244 *J. Org. Chem. Vol. 40, No. 2, 1975*

Jung and Engel

cooled. The precipitated crystals were separated by filtration, washed with ether, and dried *in vacuo.* The ir and nmr spectra of all the complexes obtained were identical with one another, similar to the mixture of RhCl(PPh₃)₃ and [RhCl(PPh₃)₂]₂, and showed no peaks assignable to indoline. The elemental analysis of the complex isolated in the reaction at 140° was also explainable by the mixture.

Anal. Calcd for the mixture of $C_{54}H_{45}ClP_3Rh$ and $C_{72}H_{60}Cl_2P_4Rh_2$ (1:3): C, 66.44; H, 4.65; N, 0.0. Found: C, 66.46; H, 4.82; N, 0.0.

A similar mixture was obtained also when RhCl(PPh₃)₃ (0.03 mmol) was heated in indoline (2.0 mmol) at 80° for 5 hr.

Anal. Found: C, 67.99; H, 4.84; N, 0.0.

When [RhCl(PPh₃)₂]₂ (0.03 mmol) was heated in indoline (2.0 mmol) at 80° for 5 hr, the dimer was recovered.

Isolation of RhCl(PPh₃)₂(pyrrolidine). RhCl(PPh₃)₃ (27.8 mg, 0.03 mmol) and pyrrolidine (142 mg, 2.0 mmol) were sealed in a Pyrex glass tube *in vacuo* and heated at 80° for 30 min. The yellow crystals isolated melted at 105–106°. The nmr spectrum of them showed three multiplets centered at τ 8.2, 6.8, and 2.7, with 1:1:8 area (in CDCl₃ with TMS as the internal standard). The ir spectrum showed bands at 2930, 2860, and 886 cm⁻¹ which are assignable to pyrrolidine.

Anal. Calcd for $C_{40}H_{39}ClNP_2Rh$: C, 65.45; H, 5.37; N, 1.91. Found: C, 65.11; H, 5.48; N, 1.83.

The same complex which was identified by elemental analysis, ir spectrum, and melting point was obtained in the similar reaction between (RhCl(PPh₃)₂)₂ and pyrrolidine.

Registry No.—RhCl(PPh₃)₃, 14694-95-2; [RhCl(PPh₃)₂]₂, 25966-16-9; [RhCl(cyclooctene)₂]₂, 12279-09-3; RhCl(PPh₃)₂(pyrrolidine), 53166-29-3; indoline, 496-15-1; cycloheptene, 628-92-2; pyrrolidine, 123-75-1.

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(10) For example, the kinetic expression derived from the fact shown in Figure 1, and the scheme which is formed by removing RhCl(PPh₃)₂(solvent) from the scheme in the text, is the type $R = a'[D][C]_0/(b'[L] + c'[D])$. This cannot explain the facts shown in Figures 2 and 4 without contradiction.
(11) Because $[VI] = K_6 [II][S]$.
(12) It has been reported⁹ᵈ that the dissociation constant, K, equals 1.4×10^{-4} mol 1.⁻¹.
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# Catalytic Hydrogenolysis–Reduction of Aryl Phosphate Esters[1]

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The platinum-catalyzed hydrogenolysis–reduction of aryl phosphate esters has been investigated with a view toward the determination of the sequence of reaction steps. The aromatic hydrocarbons related to the ester functions have been isolated and identified as intermediates; these arenes, when subjected to facilitated reaction conditions, yield reduction products in the same proportions as observed in the hydrogenolysis reaction systems. The course of intermediate formation and decay has been followed and the stereoregularity of the reduction process has also been investigated.

The hydrogenolysis–reduction of aryl esters of phosphorus-containing acids over platinum catalysts (eq 1) is a
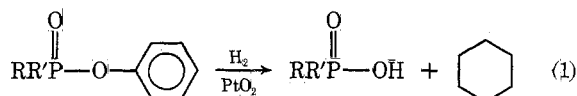
reaction which has been of significant utility in the synthesis of numerous organophosphorus compounds; the phenyl ester linkage is cleaved yielding the free acid while the original aromatic ring is reduced to cyclohexane. Its utility arises as it allows the protection of a phosphorus acid function with an ester linkage at an early stage in a synthetic sequence and at a later stage allows the generation of the free acid without resorting to hydrolytic conditions.

One example of this utility is shown in the synthesis of dihydroxyacetone phosphate.[2] At an early stage of the synthetic route the critical phosphate linkage is introduced by the reaction of diphenyl phosphorochloridate with an aliphatic alcohol. The alkyl position is then properly functionalized and at a latter stage the phenyl groups are removed by hydrogenolysis generating the free acid (eq 2).
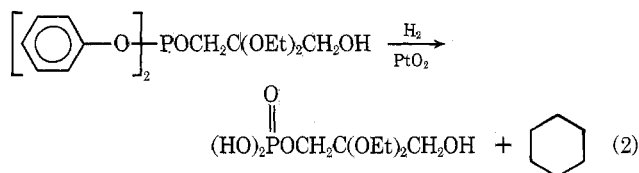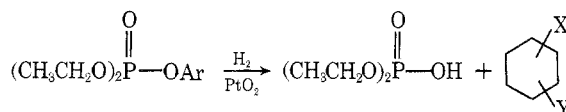
The hydrolytic removal of either aryl or alkyl protecting ester linkages is not feasible as the critical phosphate linkage in the desired product would also be cleaved.

A most interesting aspect of this reaction is the overall reduction of the phenyl ring to cyclohexane under the relatively mild reaction conditions. Thereby it is rather surprising that so little attention has been given to this point. No efforts have been reported to elucidate the course of this overall reaction, and it appears that, aside from phenyl esters themselves, only *p*-nitrophenyl esters have been used in this reaction;[3] in this latter work it was presumed that hydrogenolysis–reduction yielded cyclohexylamine although this was not shown definitively.

As it is known that aromatic hydrocarbons undergo com-

Table I

$$(CH_3CH_2O)_2\overset{\displaystyle O}{\overset{\|}{P}}\!\!-\!\!OAr \xrightarrow[\text{PtO}_2]{H_2} (CH_3CH_2O)_2\overset{\displaystyle O}{\overset{\|}{P}}\!\!-\!\!OH +$$

Ar	Compd	Rel % cis-HC[a]		Rel % trans-HC[a]		Overall hydrocarbon yield,[b] %	
		1 atm H2	4 atm H2	1 atm H2	4 atm H2	1 atm H2	4 atm H2
	I	84.2	90.5	15.8	9.5	71.8	36.2
	II	83.2	90.0	16.8	10.0	75.2	27.8
	III	73.0	78.4	27.0	21.6	90.1	31.9
	IV	75.6	79.3	24.4	20.7	93.8	68.3
	V	75.9	81.0	24.1	19.0	57.8	24.3
	VI	69.2	72.7	30.8	27.3	76.3	67.4
	VII	83.6	87.8	16.4	12.2	89.0	65.0
	VIII	82.3	85.0	17.7	15.0	76.6	65.3

[a] Dimethylcyclohexane for xylene reactions and decalin for naphthalene reactions. [b] Average value for a reaction time of 24 hr under reaction conditions described in the Experimental Section.

plete reduction over platinum catalysts at low hydrogen pressure if an acidic solvent is used or there is present a strong acid (provided the accompanying anion is not inhibitory),[4,5] a reasonable possibility for the sequence in aryl phosphate hydrogenolysis appears to be (a) initial cleavage of the aryl ester linkage yielding arene and the phosphorus-containing acid, followed by (b) the acid-facilitated reduction of the arene. To investigate this hypothesis the complete series of diethyl xylyl phosphate esters were prepared and subjected to hydrogenolysis, the amounts of *cis-* and *trans-* dimethylcyclohexanes formed being measured. Similarly, the two naphthyl diethyl phosphate esters were prepared and subjected to hydrogenolysis, and the amounts of decalins formed were measured.

Two comparisons were to be made using the data thus obtained. First, the cis:trans ratios for the dimethylcyclohexanes (and the decalin) were to be compared with those from the facilitated reduction of the corresponding xylene (or naphthalene) which were the proposed intermediates. Second, the product ratios for the two xylyl esters with methyl groups in an ortho relationship were to be compared with each other as were the product ratios for the three xylyl esters with methyl groups in a meta relationship. The latter comparison would provide information concerning the possibility of a common intermediate in each of the two sets of reactions as is necessitated by the postulated route.

Finally, direct evidence (detection, isolation) for the structure of any intermediate involved was to be obtained.

Results and Discussion

The diethyl xylyl phosphates (I–VI), which have not been reported previously, and the diethyl naphthyl phos-

phates[6] (VII, VIII) were prepared using a modification of a standard method.[7] These were subjected to hydrogenolysis–reduction over Adams catalyst in absolute ethanol solution at 1 and 4 atm pressure of hydrogen. The reaction solutions contained an internal reference of cyclohexane for gas–liquid chromatographic (glc) analysis. The overall yield and hydrocarbon product distribution data for these reactions are summarized in Table I.

Similarly, the xylenes and naphthalene were subjected to catalytic hydrogenation over Adams catalyst in absolute ethanol solution with diethyl phosphoric acid added for facilitation of reaction.[4] Again, cyclohexane was used as an internal reference for glc analysis of the reduction products. The data for these reactions are summarized in Table II.

First should be noted the close correlation of product distribution under both sets of reaction conditions for the two compounds (I and II) containing methyl groups in an ortho relationship, for the three compounds (III–V) containing methyl groups in a meta relationship, and finally for the two naphthyl compounds (VII, VIII). This serves as as preliminary evidence of a common intermediae within each set. Moreover, the close correspondence with product distribution data for the xylene and naphthalene reductions is indicative of the intermediacy in each case of the free arene. It should also be noted that these relative yields are in good agreement with the work of Schuetz and Caswell[5] on xylene reductions over Adams catalyst and the distribution trends with changing pressure are in accord with those observed by Siegel, *et al.*[8]

While the previously mentioned data are *indicative* of the intermediacy of free arene, they by no means serve as *definitive proof;* this is best attained by detection and iso-
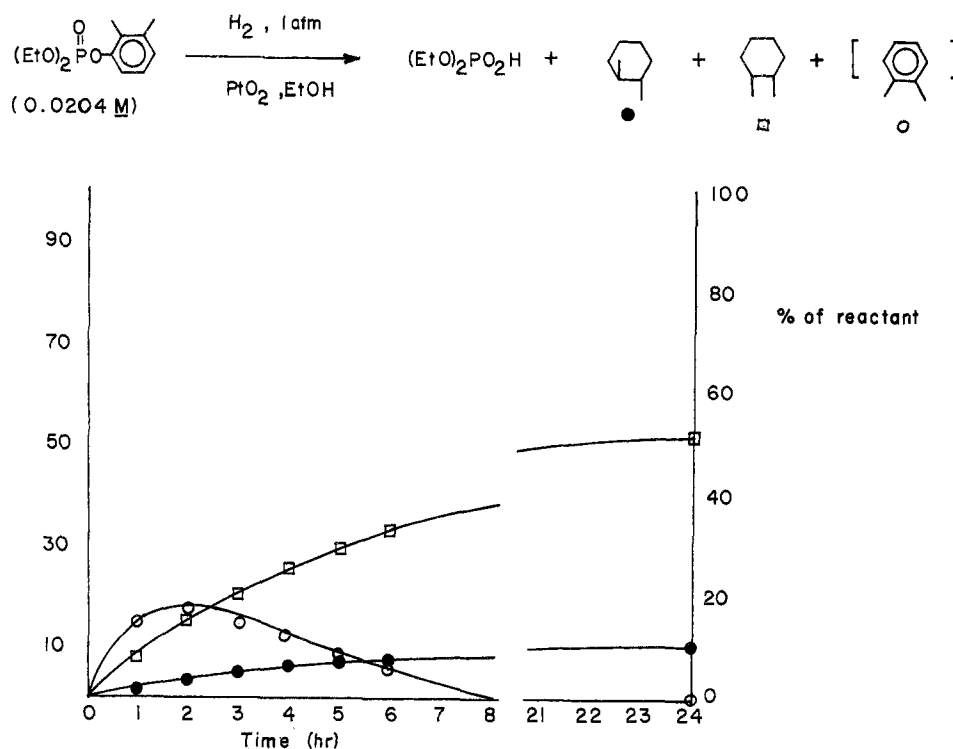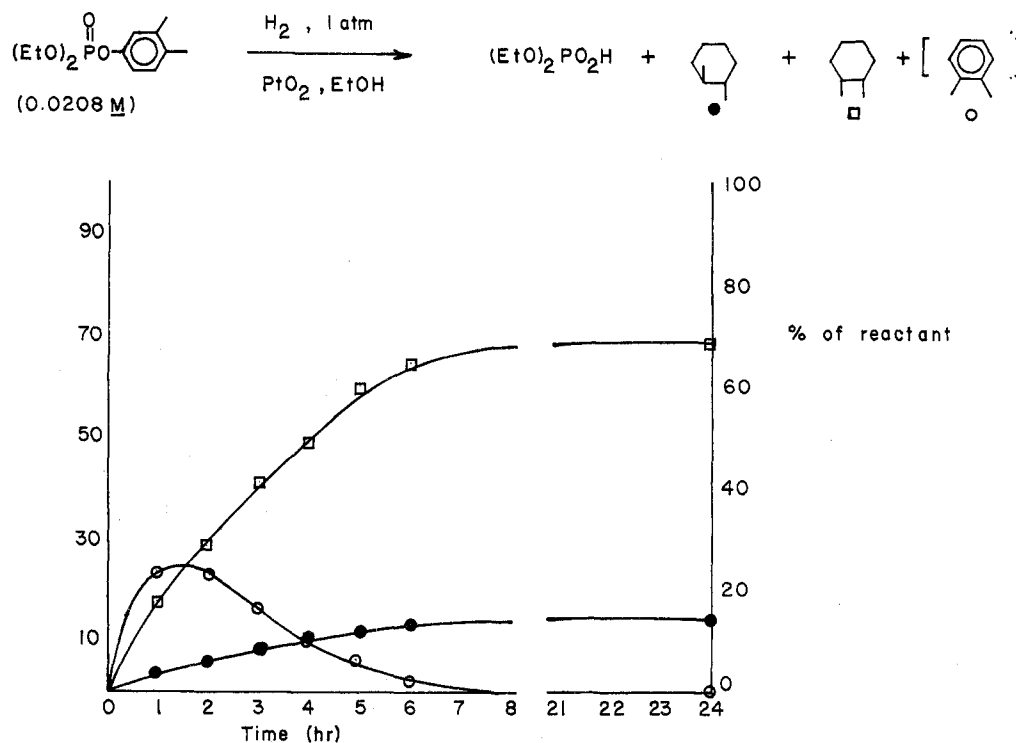
Figure 1.

Figure 2.

lation of the intermediates themselves. This situation was realized for all aryl ester reactants with the exception of compound V. (This reaction system will be discussed more fully in a succeeding paragraph.) The arenes could be intercepted during the reaction using glc and were identified by comparison of their spectral and physical properties with those of authentic samples.

For all reaction systems (with the exception of compound V) the formation and disappearance of intermediate arene, at atmospheric reaction conditions, was followed by glc analysis. Two examples of the data obtained are shown graphically in Figures 1 and 2. Similar plots are obtained

for the five other compounds from which intermediate arene may be isolated. Maxima in arene concentration for these systems (compounds I–IV, VI–VIII) were attained within 1–2 hr after reaction initiation. For the xylyl esters these maxima ranged between 8 and 30% of the concentration of the initial reactant whereas for the naphthyl esters they were about 40% of the initial reactant concentration.

As mentioned above, the diethyl 2,6-dimethylphenyl phosphate, compound V, appeared anomolous as no m-xylene could be detected although its intermediacy was indicated by the stereochemical data. This result may be rationalized in the following way. The hydrogenolysis of the

Table II
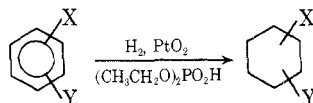
Compd	Registry no.	Rel % *cis*-HC[a]		Rel % *trans*-HC[a]		Overall yield, %	
		1 atm H$_2$	4 atm H$_2$	1 atm H$_2$	4 atm H$_2$	1 atm H$_2$	4 atm H$_2$
Me / Me	95-47-6	87.4	89.1	12.6	10.9	100.0	98.4
Me / Me	108-38-3	75.2	79.8	24.8	20.2	97.4	89.3
Me—Me	106-42-3	67.4	74.9	32.6	25.1	100.0	100.0
(naphthalene)	91-20-3		86.4		13.6		100.0

[a] Dimethylcyclohexane for xylene reactions and decalin for naphthalene reactions. [b] Average value for a reaction time of 24 hr.

Table III

Compd	Elemental analyses,[a,b] %		Yield, %	Mass spectra,[c] m/e		Bp, °C (P, mm)
	Carbon	Hydrogen		Parent	Base	
I	55.65	7.44	54	258	104	104 (0.12)
II	55.48	7.58	75	258	122	109 (0.17)
III	55.41	7.47	27	258	132	101 (0.10)
IV	55.89	7.50	38	258	122	97 (0.14)
V	55.99	7.25	43	258	104	107 (0.45)
VI	56.12	7.66	81	258	201	99 (0.05)

[a] All analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. [b] Calcd for C$_{12}$H$_{19}$O$_4$P: C, 55.81; H, 7.36. [c] All mass spectra were measured using a Varian MAT CH-7 instrument operating at 70 eV and 100-μA trap current.

ester linkage is presumed to be slow relative to the other esters investigated due to steric interference by the two methyl groups, *both* of which are adjacent to the position where cleavage reaction occurs. The *m*-xylene once formed, however, reacts at the same rate as if derived from any other source. Whereas for all other reaction systems investigated the rate-limiting step in saturated hydrocarbon production is arene reduction, for compound V the opposite situation attains and *cleavage is rate limiting*. Thus a *detectable* concentration of *m*-xylene is never present.

This rationalization is also in accord with the relatively low overall yield of saturated hydrocarbon isolated from reaction of compound V. After generation of sufficient diethylphosphoric acid for activation of the catalyst, the rate of ester cleavage remains slow; however, reduction of the aromatic ring *of the ester* may occur yielding a substituted cyclohexyl ester which does not cleave.[9] Evidence for the presence of these reduced esters in the reaction mixture has been found although detailed structural characterizations have not been made.

However, when the reaction is conducted in cyclohexane solution, *m-xylene is obtained in significant quantity from compound V*, as are the arenes from the other aromatic esters investigated. This provides an interesting and possibly useful reaction medium; in cyclohexane hydrogenolysis proceeds smoothly but reduction of the arene is retarded.

Observation of the catalyst during the two processes provides a clue to understanding this behavior. Using alcohol solvents the catalyst, upon initial reduction, begins to coagulate slightly as arene is formed; upon complete reduction of arene the finely dispersed catalyst is regenerated. In contrast, with cyclohexane as the reaction medium, upon reaction initiation, the catalyst clumps and later congeals to an oil which adheres to the glass walls of the reactor; the normal finely dispersed catalyst is *not* regenerated. This oil

retains activity for hydrogenolysis of the aryl phosphate linkage but *not* for arene reduction. As such it bears potential utility for selective isolation of arenes.

Experimental Section

General Synthesis of Diethyl Aryl Phosphates. To a solution of 0.10 mol of the substituted phenol in 400 ml of sodium-dried benzene was added 0.13 mol of sodium hydride with constant mechanical stirring. The reaction medium was stirred overnight as hydrogen was evolved. To the stirred slurry of phenolic salt was added dropwise 0.10 mol of diethyl phosphorochloridate. Upon dissolution of the salt yielding a clear solution, the reaction mixture was washed with 500 ml of water. The organic layer was separated and dried over anhydrous magnesium sulfate, and the benzene was removed by distillation at reduced pressure. The residue was then vacuum distilled to yield the diethyl aryl phosphate. Yield and analytical data are shown in Table III. Satisfactory elemental analyses and ir, nmr, and mass spectra were obtained for all compounds.

General Procedure for Atmospheric Pressure Hydrogen Reactions. The reactor used was of standard design[10] operated with manual adjustment to maintain atmospheric pressure of hydrogen in the reaction vessel. The reaction mixture was stirred throughout the reaction period using a magnetic stirrer. A reaction flask bearing a side arm fitted with a serum cap was used that samples could be removed for analysis during the course of the reaction. For the analytical experiments the reaction flask was charged with 25 ml of an absolute ethanol solution ca. 0.020 M in the compound to be investigated and ca. 0.020 M in cyclohexane which was used as the reference for glc analysis. To this was added 25 mg of PtO$_2$. For the xylene reactions the reaction solution was also prepared ca. 0.010 M in diethyl phosphoric acid. For studies involving the isolation of intermediates and products the concentra-

tion of reactant was increased to *ca.* 1 *M.* Reactions of phosphates in cyclohexane were performed at the same concentrations with the same amount of catalyst. Control experiments were performed to ensure that isomerization of initial products did not occur.

General Procedure for 4-Atm Hydrogen Reactions. All reactions were performed using a standard Parr apparatus with shaker. The pressure was adjusted manually to maintain 4 atm pressure in the reaction portion. The reaction solutions used were as described above for atmospheric pressure investigations. All systems were removed from the reactor and filtered through Celite to remove the catalyst prior to glc analysis.

Analysis. Gas–liquid chromatographic analyses (and preparative-scale glc) were performed using a 5 ft × ¼ in. column of 20% Apiezon L on Chromsorb W at column temperatures of 70–120°, varying with the compounds to be observed. For analytical data all products and intermediates were compared for relative response factors; chart areas were measured using a compensating planimeter. Control experiments were made to ensure that product interconversion was not occurring during analysis.

All ir spectra were measured using a Perkin-Elmer Model 237 B spectrophotometer, nmr spectra were measured using a Varian EM 360 spectrometer, and mass spectra were measured using a Varian MAT CH-7 instrument.

Summary

The hydrogenolysis–reduction of aryl phosphate esters has been found to proceed by initial hydrogenolysis yielding the free phosphorus-containing acid and the free arene followed by reduction of the arene. The reaction may be intercepted at the arene stage by conducting it in cyclohexane solvent; here the catalyst activity for reduction is retarded by the strong acid which is formed in the initial step.

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A Nuclear Magnetic Resonance Investigation of the Iodination of 1,2-Disubstituted Ethylenes. Evidence for a Trans Addition–Cis Elimination

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Iodine was allowed to react with olefins, in the dark, for periods of up to 10 days and their nmr spectra were periodically recorded. All of the olefins showed extensive conversion to their respective diiodides. The reaction was monitored by the disappearance of the olefin peak and the appearance of an iodinated methine proton peak. In the case of cis olefins, between the second and third days, a second halogenated methine band was observed at higher field. Its chemical shift corresponded to that of the iodinated trans olefin. Based on this evidence and supported by glc experiments, a trans addition–cis elimination mechanism is postulated for the "dark" reaction.

In spite of a gradually increasing number of papers dealing with the iodination of olefins,[1-10] most texts either ignore the reaction or state that it does not occur. In actuality certain olefins have been shown to add iodine easily, though more slowly than either bromine or chlorine. The iodinated products however are relatively unstable and can eliminate iodine on heating.

Various investigators have demonstrated that the reaction is extremely complex. Robertson[2] and others studied what they believed was the ionic reaction and found that the reaction was homogeneous in polar solvents and heterogeneous in nonpolar solvents. They were also able to show that the reaction was catalyzed by light.[1] This finding led to additional work on the free-radical iodination of olefins. Most of the recent work has concentrated on the light-catalyzed process and its kinetics and stereochemistry.[5,7] Sumrell[6] showed that the reaction of lower olefins was exothermic in the absence of solvent and was able to utilize the products to make iodohydrins in good yield.

As a result of other investigations in this laboratory it became of interest to look at the "dark" reaction, especially of unsaturated fatty acids. The reversibility of the iodination of olefins suggests itself as a possible mechanism for the biotransport of iodine in living systems. A study was therefore undertaken to follow this reaction using nuclear magnetic resonance as a probe to determine the course and stereochemistry of the reaction.

Results

A variety of unsaturated compounds with emphasis on fatty acids, their esters, and phospholipids were mixed with an equimolar quantity of iodine in an inert solvent in the absence of light and the reaction followed in an nmr instrument. Comparable saturated fatty acids and their derivatives were similarly treated as controls. In addition several related dibromo adducts were also prepared as model compounds whose stereochemistry is well known. Since the original olefinic protons and the newly halogenated ones comprised but a small proportion of the total proton content of the compounds studied, the double-resonance technique was employed to enhance the sensitivity of the nmr measurements and to give accurate chemical shifts. None of the decoupled spectra were corrected for the Bloch–Siegert shift,[11] but it is estimated that the error in the observed chemical shift is less than 0.05 ppm. The results are summarized in Table I.