Hydrocarbon Chlorinations with Phosphorus Pentachloride[1]

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Phosphorus pentachloride smoothly chlorinates a variety of alkylated aromatic and aliphatic hydrocarbons in either a thermal or catalyzed (benzoyl peroxide) reaction according to $RH + PCl_5 \rightarrow RCl + HCl + PCl_3$ to yield benzylic chlorides and aliphatic chlorides, respectively. Cumene, while reacting rapidly, undergoes a variety of side reactions which greatly diminish the yield of monochlorinated product. Mesitylene substitutes mainly by an ionic process to give 2,4,6-trimethylchlorobenzene. Competitive experiments show that this chlorinating system has about the same selectivity as photochlorination. Olefins react readily with PCl_5 at elevated ($\sim 100°$) temperatures via an ionic mechanism to give high yields of dichloro derivatives in which *trans* addition to the double bond has occurred.

Only a few reports[2,3] concerning the reactions of phosphorus pentachloride with nonolefinic hydrocarbons have appeared. These involved highly arylated compounds such as triphenylmethane and diphenylmethane which reacted readily under conditions conducive to free-radical reactions (high temperatures) to yield trityl chloride and diphenylmethyl chloride, respectively. The availability and relative ease of handling of PCl_5 made a more extensive study appear to be worthwhile and part of this paper presents the results of such an investigation made with a variety of alkylated benzenes and aliphatic hydrocarbons under different experimental conditions.

On the other hand, the reaction of PCl_5 with olefins has received considerable attention.[4-13] For the most part these reactions have been directed towards the synthesis of olefinic phosphonic acid derivatives or their β-chloro derivatives. In certain instances, however, dichlorinated compounds were also detected among the products.[8,12] Reactions of this type have been reinvestigated in order to determine whether the chlorination could be made to be predominant and, if so, whether the addition would be stereoselective.

Results

The hydrocarbon chlorination data are compiled in Table I. Chlorobenzene showed no detectable reaction even after prolonged treatment and as a matter of convenience it or o-dichlorobenzene were often used as solvents.

The aliphatic compounds cyclohexane and n-heptane dissolved very little PCl_5 even at their boiling points and the thermal reactions gave very low yields of chlorinated products. When the reactions were run under

(1) This program was supported in part by the Office of Naval Research Contract No. Nonr 2693(00).

(2) L. H. Cone and C. S. Robinson, *Ber.*, **40**, 2160 (1907).

(3) M. Colson and H. Gauthiér, *Anal. Chim. Acta*, [6] **11**, 23 (1887).

(4) B. M. Mikhailov and M. Sh. Promyslov, *Zh. Obshch. Khim.*, **20**, 338 (1950).

(5) W. H. Woodstock, U. S. Patent 2,471,472; *Chem. Abstr.*, **43**, 7499, (1949).

(6) G. M. Kosolapoff, U. S. Patent 2,486,657; *Chem. Abstr.*, **44**, 2009, (1950).

(7) G. M. Kosolapoff and L. F. McCullough, *J. Am. Chem. Soc.*, **73**, 855 (1951).

(8) G. M. Kosolapoff and W. E. Huber, *ibid.*, **68**, 2540 (1946).

(9) K. N. Anisimov and G. K. Fedorova, *Dopovidi Akad. Nauk Ukr. RSR*, 1245 (1960).

(10) K. N. Anisimov, G. M. Kunitskaya, and N. A. Slovokhotova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **64**, (1961).

(11) G. K. Fedorova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **30**, 4044 (1960).

(12) Yu. M. Zinov'ev, U. N. Kulakova, and L. Z. Soborovskii, *ibid.*, **27**, 151 (1957).

(13) E. Bergman and A. Bondi, *Ber.*, **63B**, 1158 (1930).

homogeneous conditions in o-dichlorobenzene solvent, the yields obtained in the thermal reactions were increased significantly over those obtained in the absence of a solvent, but they were still quite low compared with those obtained under the same conditions with the alkylated aromatic compounds. In general the per cent chlorination under these conditions varied directly with the time of reaction. The decreased yields with these compounds mostly can be attributed to the lower reflux temperatures prevailing during the experiments. When the reactions were catalyzed by small amounts of benzoyl peroxide the rates of chlorination were greatly increased.

The yields of chlorinated products obtained with the alkylated aromatic derivatives also varied with the time of reaction but were always much higher than those encountered with the lower boiling aliphatic systems. While the rates could be increased by catalysis with benzoyl peroxide, good yields were obtained with ~ 16-hour reaction periods via the thermally induced reaction. Thus, toluene reacted readily by the thermal or catalyzed reaction to give good (60–70%) yields of benzyl chloride. Similar behavior was exhibited by p-xylene and 60–70% yields of p-methylbenzyl chloride were obtained. In the presence of an excess of PCl_5 it was possible to chlorinate the second methyl group to give α,α'-dichloro-p-xylene. No evidence for the formation of benzal dichlorides was found.

Ethylbenzene yielded α-phenethyl chloride almost exclusively with only 0.5% of the β-derivative being formed. Similarly, p-ethyltoluene reacted smoothly to give a mixture of p-methyl-α-phenethyl chloride and p-ethylbenzyl chloride (34.8% and 25.2%, respectively). Only small traces of the β-phenethyl derivative were found.

Cumene reacted very readily and hydrogen chloride was rapidly evolved in large quantities. Upon work-up, however, it was found (either on a small scale with analysis by v.p.c. or in a preparative reaction) that only low or modest yields (20–30%) of the expected phenyldimethylcarbinyl chloride were obtained and that the major products were a mixture of compounds which were relatively high boiling, 120–135° (15 mm.). This mixture was examined via n.m.r. The lower boiling component, 120–130° (15 mm.), showed evidence of a benzylic or conjugated $-CH_2Cl$ (sharp singlet at τ 5.65), an uncoupled methyl group (τ 8.0), along with much smaller quantities of vinyl protons (centered at τ 3.78). The higher boiling portion, 130–135° (15 mm.), showed a diminished methyl singlet (τ 7.98),

TABLE I
HYDROCARBON CHLORINATIONS

Hydrocarbon	Moles hydrocarbon moles PCl₅	Solvent[c]	Temp., °C.	Time, hr.	Products, % yield based on PCl₅
Chlorobenzene	2		120	12	99% Recovery of C₆H₅Cl
Cyclohexane	1.56	ODCB	90	8	C₆H₁₁Cl (13)
Cyclohexane	3		88	5	C₆H₁₁Cl (~1)
Cyclohexane[a]	3	ODCB	88	7	C₆H₁₁Cl (70.2)
Cyclohexane	2	ODCB	88	13	C₆H₁₁Cl (20)
n-Heptane	3		90	8	Mixed chloroheptanes (~2)
n-Heptane	3	ODCB	90	14	Mixed chloroheptanes (23)
n-Heptane[a]	3	ODCB	90	8	Mixed chloroheptanes (73.2)
p-Xylene	1.2		110	10	p-Methylbenzyl chloride (30.8) + α,α'-dichloro-p-xylene (6.5)
p-Xylene	1.0	C₆H₅Cl	110	16	p-Methylbenzyl chloride (67.3) + α,α'-dichloro-p-xylene (0.2)
p-Xylene	0.6		110	16	p-Methylbenzyl chloride (50.4) + α,α'-dichloro-p-xylene (14.8)
Toluene	3		100	16	Benzyl chloride (65.1)
Toluene[a]	3		100	7	Benzyl chloride (72.1)
Ethylbenzene	4		105	16	α-Phenethyl chloride (60) + β-phenethyl chloride (0.5)
p-Ethyltoluene	2		105	16	p-Methyl-α-phenethyl chloride (34.8) + p-ethylbenzyl chloride (25.2)
Mesitylene	1.5		110	16	2,4,6-Trimethylchlorobenzene (37) + 3.5-dimethylbenzyl chloride (25.2)
Mesitylene	1.0	C₆H₅Cl	110	16	2,4,6-Trimethylchlorobenzene (35) + 3,5-dimethylbenzyl chloride (23)
Mesitylene	1.2	MDNB	90	10	2,4,6-Trimethylchlorobenzene (63)
Mesitylene[a,b]	3		88	8	3,5-Dimethylbenzyl chloride (59.2) + 2,4,6-trimethylchlorobenzene (3) + dichloronated product [1.1]
Toluene + ethylbenzene	4		115	16	Benzyl chloride (34.8) + α-phenethyl chloride (28.4) + β-phenethyl chloride (0.5)
Toluene + cyclohexane	5.6		88	13	Benzyl chloride (4.85) + cyclohexyl chloride (22.6)
Toluene + cyclohexane[a]	2	MDNB	85	8	Benzyl chloride (8) + cyclohexyl chloride (17.6)
Cumene	2		110	14	Phenyldimethylcarbinyl chloride (28.5) + higher chlorinated products

[a] Reaction catalyzed with benzoyl peroxide. [b] Reaction with SO₂Cl₂ instead of PCl₅. [c] ODCB = o-dichlorobenzene; MDNB = m-dinitrobenzene.

two very small –CH₂Cl (tentatively assigned) peaks at τ 5.65 and τ 5.80 and only very small quantities of vinyl protons. Neither the n.m.r. nor infrared spectra indicated any significant amounts of ring chlorination and it is concluded that the major products of the cumene–PCl₅ reaction were a mixture of highly chlorinated derivatives containing some chloro olefins (vide infra).

Mesitylene underwent substitution very readily in the thermal reaction to give a 60–70% total yield of products in which the ring chlorinated isomer, 2,4,6-trimethylchlorobenzene, was predominant. In contrast, a chlorination with SO₂Cl₂ catalyzed by benzoyl peroxide gave mainly 3,5-dimethylbenzene chloride with only ~3% ring chlorination. When the reaction was conducted in the presence of m-dinitrobenzene, 2,4,6-trimethylchlorobenzene was obtained as the sole product in 63% yield (by actual isolation).

A series of competitive experiments were performed with excesses of equimolar mixtures of toluene and ethylbenzene, and toluene with cyclohexane. The former gave a mixture containing benzyl chloride (34.8%), ~-phenethyl chloride (28.4%), and only 0.5% of β-phenethyl chloride. The latter mixture gave 22.6% cyclohexyl chloride and 4.85% benzyl chloride when reacted thermally without solvent and 17.6% cyclohexyl chloride and 8% benzyl chloride when reacted in the presence of m-dinitrobenzene and catalyzed by benzoyl peroxide.

In all of these reactions phosphorus trichloride and hydrochloric acid were products and each was isolated

and/or trapped and identified. In all cases distillation could be carried out virtually to completion with only negligible residues remaining. This along with n.m.r. and infrared spectral data is excellent evidence for the lack of formation of organophosphorus compounds in these reactions.

Three olefins, octene-1, cyclohexene, and trans-stilbene, were investigated and the results are shown in Table II. The yields listed were based upon actual isolation of the products. Octene-1 was very readily converted to 1,2-dichlorooctane in 83% yield at the reflux temperature (91°) of the reaction mixture (using chlorobenzene as solvent). Only negligible amounts of other products were obtained.

TABLE II
OLEFIN CHLORINATIONS

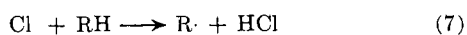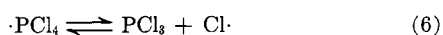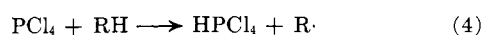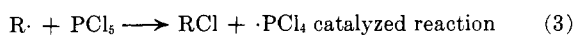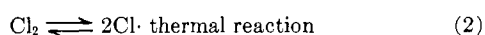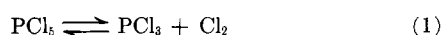| Hydro-carbon	Moles PCl₅ moles olefin	Sol-vent	Temp., °C.	Time, hr.	% yield based on PCl₅[a]
Octene-1	0.5	C₆H₅Cl	91	6	1,2-Dichlorooctane (83)
Cyclo-hexene	1	MDNB[b]	80	10	trans-1,2-Dichloro-cyclohexane (87)
trans-Stilbene	0.5	C₆H₅Cl	124	12	meso-1,2-Dichlorostil-bene (85) + dl-1,2-dichlorostilbene (13.1)

[a] Yields based on actual isolation of products. [b] Actually a catalytic amount (0.05 mole) was used.

The reaction with cyclohexene was conducted in the presence of a small amount of m-dinitrobenzene and an 87% yield of trans-1,2-dichlorocyclohexane was obtained. None of the cis isomer was detected and if it was present it was there in very small quantities. There is a small but significant difference in boiling points of the two isomers[14] but only a single peak was found via v.p.c.

Two isomers (in nearly quantitative total yield) were found when trans-stilbene reacted with PCl_5 at reflux (124°) in chlorobenzene. The major component was meso-1,2-dichlorostilbene (85%) while the minor component was the dl mixture (13.1%). When the dl mixture was heated in chlorobenzene in the presence of catalytic amounts of PCl_5, it was found that no detectable amount of isomerization had occurred.

Discussion

The competitive reaction between cyclohexane and toluene in photochlorination has been reported.[15] With toluene assigned a relative reactivity value of 1.0 per replaceable methyl hydrogen, it was found that each hydrogen in cyclohexane was 2.8 times as reactive. This result demonstrates that resonance stabilization is not important in the transition state which in turn reflects the highly exothermic nature of the reactions of carbon–hydrogen bonds with chlorine atoms.[16] With PCl_5 in a thermal reaction, the reactivity per C–H in cyclohexane was found to have a value of 3.0 compared to the methyl C–H bonds in toluene again with an assigned relative reactivity of 1.0. Thus, the systems are very similar in their over-all behavior. This then implies that the attacking radical in the PCl_5 reaction is either a chlorine atom or a substance with about the same activity as a chlorine atom. The following scheme (equations 1–7) seems reasonable.
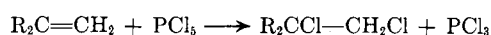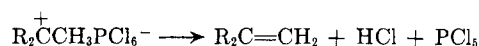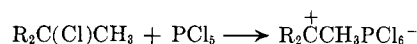
$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad (1)$$

$$Cl_2 \rightleftharpoons 2Cl\cdot \text{ thermal reaction} \qquad (2)$$

$$R\cdot + PCl_5 \longrightarrow RCl + \cdot PCl_4 \text{ catalyzed reaction} \qquad (3)$$

$$PCl_4 + RH \longrightarrow HPCl_4 + R\cdot \qquad (4)$$

$$HPCl_4 \longrightarrow HCl + PCl_3 \qquad (5)$$

$$\cdot PCl_4 \rightleftharpoons PCl_3 + Cl\cdot \qquad (6)$$

$$Cl + RH \longrightarrow R\cdot + HCl \qquad (7)$$

It is difficult per se to distinguish whether steps 4 and 5 are important or whether $\cdot PCl_4$ first decays rapidly to PCl_3 + $Cl\cdot$ as in step 6. The competitive experiments imply that step 6 is the important one, although the depicted equilibria may be of considerable importance and many reactive species may be involved in a complex manner.[17] Interestingly, the same question appears with chlorinations conducted with sulfuryl

(14) H. C. Stevens and O. Grummitt, J. Am. Chem. Soc., 74, 4876 (1952).

(15) G. A. Russell and H. C. Brown, ibid., 77, 4578 (1955).

(16) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 370.

(17) As pointed out by one of the referees, the bond reactivity data, obtained from competitive chlorination experiments between toluene and cyclohexane, tend to support step 6, but the isomer distributions of the products obtained from the chlorination of ethylbenzene and p-ethyltoluene do not. Whether the marked preference for benzylic substitution in these compounds is due to reaction with ·PCl₄, which would be expected to be less reactive than Cl·, or to an energy lowering coordination²¹,²² of Cl· and/or ·PCl₄ with the ring prior to hydrogen abstraction is not discernible from the present data. Experiments designed to help clarify these interesting observations are in progress.

chloride[18] wherein most, but not all, of the results are explicable by a step involving $SO_2Cl\cdot \rightarrow SO_2 + Cl$.

The relative rates of the thermal reactions varied directly with temperature. This result is entirely consistent with steps 1 and 2. The ability of PCl_5 to chlorinate a variety of hydrocarbons in a thermal reaction is one of the areas in which it differs fundamentally from other chlorinating agents such as sulfuryl chloride.[19] This of course is partly due to the higher reflux temperatures available by use of this reagent.

A benzoyl peroxide-catalyzed competitive experiment between cyclohexane and toluene was performed in the presence of m-dinitrobenzene. As expected, the over-all yields were decreased because nitrated aromatic solvents are poor media for radical substitution reactions.[20] The results showed that under these conditions toluene was 1.8 times more reactive per CH_3 hydrogen than was cyclohexane, a result practically opposite that obtained in the reaction conducted in the absence of m-dinitrobenzene. It has been previously reported that certain solvents (usually aromatic) can form complexes with chlorine atoms to lower their energy and increase their selectivity.[21,22] It is quite probable that a type of coordination occurs in this system and involves the nitro compound. Whether this might involve ·PCl_4 or ·Cl or both cannot be estimated.

While the chlorinations of most of the hydrocarbons took place smoothly to yield the expected products there were significant exceptions. Cumene reacted readily but only a relatively small yield of the expected phenyldimethylcarbinyl chloride was isolated. Most of the product was a more extensively chlorinated mixture. Cumene, of course, can be chlorinated readily either photochemically with chlorine[15] or with sulfuryl chloride[15] to give predominantly the tertiary chloride. The results with PCl_5 are interpretable on the basis of a series of dehydrohalogenation reactions catalyzed by PCl_5 with subsequent additions of chlorine across the double bonds.

$$R_2C(Cl)CH_3 + PCl_5 \longrightarrow R_2\overset{+}{C}CH_3PCl_6{}^-$$

$$R_2\overset{+}{C}CH_3PCl_6{}^- \longrightarrow R_2C{=}CH_2 + HCl + PCl_5$$

$$R_2C{=}CH_2 + PCl_5 \longrightarrow R_2CCl{-}CH_2Cl + PCl_3$$

Ability of PCl_5 to function as a Lewis acid (albeit a weak one) is well established,[23] while the halogen addition to olefins is discussed subsequently.

Mesitylene when chlorinated by sulfuryl chloride gave good yields of 3,5-dimethylbenzyl chloride with only about 3% ring chlorination. On the other hand, the thermal reaction with PCl_5 gave a mixture which was predominantly the ring substituted compound, 2,4,6-trimethylchlorobenzene (in a ratio of about 1.5:1). When the reaction was conducted in the presence of m-dinitrobenzene the product was exclusively 2,4,6-trimethylchlorobenzene. It is quite evident that in this case an ionic reaction competes with the free-radical substitution. The addition of a polar com-

(18) Ref. 16, pp. 380–381.

(19) M. S. Kharasch and H. C. Brown, J. Am. Chem. Soc., 61, 2142 (1939).

(20) Ref. 16, p. 352.

(21) G. A. Russell, J. Am. Chem. Soc., 80, 4987 (1958).

(22) C. Walling and M. F. Mayahi, ibid., 81, 1485 (1959).

(23) M. Boaz, V. Gutmann, and J. R. Masaguer, Monatsh., 92, 582 (1961).

ponent, m-dinitrobenzene, which enhances ionic reactions but strongly inhibits free radical ones,[20] completely suppressed the free-radical path. This apparently is a manifestation of the activity of the mesitylene ring toward electrophilic attack and the reaction is akin to ring chlorinations by other more obvious Friedel–Crafts catalysts as reported by Kovacic.[24–27]

It has been known for a long time[4–13] that PCl₅ reacts with olefins in the cold to give compounds in which the elements of Cl–PCl₄ have been added. Surpris-

$$R-CH=CH_2 + PCl_5 \xrightarrow{} RCHCl-CH-PCl_4 \xrightarrow{H_2O} RCHCl-CH_2-PO_2H$$

ingly, little emphasis has been placed on the use of this reaction for the simple chlorination of olefins, and while a few examples[8,12] of 1,2-dichlorination in the system have been reported, no attempts to investigate the scope and general utility of the reaction have been made.

Merely heating octene-1 with PCl₅ in chlorobenzene gave 1,2-dichlorooctane in 83% yield (isolated). No evidence for more than trace amounts of other compounds was found. Similarly, cyclohexene when heated with PCl₅ in the presence of m-dinitrobenzene gave an 87% yield of 1,2-dichlorocyclohexane which was apparently solely the trans isomer (infrared, refractive index, v.p.c.). The reaction of trans-stilbene (in chlorobenzene) gave an 85% yield of meso-1,2-dichlorostilbene (trans addition) and 13.1% of the dl mixture (cis addition). Thus the reactions proceed very readily and are highly stereoselective. At least in the case of cyclohexene–m-dinitrobenzene (and octene-1) they are obviously ionic. It has been postulated that the formation of gem-dichloride by reaction of PCl₅ with ketones involves $\overset{+}{PCl_4}$ from $2 PCl_5 \rightleftharpoons \overset{+}{PCl_4}\overset{-}{PCl_6}$.[28] Based on this argument, it would be expected that $\overset{+}{PCl_4}$ would add to olefins to form a bridged cationic intermediate. Attack of a chloride ion on this would be from the side opposite of the very bulky PCl₄ group, thus giving the over-all trans addition. This is of course basically the mechanism accepted for ionic halogen additions to olefins. Phosphorus trichloride must then be eliminated by a SNi process as shown in equation 8.
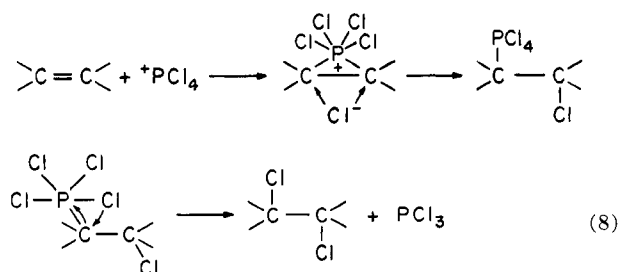
While trans-stilbene would be expected to yield the same result by the same mechanism, small but significant quantities of the dl compound arising from cis addition were found. Isomerization of the trans dichloride to the cis dichloride is not thermodynamically

(24) P. Kovacic and A. K. Sparks, J. Am. Chem. Soc., 82, 5740 (1960).

(25) P. Kovacic and A. K. Sparks, J. Org. Chem., 26, 1310 (1961).

(26) P. Kovacic and A. K. Sparks, ibid., 26, 2541 (1961).

(27) P. Kovacic, C. Wu, and R. W. Stuart, J. Am. Chem. Soc., 82, 1917 (1960).

(28) M. S. Newman and L. L. Wood, Jr., ibid., 81, 4300 (1959).

favored and, in fact, under normal free-radical conditions, the reverse is found.[29] While many rationalizations could be put forth to explain this result, the simplest and most obvious is that at the somewhat elevated temperature at which this reaction was conducted both a free-radical and ionic addition were operative. This was apparently the situation in the reactions with mesitylene and seems a very reasonable explanation in this case.

Experimental[30]

General.—All of the liquid hydrocarbons used in this study were commercial reagent grade materials which were further purified by distillation from sodium. High purity phosphorus pentachloride (purchased from the Baker and Adamson Division of the Allied Chemical Corporation) was used as received.

The general chlorination procedure followed in all cases was to mix the reagents and then stir and reflux under nitrogen for the times listed in Tables I and II. After cooling, the reaction mixtures were either distilled directly without washing, or poured onto ice, washed with water and dilute NaHCO₃ solution, dried over anhydrous CaCl₂, and then distilled. Either method of work-up gave essentially the same results. The v.p.c. analyses were performed with a column composed of 10% Apiezon L on Anakrome ABS. Authentic samples for retention time comparisons were commercially available reagent grade compounds or were synthesized by straight forward procedures. N.m.r. spectra were obtained on a Varian A-60 spectrometer, using tetramethylsilane as an internal reference. This instrument was particularly useful and while in all cases isolation and/or v.p.c. were used for the ultimate analysis, in many cases the same results could have been obtained by this method alone. Bond reactivities in the competitive experiments were obtained by use of the nonintegrated expression,[15] $k_s/k_t([SH]/[TH])_{av} = [SCl]/[TCl]$, which corrects for losses of reagents due to causes other than chemical reaction.

A few typical examples of preparative scale experiments are given subsequently.

Chlorination of Ethylbenzene.—Ethylbenzene (135 g., 1.25 moles) was mixed with 62.5 g. of PCl₅ (0.31 mole). The mixing process was exothermic and the temperature rose to 55°. The reaction mixture was then stirred and refluxed (105°) under nitrogen for 16 hr. During this period, HCl was steadily evolved. Without washing[31] the clear light yellow solution which resulted was distilled through a helices-packed column. The first fraction was PCl₃ (b.p. 75° at atmospheric pressure). There was obtained 33 g. of it (77% yield). The next fraction, consisting of unchanged PCl₅ and ethylbenzene, was obtained at 134–135°. The final fraction, with b.p. 93–94° (15 mm.) weighed 24.5 g. The n.m.r. spectra of this colorless liquid was identical with that of an authentic sample of α-phenethyl chloride (quartet at τ 5.18, doublet at τ 8.42 in the proper intensity ratios). Analysis by v.p.c. showed that the product contained about 0.5% of β-phenethyl chloride.

Chlorination of Cyclohexene.—A mixture of cyclohexene (41 g., 0.5 mole), PCl₅ (104 g., 0.5 mole), and m-dinitrobenzene (8.4 g., 0.05 mole) was stirred and refluxed at 80° under nitrogen for 10 hr. The reaction mixture was then cooled, washed with water and dilute sodium bicarbonate solution (5%), and then dried over anhydrous calcium chloride. After stripping the unchanged cyclohexene in vacuo the product, b.p. 72–75° (15 mm.), was collected. It weighed 34 g. (87%); $n^{30}D$ 1.4873 (lit.[14] $n^{20}D$ 1.4904 for the trans isomer).

Anal. Calcd. for C₆H₁₀Cl₂: C, 47.1; H, 6.5; Cl, 46.4. Found: C, 47.19; H, 6.61; Cl, 46.21.

The infrared spectrum of this compound was identical with that listed in the literature[14] for the trans isomer. Only one peak was found via v.p.c.

Chlorination of trans-Stilbene.—A solution of trans-stilbene (22 g., 0.122 mole) and PCl₅ (51 g., 0.244 mole), in 200 cc. of

(29) R. E. Buckles, W. E. Steinmetz, and N. G. Wheeler, ibid., 72, 2496 (1950).

(30) Melting points are corrected, but boiling points are not. Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(31) Any unchanged PCl₅ codistilled out of the reaction mixture with the excess hydrocarbons.

chlorobenzene was refluxed (124°) under nitrogen for 12 hr. Upon cooling, 17.5 g. of fine, snow white crystals of *meso*-1,2-dichlorostilbene[28] separated and were isolated (m.p. 193–194). Upon evaporation of the solution to one half its original volume and chilling, a further 8.5 g. of this compound were obtained. The remaining solution was evaporated to dryness and the residue was recrystallized from petroleum ether to yield 4.0 g. of *dl*-1,2-dichlorostilbene[28] (m.p. 90–91°).

Chlorination of Cumene.—A solution of cumene (240 g., 2 moles) and PCl₅ (208 g., 1 mole) was stirred and refluxed (110°) under nitrogen for 14 hr. Hydrogen chloride was rapidly evolved during this period. After washing with water and NaHCO₃ solution, the clear yellow solution which was obtained as distilled through a short packed column. There was obtained 44 g. (28.5%) of phenyldimethylcarbinyl chloride, b.p. 95–96° (15 mm.). N.m.r. showed a sharp singlet at τ 8.22; ratio of aliphatic protons to aromatic protons 6:5. There was also obtained 95 g. of a substance boiling mainly at 120–135° (15 mm.). This colorless liquid showed greatly diminished methyl peaks in its n.m.r. and infrared spectra as well as evidence in the former for –CH₂Cl groups and small amounts of vinyl protons. It was not investigated further. These results were essentially reproducible. From the relative retention times in the v.p.c. analysis it was estimated that a mixture of di- and tri-chlorinated products had been formed.

Catalyzed Chlorination of Cyclohexane.—A mixture of cyclohexane (84 g., 1 mole) and PCl₅ (70 g., 0.33 mole) in 200 cc. of *o*-dichlorobenzene was refluxed (88°) under nitrogen for 7 hr. Small quantities of benzoyl peroxide were added periodically during this time and HCl was evolved. After cooling, the reaction mixture (which was a light yellow color at this point) was poured onto ice water. The organic layer was separated, washed consecutively with water and 5% NaHCO₃ solution, and then dried over anhydrous CaCl₂. Analysis by v.p.c. indicated a 70.2% yield of cyclohexyl chloride had been formed (based on PCl₅).

The Reaction of Ethyl Azodicarboxylate with Conjugated Dienes. II[1,2]

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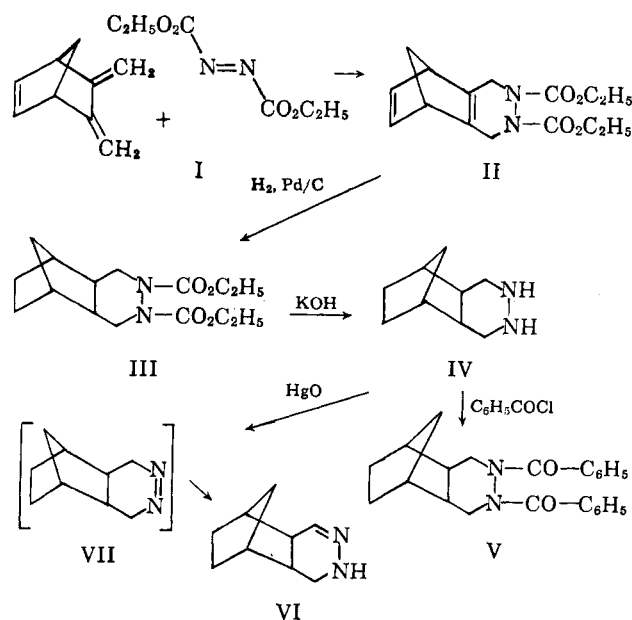*Department of Chemistry, Duquesne University, Pittsburgh 19, Pennsylvania*

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Further investigations of the reaction of ethyl azodicarboxylate (I) with conjugated dienes have been performed. The reaction of I with 5,6-dimethylenebicyclo[2.2.1]hept-2-ene gave the Diels–Alder adduct 1,2-dicarbethoxy-7,10-methano-1,2,3,6,7,10-hexahydro-4,5-benzopyridazine in 80% yield. Addition of I to bi(1-cyclohexen-1-yl) produced 1,2-dicarbethoxy-3,4,5,6-bis(tetramethylene)-1,2,3,6-tetrahydropyridazine in 80% yield. Treatment of 2,4-dimethyl-1,3-pentadiene with I proceeded by a concerted cyclic mechanism to give a mixture of isomers, 1,2-dicarbethoxy-1-[1-(4-methyl-2-methylene-3-pentenyl)]hydrazine (78.5%) and 1,2-dicarbethoxy-1-[3-(2,4-dimethyl-1,4-pentadienyl)]hydrazine (21.5%). The proofs of structure on the latter compounds were accomplished by instrumental methods and chemical degradation.

In a previous report from this laboratory,[2] it was shown that ethyl azodicarboxylate added to simple conjugated dienes by Diels–Alder or 1,4-addition, whereas, with more highly substituted conjugated dienes addition occurred by a different mechanism with a shift of the double bond.[2,4] The present report describes the results of an extension of these studies to other conjugated diene systems.

The addition of ethyl azodicarboxylate (I) to 5,6-dimethylenebicyclo[2.2.1]hept-2-ene took place with an evolution of heat and gave an 80% yield of the Diels–Alder adduct, 1,2-dicarbethoxy-7,10-methano-1,2,3,6,-7,10-hexahydro-4,5-benzopyridazine (II). The adduct II was hydrogenated over palladium-on-charcoal catalyst in ethanol to form 1,2-dicarbethoxy-7,10-methano-decahydro-4,5-benzopyridazine (III) in 82% yield. Hydrolysis of III was accomplished by refluxing in ethanolic potassium hydroxide solution for 11.5 hours. The cyclic hydrazine, 7,10-methanodecahydro-4,5-benzopyridazine (IV), was thus obtained in 84% yield. The dibenzoyl derivative of IV, 1,2-dibenzoyl-7,19-methanodecahydro-4,5-benzopyridazine (V) was prepared in 80% yield. Oxidation of IV was performed under a nitrogen atmosphere using yellow mercuric oxide in anhydrous ether. The only compound isolated was the cyclic hydrazone, 7,10-methano-Δ²-octahydro-4,5-benzopyridazine (VI) in 63.5% yield, which was characterized by its infrared and ultraviolet spectra. The isolation of VI indicated that the azo compound VII had probably formed, but facile isomerization to the more stable structure VI, had taken place under the reaction conditions.