in order to see whether VI was formed directly from V or *via* conversion of V to VII and then rearrangement of VII to VI. The results of these studies indicated that most of the VI formed was formed directly from V but that some might have been formed by the route through VII.

From the above facts we believe that the primary product of the reaction of V with phosphorus pentachloride in methylene chloride is the 1,4-dichloride VI, whereas in carbon tetrachloride the product is the 1,1-dichloride VII. It could be argued that in both solvents the 1,1-dichloride VII is the primary product and that in methylene chloride VII isomerizes to VI because of the $POCl_3$ formed during the reaction. There are two reasons why we believe that the primary products are different in the two solvents. The first is that, when the products of the reaction in methylene chloride were examined after short periods of time, the 1,4-chloride VI was the main product. Because of the slow rate of rearrangement of VII to VI in methylene chloride containing phosphorus oxychloride, we think that if VII were the primary product more would have been found after short reaction periods. The second reason stems from the fact that phosphorus pentachloride has been shown to exist mainly as dimer in carbon tetrachloride and monomer in methylene chloride.[8] This fact permits a rationalization of the formation of VI and VII in the two solvents in question as shown in eq 1 and 2.



We believe that intermediate A is formed from monomeric phosphorus pentachloride in methylene chloride and that A goes directly to VI *via* a six-centered transition state as shown in eq 1. In carbon tetrachloride dimeric phosphorus pentachloride reacts with V to form intermediate B (the bridging chlorines are prob-

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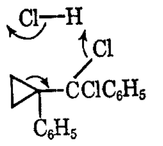
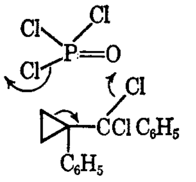
[7] In one case, however, a 28% yield of VII was present in addition to 57% of VI. In general the reproducibility of results with great accuracy was not possible probably because of the heterogeneous (owing to insolubility of PCl_5) nature of the reactions. In order to run any kinetic studies much more dilute solutions would have been required.

[8] V. P. Petro, J. Howatson, and S. G. Shore, *J. Am. Chem. Soc.*, in press.

ably in front of and behind the plane of the paper in B) which collapses to VII, POCl$_3$, and PCl$_5$ monomer as shown in eq 2. Intermediates A and B are probably formed from the ketone and phosphorus halide by attack of the carbonyl oxygen on phosphorus to displace a chloride ion which subsequently (or simultaneously) adds to the carbon of the carbonyl group. Alternately, intermediates A and B could be formed by the route drawn in eq 2 and 3 in ref 3.

The rearrangement of VII to VI catalyzed by phosphorus oxychloride and hydrogen chloride in methylene chloride can be explained by similar cyclic mechanisms as shown below. It is difficult, however, to see why the change occurs in methylene chloride but not in carbon tetrachloride.[9]

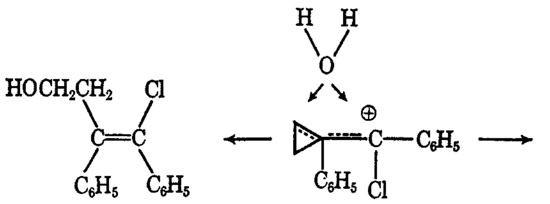




As a result of the above discussion, we do not think that free chlorocarbonium ions, as discussed previously,[3] are involved in the reactions of the cyclopropyl ketones mentioned with phosphorus pentachloride, since alternate explanations appear more reasonable.

A puzzling feature of the mechanism of formation of dichloride VI pictured in eq 1 is the stereospecificity. The isomer shown (with *cis*-phenyl groups) is formed exclusively. Examination of molecular models reveals no reason why this stereoisomer should predominate. The rearrangement of cyclopropyl phenyl ketone is also quite stereospecific and in the same sense as in the rearrangement of V. In both cases the group attached to that cyclopropyl carbon which is attached to the ketonic function ends up *cis* to the phenyl group, *e.g.*, hydrogen in the cyclopropyl phenyl ketone case and phenyl in the case of V.

The rearrangements of VII to VI in ethanol, aqueous dioxane, and acetic acid without appreciable formation of oxygenated products indicates that if ionization occurs an extremely tight ion pair is involved. When an ether solution of VII was treated with aqueous alcoholic silver nitrate, an immediate precipitate of silver chloride appeared. The crude product showed both carbonyl and hydroxyl absorption in the infrared. After treatment with thionyl chloride, vpc analysis showed that 1-phenylcyclopropyl phenyl ketone (V, 34%) and acyclic dichloride (VI, 59%) were present. The dichloride undoubtedly arose from reaction of thionyl chloride with 4-chloro-3,4-diphenyl-3-butenol, although the latter was not isolated and identified since the hydroxyl absorption in the infrared and conversion to the known dichloride, VI, by thionyl chloride were considered as adequate proof of its presence. In the above silver nitrate reaction, the chlorocarbonium ion is undoubtedly involved, as shown in eq 3.



(3)

One feature of interest in connection with the synthesis of the required 1-phenylcyclopropyl cyanide by alkylation of phenylacetonitrile with ethylene dibromide and sodium amide in ether lies in the reaction temperature. When the reaction is carried out at 30–35°, a yield of 44% is obtained.[10] However, when the reaction temperature was maintained in the −40 to −20° range, the yield was 71%. We explain the improvement by assuming that the ratio of the rate of displacement of bromide ion to rate of proton abstraction (leading to elimination of bromide ion) for the anion of phenylacetonitrile is greater at the lower temperature than at the higher. A similar argument has been invoked to explain improved alkylation of phenylmethylacetonitrile with γ-bromobutyronitrile at low temperatures.[11]

The structure of the major component of the reaction of cyclopropyl phenyl ketone with phosphorus pentachloride was assigned the *trans*-III structure on the following bases: elemental analyses, spectral analyses, hydrolysis to γ-chlorobutyrophenone, conversion of γ-chlorobutyrophenone to a mixture of *cis*- and *trans*-III by treatment with phosphorus pentachloride, and study of the products obtained by reaction of III with magnesium in ether.[12] The absence of absorption in the 1.624–1.650-μ region of the near-infrared spectrum of III showed that no cyclopropyl ring was present.[13] The nmr spectrum showed the following: 5 H, multiplet with maximum at τ 2.78 (-C$_6$H$_5$); 1 H, triplet centered at τ 4.02 (=CH); 2 H, triplet centered at τ 6.60 (-CH$_2$Cl); 2 H, quartet centered at τ 7.37 (—CH$_2$—$\overset{|}{\text{C}}$=). The τ value of 4.02 for the vinylic hydrogen indicates a *trans*-III structure by comparison with the work of Stevens.[14]

When butyrophenone was treated with phosphorus pentachloride in carbon tetrachloride, an 82% yield of *cis*- and *trans*-1-chloro-1-phenyl-1-butene was obtained. Vpc analysis showed this to be a 29:71 mixture of

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(9) All of the above arguments concerning mechanism should be regarded merely as guides to further research, as extremely subtle effects are undoubtedly involved. The difference in dielectric constant for methylene chloride (8.7) and carbon tetrachloride (2.2) [S. O. Morgan and H. H. Lowry, *J. Chem. Phys.*, **34**, 24131 (1930)] is undoubtedly of importance, as suggested by a referee. However, in one experiment, the reaction of V with PCl$_5$ was slightly slower in nitromethane than in methylene chloride. This points up the complexity of these reactions.

(10) E. C. Knowles and J. B. Cloke [*J. Am. Chem. Soc.*, **54**, 2028 (1932)] obtained a 44% yield using 1-bromo-2-chloroethane.

(11) M. S. Newman and R. D. Closson, *ibid.*, **66**, 1553 (1944).

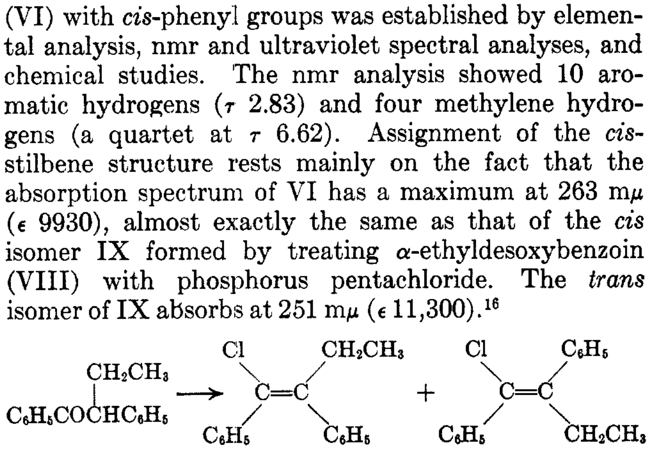
(12) This work is reported in another article: M. S. Newman and G. Kaugars, *J. Org. Chem.*, **30**, 3295 (1965). The products produced were 1-phenylcyclobutene, *trans*-1-chloro-1-phenyl-1-butene, *cis*- and *trans*-1-phenyl-1-butene, and 1-phenyl-1,3-butadiene.

(13) W. H. Washburn and M. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958). P. G. Gassman [*Chem. Ind.* (London), 740 (1962)] has found that each of 16 compounds containing cyclopropyl rings absorb in the 1.624–1.650-μ region.

(14) In a private communication, Dr. T. E. Stevens, Rohm and Haas Co., Huntsville, Ala., informed us that on treatment of propiophenone with phosphorus pentachloride in benzene at reflux a mixture of the two isomers of 1-chloro-1-phenyl-1-propene was obtained in which the *trans* isomer (phenyl and methyl groups *trans*) was largely present (*ca.* 10:1). The nmr proton signal of the vinylic hydrogen of the major isomer occurred at a lower τ value (quartet centered at τ 3.87) than that of the vinylic hydrogen of the minor isomer (quartet centered at τ 4.02). The minor isomer was assigned the *cis* structure (phenyl and methyl *cis*) from the fact that treatment of *trans*-1-phenyl-1-propene with chlorine to form a dichloride followed by elimination of 1 mole of hydrogen chloride yielded the minor isomer. Such a treatment is involved in the conversion of *trans* to *cis* olefins as described by M. C. Hoff, K. W. Greenlee, and C. E. Boord [*J. Am. Chem. Soc.*, **73**, 3329 (1951)] and would be expected to lead to the isomer in which the phenyl and methyl groups are *cis*.

cis:trans isomers, whereas nmr analysis showed it to be 24:76 *cis:trans*. The vinyl proton signal of the *cis* isomer occurred at τ 4.18, whereas that of the *trans* isomer was at τ 4.04, in agreement with the fact that the τ value of the vinylic hydrogen in the corresponding *cis*- and *trans*-1-chloro-1-phenyl-1-propenes occurred at a higher τ value for the *cis* isomer.[12,14] Furthermore, when the sample of 1-chloro-1-phenyl-1-butene obtained after treating the major isomer of III with magnesium and treatment of the resulting Grignard reagent with water was examined by nmr analysis, the vinylic proton absorbed at τ 3.98.[15] Since conversion of III to a monomagnesium derivative and hydrolysis thereof cannot affect the stereochemistry at the vinyl group, further support for the *trans* structure for the major isomer was at hand.[12]

The structure of 1,4-dichloro-1,2-diphenyl-1-butene (VI) with *cis*-phenyl groups was established by elemental analysis, nmr and ultraviolet spectral analyses, and chemical studies. The nmr analysis showed 10 aromatic hydrogens (τ 2.83) and four methylene hydrogens (a quartet at τ 6.62). Assignment of the *cis*-stilbene structure rests mainly on the fact that the absorption spectrum of VI has a maximum at 263 mμ (ϵ 9930), almost exactly the same as that of the *cis* isomer IX formed by treating α-ethyldesoxybenzoin (VIII) with phosphorus pentachloride. The *trans* isomer of IX absorbs at 251 mμ (ϵ 11,300).[16]



VIII *cis*-IX *trans*-IX

The assignment of the *cis* structure to that isomer of IX which absorbs at 263 mμ is strengthened by nmr analysis. The allylic methylene hydrogens of *cis*-IX and *trans*-IX fall at τ 7.23 and 7.65, respectively. Suzuki has shown that the allylic hydrogens in *cis*-dimethylstilbene (τ 7.86) and *cis*-diethylstilbene (τ 7.43) fall at lower values than those of the *trans* analogs (8.26 and 7.75).[17]

Experimental Section[18]

***cis*- and *trans*-2,5-Dichloro-2-pentene (I).**—To 41.7 g of phosphorus pentachloride in 80 ml of methylene chloride at 0° was added 16.8 g of cyclopropyl methyl ketone,[19] bp 109–112°, prepared by the reaction of cyclopropyl cyanide with methylmagnesium bromide in 49% yield. After standing at 0–5° for 2 days, the mixture was treated with ice water and worked up as usual[18] to yield 21.9 g (79%) of crude I. Gas chromatography showed the product to consist of 4% starting ketone, 68% *cis*-I, and 28% *trans*-I in this order regarding retention time. Separation on a 6 ft × $^3/_8$ in. Carbowax 4000 column on a F & M Model 500 gas chromatograph yielded pure *cis*-I [nmr signals at τ 7.87 (3 H), 7.39 (2 H), 6.52 (2 H), 4.47 (1 H); *J* for methyl-vinyl H *trans* coupling was -1.27 cps] and pure *trans*-I [τ 7.91 (3 H), 7.51 (2 H), 6.52 (2 H), 4.51 (1 H); *J* for methyl–vinyl H *cis* coupling was -1.78 cps].

Anal. Calcd for $C_5H_8Cl_2$: C, 43.2; H, 5.8; Cl, 51.0. Found (for *cis*-I): C, 44.5, 44.3; H, 5.6, 5.5; Cl, 48.8, 49.0. Found (for *trans*-I): C, 43.4; H, 5.9; Cl, 50.8.

The sample of *cis*-I was slightly contaminated with Carbowax which was eluted from the column.

When the reaction of cyclopropyl methyl ketone was carried out with phosphorus pentachloride in carbon tetrachloride at reflux for 2 hr, a similar work-up yielded a mixture of 23% of starting ketone, 26% of *cis*-I, 15% of *trans*-I, and 36% of II. After standing 1 week at room temperature all II had disappeared, and the ratio of *cis*-I:*trans*-I was 69:31.

***cis*- and *trans*-1,4-Dichloro-1-phenyl-1-butene (III). A.**—To 50.8 g of phosphorus pentachloride in 40 ml of methylene chloride was added 32.3 g of cyclopropyl phenyl ketone[20] at 0°. After standing at room temperature for 2 days with occasional shaking, the usual work-up[18] afforded 38.2 g (86%) of *cis*- and *trans*-III, bp 97–102° (1 mm). Gas chromatography of different runs showed this material to be mainly (90–98%) *trans*-III. An analytical sample boiled at 106–107° (1.5 mm): nmr signals, γ 7.37 (2 H), 6.60 (2 H), 4.02 (1 H), 2.78 (5 H).

Anal. Calcd for $C_{10}H_{10}Cl_2$: C, 59.7; H, 5.0; Cl, 35.3. Found: C, 59.5; H, 5.0; Cl, 35.5.

B.—To 125.0 g of phosphorus pentachloride in 400 ml of carbon tetrachloride was added 73.1 g of cyclopropyl phenyl ketone. After refluxing for 24 hr, 300 ml of solvent was distilled and the remaining mixture was worked up essentially as in A to yield 95.6 g (95%) of III, bp 91–94° (1 mm). Glpc showed this to be a 11% *cis*- and 89% *trans*-III mixture. In other similar runs the proportion of *trans*-III was greater.

C.—A solution of 22.9 g of phosphorus pentachloride and 18.3 g of γ-chlorobutyrophenone[21] in 50 ml of methylene chloride was allowed to stand at room temperature for 1 day with occasional shaking. After a work-up similar to that in A, distillation afforded 18.7 g (93%) of III which glpc analysis showed to be 95% *trans*-III.

After treatment of 3 drops of a mixture of *cis*- and *trans*-III with 2 ml of concentrated sulfuric acid for 30 min, an ether extract of the diluted reaction mixture was treated with 2,4-DNPH (2,4-dinitrophenylhydrazine) reagent. The resulting solid on recrystallization from ethanol yielded a 2,4-DPNH derivative, mp 164–166°, identical with that prepared from γ-chlorobutyrophenone.[22]

1,4-Dichloro-1-(*m*-nitrophenyl)-1-butene.—A solution of 3.66 g of phosphorus pentachloride and 2.81 g of cyclopropyl *m*-nitrophenyl ketone in 10 ml of methylene chloride was allowed to stand at room temperature for 13 days. The usual work-up afforded 3.47 g of crude product which was purified by chromatography over Woelm grade I alumina to yield 2.68 g (74%) of 1,4-dichloro-1-(*m*-nitrophenyl)-1-butene, mp 46–47°, and 0.43 g (15%) of starting ketone. Recrystallization from ethanol yielded the analytical sample: mp 48–49°; nmr signals, τ 7.13 (2 H), 6.32 (2 H), 3.60 (1 H), 1.67–2.63 (4 H).

Anal. Calcd for $C_{10}H_9Cl_2NO_2$: C, 48.8; H, 3.7; Cl, 28.8. Found: C, 48.8; H, 3.7; Cl, 28.8.

Cyclopropyl *m*-Nitrophenyl Ketone.—To a solution of 25 ml of fuming nitric acid in 25 ml of concentrated sulfuric acid was added 12.69 g of cyclopropyl phenyl ketone at 0–5° during 50 min. After 1 hr at 0° the mixture was poured on ice. After isolation by the usual procedure, 7.76 g (47%) of desired ketone,[23] mp 69–72°, was obtained. The analytical sample, mp 72.5–73.5°, was obtained after recrystallization from Skellysolve B (petroleum ether, bp 65–70°) and from methanol. The ketone absorbed at 1.627 μ in the near-infrared spectrum.[13]

Anal. Calcd for $C_{10}H_9NO_3$: C, 62.8; H, 4.7; N, 7.3. Found: C, 62.9; H, 4.9; N, 7.4.

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[15] The shift of 0.06 ppm in all τ values in this determination was caused by a concentration effect. See L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, p 119.

[16] H. Suzuki [*Bull. Chem. Soc. Japan*, **33**, 379 (1960)] shows that dimethyl- and diethyl-*cis*-stilbene absorb at longer wavelengths, 252 and 244 mμ, and with lower ϵ values, 8780 and 7740, than the *trans* analogs, 243.5 and 237.5 mμ (ϵ 12,260 and 11,020, respectively).

[17] These values are calculated from data in ref 16.

[18] All microanalyses were by Galbraith Laboratories, Knoxville, Tenn. All melting points were uncorrected. The methylene chloride used was distilled from phosphorus pentoxide and stored over anhydrous magnesium sulfate. The term "worked up in the usual way" means that the organic products were taken up in ether or ether–benzene. This solution was washed with dilute acid and/or base and with saturated sodium chloride solution, filtered through anhydrous magnesium sulfate, and stripped of solvent by distillation or on a rotary evaporator. The residue was then treated as indicated in the text.

[19] P. Bruylants [*Bull. Soc. Chim. Belges*, **36**, 519 (1927)] reports a boiling point of 111.6–111.8° at 752 mm.

[20] W. J. Close, *J. Am. Chem. Soc.*, **79**, 1455 (1957).

[21] Purchased from the Aldrich Chemical Co. It was also prepared as described by N. Kishner, *Zh. Obshch. Khim.*, **43**, 1163 (1911).

[22] C. F. H. Allen and R. V. V. Nicholls [*J. Am. Chem. Soc.*, **56**, 1409 (1934)] report a melting point of 167°.

[23] In ref 21, a melting point of 77° is recorded for this ketone.

3,6-Dichloro-1-phenyl-1,3-hexadiene (IV).—To a suspension of 22.9 g of phosphorus pentachloride in 75 ml of carbon tetrachloride at reflux was added a warm solution 17.2 g of cyclopropyl styryl ketone[24] in 50 ml of carbon tetrachloride. After 4 hr at reflux, 110 ml of solvent was distilled and the cooled remainder worked up as usual to yield 14.3 g (62%) of IV: bp 128–131° (<1 mm); nmr, τ 7.28 (2 H), 6.52 (2 H), 4.18 (1 H), 3.14 (2 H), 2.66 (5 H).

This product, 5.0 g, was immediately added to 2.0 g of maleic anhydride and the mixture was left for 5 days at room temperature by which time it was mainly crystalline. Recrystallization from Skellysolve B-benzene afforded 5.3 g (80%) of adduct, mp 150–152°. Further recrystallizations from benzene did not raise the melting point. Nmr (in hexadeuteriodimethyl sulfoxide) signals were at τ 7.52 (2 H), 6.95 (1 H), 6.14 (5 H), 3.50 (1 H), and 2.65 (5 H). These values are consistent with a structure of 3-(β-chloroethyl)-4-chloro-6-phenyl-1,2,3,6-tetrahydrophthalic anhydride, but no attempt to assign stereochemistry was made.

Anal. Calcd for $C_{16}H_{14}Cl_2O_3$: C, 59.1; H, 4.3; Cl, 21.8. Found: C, 59.0; H, 4.4; Cl, 21.6.

Dichloro-1-phenylcyclopropylmethane.—To 12.5 g of phosphorus pentachloride was added a solution of 7.3 g of 1-phenylcyclopropylcarboxaldehyde, bp 89–93° (5 mm), prepared in 59% yield essentially as described.[25] The reaction mixture refluxed spontaneously for a few minutes and was allowed to stand at room temperature for 17 hr. After the usual work-up, distillation afforded 7.5 g (74%) of dichloro-1-phenylcyclopropylmethane, bp 77–79° (1 mm). Sublimation under vacuum yielded the analytical sample, mp 41.5–42.5°, which absorbed at 1.634 μ in the infrared spectrum.[13] The nmr spectrum had singlets at τ 9.05 (4 H) and 4.73 (1 H) and a multiplet at τ 2.50–2.90 (5 H).

Anal. Calcd for $C_{10}H_{10}Cl_2$: C, 59.7; H, 5.0; Cl, 35.3. Found: C, 59.6; H, 4.8; Cl, 35.4.

A comparable yield of identical product was obtained when the reaction was carried out in carbon tetrachloride at reflux for 19 hr.

1-Phenylcyclopropyl Cyanide.—Several experiments on the alkylation of phenylacetonitrile with ethylene dibromide[10] were run. The best yield (71%) of 1-phenylcyclopropylcyanide, bp 85–88° at 0.6 mm (97% pure by vpc) was obtained by allowing 0.4 mole of phenylacetonitrile in 250 ml of dry ether to react with 0.8 mole of sodium amide at reflux for 5 hr. The mixture was then cooled in Dry Ice–acetone, 0.4 mole of ethylene dibromide was added, and the temperature was allowed to rise to the −40 to −20° range. The evolution of ammonia was vigorous in this range but could be controlled by external cooling. After the evolution of ammonia was essentially complete, the reaction mixture was warmed to reflux for 1 hr and then worked up as usual.

1-Phenylcyclopropyl Phenyl Ketone (V).—This ketone was prepared in 53% yield from the above nitrile and phenylmagnesium bromide as described.[26] An alternate experiment involved the alkylation of desoxybenzoin, as follows. To the 0–5° solution obtained by stirring 8.2 g of sodium amide and 150 ml of pure dimethyl sulfoxide at room temperature for 15 min was added 20.0 g of desoxybenzoin. After stirring for 30 min at 0–5°, 14.8 g of 1-bromo-2-chloroethane was added during 2 hr. After the usual work-up a 45% yield of V was obtained. In view of the superior results obtained at low temperatures in the preparation of 1-phenylcyclopropyl cyanide above described, an improved synthesis of V could probably be effected were the reaction carried out at lower temperatures.

***cis*-1,4-Dichloro-1,2-diphenyl-1-butene (VI).**—In a typical experiment 37.9 g of V was added to 42.5 g of phosphorus pentachloride in 100 ml of methylene chloride. The mixture was allowed to stand at room temperature for 5 days with occasional shaking. Most of the solvent was then removed on a rotary evaporator and the residue was treated with ice. After the usual work-up crystallization from Skellysolve B yielded 36.8 g (78%) of VI, mp 79–81°. Chromatography of the oily residue over Woelm alumina yielded a further 3.7 g (8%) of VI. Some of this VI may have been produced during chromatography from any VII which might have been present. The near-infrared spectrum showed no absorption in the cyclopropane region.[13]

Anal. Calcd for $C_{16}H_{14}Cl_2$: C, 69.3; H, 5.1; Cl, 25.6. Found: C, 69.5; H, 5.1; Cl, 25.5.

Phenyl(1-phenylcyclopropyl)dichloromethane (VII).—A mixture of 22.9 g of phosphorus pentachloride, 22.2 g of 1-phenylcyclopropyl phenyl ketone, and 125 ml of carbon tetrachloride was held at reflux for 4 hr. The solvent was removed on a rotary evaporator, and the residue was worked up as usual. Recrystallization from Skellysolve B afforded 17.6 g (64%) of VII, mp 122–126°, and 7.7 g (28%) of VI, mp 77–80°. The analytical sample of VII, mp 124.5–126.0°, had a band at 1.63 μ,[13] and the nmr spectrum showed multiplets centered at τ 8.91 (2 H), 8.32 (2 H), and 3.04 (10 H).

Anal. Calcd for $C_{16}H_{14}Cl_2$: C, 69.3; H, 5.1; Cl, 25.6. Found: C, 69.3; H, 5.2; Cl, 25.5.

A mixture of 1.00 g of VII in 25 ml of absolute alcohol was refluxed until solution was effected. After 2 days at room temperature, 0.80 g of VI was obtained. Similarly, after a solution of 1.00 g of VII in 30 ml of dioxane and 3 ml of water had stood for 2 days, a 75% yield of VII was obtained. A mixture of 0.55 g of VII, 0.21 g of phosphorus pentachloride, 5 drops of phosphorus oxychloride, and 2 ml of methylene chloride was allowed to stand for 4 days at room temperature. After the usual work-up 0.48 g (87%) of VI was obtained. The same result was obtained when the phosphorus pentachloride was omitted. When similar experiments were carried out in carbon tetrachloride, high yields of VII were recovered. In all cases identity of VI with an authentic sample was established by mixture melting point, infrared spectrum, or both.

A mixture of 0.50 g of VII, 10 ml of acetic acid, and 10 ml of acetic anhydride was heated to dissolve the VII. After cooling to room temperature an acetic acid solution of silver nitrate was added. Only slight cloudiness developed after 1 hr. After the usual work-up a 92% yield of VI was obtained. When a solution of 0.50 g of VII in 20 ml of ether was added to 30 ml of a 5% alcoholic silver nitrate solution containing 5 ml of water, an immediate precipitate of silver chloride formed. After 1 hr the usual work-up afforded an oil after removal of all solvent. The infrared spectrum showed that, in addition to 1-phenylcyclopropyl phenyl ketone, a hydroxyl band was present. The oil was heated with thionyl chloride for 1 hr, and the resultant oil showed on glpc analysis 34% of 1-phenylcyclopropyl phenyl ketone, 59% of VI, and 7% of an unidentified substance.

A mixture of 10.4 g of phosphorus pentachloride, 7.0 g of V, and 25 ml of methylene chloride was allowed to stand in a stoppered flask at room temperature. Aliquots were removed after 2.0 and 3.0 hr and analyzed for ketone V and unrearranged dichloride VII by using the fact that both V and VII absorb at 1.630 μ with extinction coefficients of 0.646 and 0.862, respectively.[27] In addition, the amount of V present was checked by vpc. If the absorption at 1.630 μ were greater than that expected on the basis of the known amount of V present, one can conclude that VII was present since it has a greater absorbance than V, and VI does not absorb at all in this region. The results indicated that small amounts of VII were formed, but not sufficient to account for the amount of ketone V which had reacted (14% after 3 hr).

In another experiment,[27] a solution of VII in methylene chloride containing phosphorus pentachloride and phosphorus oxychloride was allowed to stand at room temperature. After 3 hr the absorbance at 1.630 μ indicated that 28% of the dichloride VII had rearranged (as judged by the decrease in absorbance). After 3 hr the phosphorus pentachloride had all dissolved, and thereafter the rate of rearrangement of VII decreased (14% in the next 3 hr). Thus, heterogeneity plays a part in these reactions but has not been investigated.

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[24] L. I. Smith and E. R. Rogier, *J. Am. Chem. Soc.*, **73**, 3831 (1951).

[25] D. I. Schuster and J. D. Roberts, *J. Org. Chem.*, **27**, 51 (1962).

[26] S. C. Bunce and J. B. Cloke, *J. Am. Chem. Soc.*, **76**, 2244 (1954). The preparation of I as described[20] is preferable to this method.

[27] We thank Bernard Ream for performing these experiments.