

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  $\times$   $\frac{1}{4}$  in. column of 20% Apiezon L on Chromosorb 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 yield-

ing 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.

**Registry No.**—I, 53336-80-4; II, 14143-06-7; III, 53336-81-5; IV, 53336-82-6; V, 39604-15-4; VI, 53336-83-7; VII, 33650-14-5; VIII, 16519-26-9.

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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,<sup>1-10</sup> 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<sup>2</sup> 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.<sup>1</sup> 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.<sup>5,7</sup> Sumrell<sup>6</sup> 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,<sup>11</sup> 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.

**Table I**  
Chemical Shift ( $\delta$ ) Data for the Halogenated Ethylenes

Compd	Halogen	Olefin type	X-C-H shift, ppm
4-Octene	Br <sub>2</sub>	Trans	4.16
4-Octene	I <sub>2</sub>	Trans	4.18
Oleic acid	Br <sub>2</sub>	Cis	4.22
Oleic acid	I <sub>2</sub>	Cis	4.5, 4.15
Methyl oleate	I <sub>2</sub>	Cis	4.5, 4.15
Elaidic acid	Br <sub>2</sub>	Trans	4.16
Methyl elaidate	I <sub>2</sub>	Trans	4.17
Nervonic acid	Br <sub>2</sub>	Cis	4.20
Nervonic acid	I <sub>2</sub>	Cis	4.5, 4.18
Methyl nervonate	I <sub>2</sub>	Cis	4.5, 4.18
Olive oil	I <sub>2</sub>	Cis	4.5
Cottonseed oil	I <sub>2</sub>	Cis	4.5
Dioleoyl lecithin	I <sub>2</sub>	Cis	4.5
Egg lecithin	I <sub>2</sub>	Cis	4.5
Beef heart lecithin	I <sub>2</sub>	Cis	4.5
Controls			
Arichidic acid	I <sub>2</sub>	Satd	
Behenic acid	I <sub>2</sub>	Satd	
Ethyl myristate	I <sub>2</sub>	Satd	
Tristearin	I <sub>2</sub>	Satd	
Dipalmitoyl lecithin	I <sub>2</sub>	Satd	

The iodine was allowed to react at 20° with the olefins for periods up to 10 days with periodic spectra of the samples being recorded. All of the olefins showed extensive conversion to their respective diiodides but the trans isomers reacted noticeably slower than the cis isomers. The cis compounds showed immediate formation of diiodide compound with 50% conversion occurring in as little as 60 min. Under these conditions the final conversion to diiodide ranged from 70 to 90% for periods up to 10 days. Loss of solvent prevented measurements of longer duration.

The reaction was followed by the disappearance of the olefin peak (5.4 ppm) and by the simultaneous appearance of a halogenated methine proton (4.1–4.5 ppm). Without decoupling, these bands appeared as weak, diffuse triplets. Since the methylene protons vicinal to both the olefinic and halogenated methine protons have chemical shifts in the 1.7–2.0-ppm range, a single H<sub>2</sub> frequency (1.9 ppm) was sufficient simultaneously to decouple both of the protons being studied. The total integral for the olefinic and methine protons remained constant.

As Table I shows, the iodinated methine proton resulting from the cis isomers gave similar chemical shifts regardless of the compound employed. The trans compounds also gave consistent but different shifts for the methine proton. The saturated compounds showed no changes in their nmr spectra over a period of many days. The dibromo compounds gave similar but smaller differences between the cis and trans adducts.

During the course of the iodination of the cis olefins, an unusual phenomenon occurred. Between the second and third days of the iodination, a second halogenated methine band was observed at higher field than the original band. Between the second and tenth days, this band continued to grow at the expense of both the olefinic and initial methine peaks. Again the total integral of the three peaks remained constant. Eventually, most of the original methine band was lost and the new peak predominated. The chemical shift of this new peak (4.16 ppm) was coincidental with that observed for the iodinated trans olefins and was tentatively assigned as such. A similar interconversion of the trans-diiido compound was not observed.

To verify this apparent isomerization, parallel experiments were run using gas chromatography. A column was

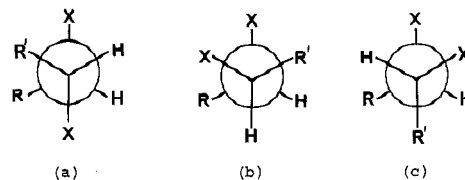


Figure 1. Three rotamers.

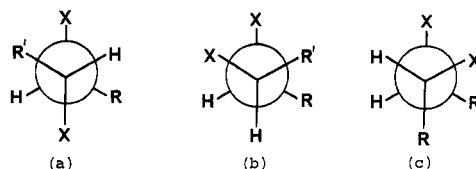


Figure 2. Erythro rotamers.

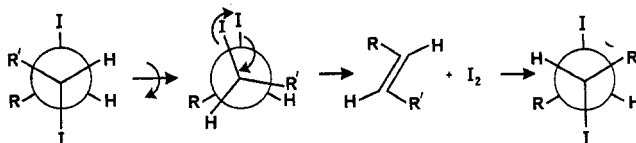


Figure 3. Cis elimination mechanism.

found which could separate methyl oleate (cis) from methyl elaidate (trans). The methyl oleate was partially iodinated for several hours and checked by nmr to verify that no rearrangement had occurred. This sample was then analyzed by glc; only one peak was observed, indicating that the diiodo compound was thermally degraded to oleate without rearrangement. Samples of diiodide containing varying amounts of isomeride were then subjected to simultaneous thermal degradation and glc analysis and in every case the nmr ratio of oleate to elaidate was the same by both methods.

## Discussion

It is apparent from the chemical shifts of the *cis*- and *trans*-diiido adducts that the addition must be occurring stereospecifically. That the addition is probably *trans* is inferred by analogy with bromine<sup>5</sup> and chlorine addition reactions. Anet<sup>12</sup> and Bothner-By<sup>13</sup> used nmr to study the dibromobutanes. They demonstrated that a proton gauche to a methyl group and a bromine atom will resonate at higher field than will a proton gauche to a hydrogen and a bromine. In Figure 1 the relevant conformers for the *trans* addition product of iodine to a *cis* olefin are shown. Conformer 1a probably makes the greatest contribution since in this form the iodines are anti to each other. In this conformer, the methine proton is gauche to a proton and an iodine and the result should be a deshielded proton. That this isomer gives the most deshielded methine proton permits its assignment as the threeo compound.

Figure 2 depicts the conformers which would result from the *trans* addition of iodine to a *trans* olefin. In this case conformer 2a fits the observed spectrum best. The chemical shift (at high field) correlates well with those seen for the other dihalides and this conformer is obviously the most stable since it again has the iodine atoms anti to each other as well as the alkyl groups. It then follows that iodination of *trans* olefins leads to erythro isomers.

In the observed isomerization reaction, the three diiodo compound is slowly converted into its erythro isomer. Assuming *trans* addition, the conversion must be occurring via *cis* elimination followed by a second *trans* iodination as shown in Figure 3. This *trans* addition–*cis* elimination mechanism accounts for the isomerization of *cis* olefins to

trans olefins. Further support for this mechanism comes from the observation that the olefin isomerization seems to occur only from cis to trans and not the reverse. If conformers **1a** and **2a** (the two most stable for the threo and erythro compounds) are compared, it is apparent that **2a**, the erythro compound, is more stable than **1a**, the threo compound. Thus the isomerization would be most likely to proceed in the direction leading to the more stable compound.

The obvious differences between the "dark" reaction studied here and the light-catalyzed reaction studied by others argues for two fundamentally different mechanisms, namely, ionic and free radical. Although none of the work reported here unambiguously indicates an ionic reaction course, it seems reasonable to so assign it until such time as it can be more definitely established.

As a result of these studies and earlier ones, it now appears that the addition of iodine to double bonds occurs trans regardless of whether the mechanism is free radical or ionic. In the reverse reaction, however, elimination of halogen can occur either trans (free radical) or cis (ionic).

### Experimental Section

**Materials.** *trans*-2-Pentene was prepared by the dehydration of 2-pentanol; the product was fractionated and analyzed by gas chromatography. *trans*-4-Octene (99%) was obtained from the Aldrich Chemical Co. Oleic, nervonic, and elaidic acids were obtained from Applied Science Laboratories, Inc. All other esters were secured from Supelco Inc. All compounds were checked by nmr.

The dibromo adducts were all prepared by the slow addition of a bromine solution (in  $\text{CHCl}_3$ ) to the olefins in  $\text{CHCl}_3$  in the absence of light. The products were solvent stripped to remove the slight excess of bromine and the residues were analyzed by nmr without further purification.

**Iodination Reactions.** Oleic acid was initially iodinated accord-

ing to the method of Sumrell, *et al.*<sup>6</sup> All other iodination reactions were carried out in chloroform or deuteriochloroform solutions. A Perkin-Elmer R-12 nmr spectrometer equipped with a double-resonance accessory was used for the analyses. Tetramethylsilane (TMS) was used as the internal reference standard from which all chemical shifts were measured.

**Gas-Liquid Chromatography.** Gas-liquid chromatography was performed using a Packard Model 846 with an 8 ft long glass column packed with 10% SP-2340 on 100 mesh Supelco support. Argon at 25 lb pressure was used as the carrier gas. Temperature programming was carried out from 140 to 180° at 0.5°/min. Standards obtained from various sources were used to establish the correct retention time for the methyl esters of oleic and elaidic acids. The mixture was dissolved in 5 ml of ether and 5–10  $\mu\text{l}$  was injected directly.

**Registry No.**—Iodine, 7553-56-2; bromine, 7726-95-6; oleic acid, 112-80-1; methyl oleate, 112-62-9; elaidic acid, 112-79-8; methyl elaidate, 1937-62-8; nervonic acid, 506-37-6; methyl nervonate, 2733-88-2; *trans*-4-octene, 14850-23-8.

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