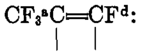
boiled at 11.5°. The n.m.r. spectrum was for  $\begin{array}{c} CF_3{}^aC{=}CF^d: \\ | \quad\ \ | \\ F_2C^b{-}CF_2{}^c \end{array}$ [(a), −16.0, (3.1)], [(b), 23.1, (2.0)], [(c), 39.8, (1.9)], [(d), 43.5, (1.0)].

Anal. Calcd. for C_5H_8: C, 28.3; F, 71.7. Found: C, 28.7; F, 71.0.

Perfluoropentyne-2 (VII) was prepared by isomerizing V or VI over CsF at 240°. In a typical reaction, 9.6 g. (0.045 mole) of V was passed over CsF at 240° in 3.6 hr. equivalent to a theoretical contact time of 150 sec. Almost pure VII was obtained in 98% conversion. It boiled at 3.5°, had mol. wt. 212 (calcd. 212), and absorbed in the infrared very weakly between 4.9–5.1 μ (believed to be characteristic of the C≡C grouping). The n.m.r. spectrum was for $CF_3{}^aC{\equiv}CCF_2{}^bCF_3{}^c$: [(a), −21.2, (3.1)], [(b), 29.7, (2.0)], [(c), 10.1, (2.9)].

Perfluorolevulinic acid (X, $CF_3COC_2F_4COOH$) was prepared from VII as follows. Into a round-bottom flask fitted with a cold head was frozen a mixture of dry acetone and $KMnO_4$. Then 7.0 g. of VII was condensed in the flask. The flask was warmed cautiously until no further reflux was noted dropping from the cold head maintained at −78°. The reaction mixture was acidified with a slight excess of H_2SO_4 and filtered. The filtrate was extracted with ether. The ether phase was vacuum stripped and a residue, amounting to 4.3 g., which boiled between 134 and 137° was obtained. This product formed an hydrozone m.p. 149.6–150.0°, readily. The infrared spectrum of the dry acid showed C=O absorptions and one OH absorption. A titration of the acid in water with standard base potentiometrically indicated two end points at about pH 2 and pH 8. Titration with an indicator of color change pH 2–3 gave a molecular weight of 266 (calcd. for the dry acid is 242 and for the hydrate $CF_3C(OH)_2CF_2CF_2COOH$ is 260). The n.m.r. spectrum of the neat, dry acid was for $CF_3{}^aCOCF_2{}^bCF_2{}^cCOOH$: [(a), 4.4, (3.0)], [(b), 41.5, (2.0)], [(c), 46.4, (2.0)].

The γ Irradiation of C_5F_8 Isomers.—Each isomer was exposed to a dose of 10^7-r. γ radiation from a cobalt-60 source. No gross changes (greater than 0.5%) were observed when 3.1 g. of VI 7.5 g. of VIII, and 10.6 g. of IX were exposed in heavy-wall glass ampoules as liquids. V (10.5 g.) under similar conditions formed about 0.5 g. of brownish polymeric substance, while half of a 6.0-g. sample of VII ($CF_3C{\equiv}CCF_2CF_3$) was converted to a soft waxy polymer which on heating began to shrink at 428° and to form a liquid at 434°. At this point the color began to darken until at 458° gas was visibly evolved as the liquid turned brown. An infrared spectrum of the powder between NaCl plates showed no absorptions in the 5.0–6.0-μ region or below.

A portion of this powdered polymer was subjected to X-ray analysis. It demonstrated to diffuse primary spacing of 8.67 ± 1.13 A. It is possible that this represents a fusion of two spacings. The second- and third-order peaks were broad and diffuse. The spectrum was scanned from 1.3–40.0 Å. with no other peaks observed. Microscopic examinations of the polymer showed the material to be isotropic with a refractive index between 1.33 and 1.40 which is high for fluorocarbon material and suggests the formation of strained rings rather than unsaturation.

Acknowledgment.—The authors are most grateful to Dr. W. S. Brey and his students for the n.m.r. spectra reported in this paper. The help of Dr. J. H. Gross of the International Minerals Corporation, Mulberry, Florida, in obtaining the X-ray spectrum of the perfluoropentyne-2 polymer is gratefully acknowledged.

Retention of Configuration in Nucleophilic Vinylic Halide Substitution. Proton Magnetic Resonance Spectra of *cis*- and *trans*-β-Styryldiphenylphosphine Oxides

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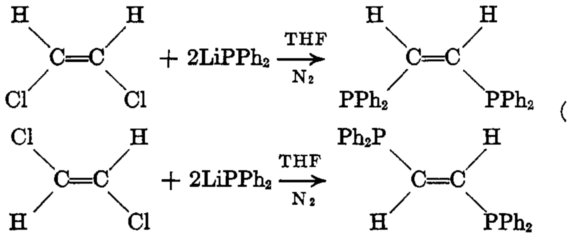
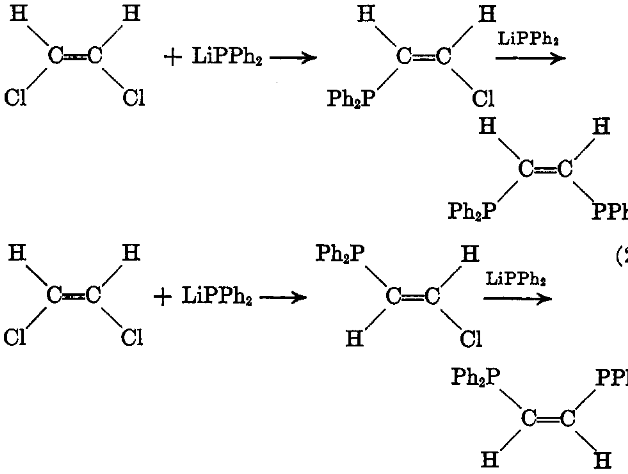
cis- and *trans*-β-bromostyrene were found to react with lithium diphenylphosphide in tetrahydrofuran to produce *cis*- and *trans*-β-styryldiphenylphosphine (isolated as the oxides), respectively, uncontaminated with the other isomer in each case. P.m.r. spectra at 60 Mc. and 100 Mc., along with "spin tickling" results at 100 Mc., are reported for these compounds. Possible mechanistic explanations for the observed retention of configuration are discussed. The addition of lithium diphenylphosphide to the styryldiphenylphosphines and oxides, giving rise to phenylethylenebis(diphenylphosphine) dioxide, is reported and discussed, as is isomerization of *cis*-β-styryldiphenylphosphine to the *trans* isomer by lithium diphenylphosphide.

We recently reported the stereospecific substitution of the vinylic chlorides in *cis*- and *trans*-1,2-dichloroethene by the diphenylphosphide ion[1] (eq. 1).



(1)

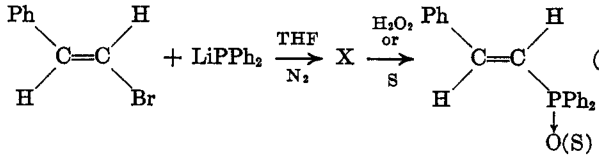
The over-all retention of configuration observed could arise from two replacements with retention of or inversion of configuration at each carbon (eq. 2).



(2)

Attempts at isolation of the possible intermediate, β-chlorovinylphosphines (or derivatives) have failed.

In an attempt at clarification of this problem, the replacement of the vinylic bromine in *trans*-β-bromostyrene by the diphenylphosphide ion was studied.[2]



(3)

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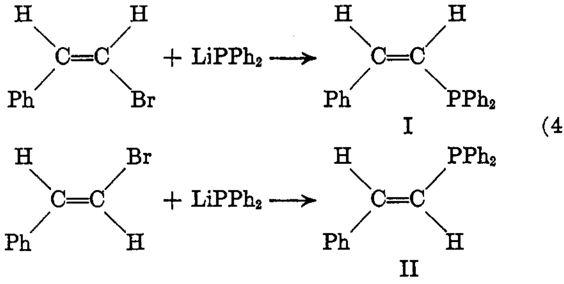
[1] A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).

[2] A. M. Aguiar and D. Daigle, *J. Org. Chem.*, **30**, 2826 (1965).

This reaction (3) led to high yields of *trans*-β-styryldiphenylphosphine oxide and sulfide (as derivatives).

Although it was shown that the starting material did not isomerize prior to reaction with the phosphide, no conclusive evidence was obtained that *trans*-β-styryldiphenylphosphine was initially produced.[2] The *cis* isomer could have been produced initially and then isomerized by the conditions employed in the reaction, derivatization, isolation or gas–liquid partition chromatographic analysis of the reaction products.[2]

We now wish to report that *cis*-β-bromostyrene reacts with lithium diphenylphosphide in tetrahydrofuran to produce *cis*-β-styryldiphenylphosphine (I) uncontaminated with *trans*-β-styryldiphenylphosphine (II) and *vice versa* (eq. 4).



(4)

Pure *cis*-β-bromostyrene, prepared by the method of Cristol and Norris,[3] reacted with lithium diphenylphosphide[4] to give *cis*-β-styryldiphenylphosphine oxide (Ia) after dilute aqueous peroxide treatment of the residual material. After recrystallization from cyclohexane, Ia melted at 103–104° and was shown (elemental analysis and molecular weight) to be isomeric with *trans*-β-styryldiphenylphosphine oxide (IIa).[2]

The proton magnetic resonance spectrum of a deuteriochloroform solution of Ia at 60 Mc. showed two broad phenyl proton complexes centered at $\delta = 7.3$ and 7.75 p.p.m., along with two small peaks at $\delta = 6.08$ and 6.4 p.p.m., and two larger ones at $\delta = 6.3$ and 6.63 p.p.m. No other bands were present between these and the resonance peak of the tetramethylsilane used as a standard. The areas of integration were approximately in a ratio of 6:10:1. The vinyl proton resonance peaks are partially hidden by the phenyl proton peaks. Griffin observed a similar four-line pattern for a vinyl hydrogen of *trans* diesters of β-styrylphosphonates.[5] He assigned the low-field vinyl proton resonance to the proton α to the phenyl group.[5]

Employing a Varian model HA-100 instrument, the two types of phenyl protons and the quartet due to one of the vinyl hydrogens in the *trans* isomer, IIa, were resolved. The "spin tickling" technique was used to locate the four hidden resonances. Assignments were made on the basis of the tilting seen within the patterns. In both Ia and IIa there is vinyl proton overlap with both sets of phenyl protons.

The magnitude of the phosphorus–proton coupling constants observed in the open four-line pattern and tabulated from the spin-tickling results are shown in Table I and are in accordance with those determined by Anderson, *et al.*, for trivinylphosphine[6] (Table I).

TABLE I

Compd.	$J_{H,H}$ (*cis*)	$J_{H,H}$ (*trans*)	$J_{P,H}$ (*gem*)	$J_{P,H}$ (*cis*)	$J_{P,H}$ (*trans*)
Ia (*cis*)	14.0	. . .	19.3	. . .	40.3
IIa (*trans*)	. . .	17.4	22.3	19.5	. . .
Trivinylphosphine[a]	11.6	18.4	11.7	13.6	30.2

[a] Reference 6.

The full spectra were obtained under field-sweep operation while the spin-tickling results were run in the frequency-sweep mode. The spin-decoupling field was provided by an external audiooscillator whose frequency was counted with a 10-sec. time base.

Treatment of Ia with phosphorus trichloride did not cause isomerization.[7] Isomerization of Ia to IIa was achieved with phosphorus pentachloride.

At 190°, employing a 3% SE-30 on Chromosorb, $^1/_8$ in. × 4 ft. column, Ia has a considerably shorter retention time than IIa and is not isomerized. Similar gas chromatographic analysis of the crude reaction mixtures from the *trans*- and *cis*-β-bromostyrene runs show that no *trans*-β-styryldiphenylphosphine (II) is produced from *cis*-β-bromostyrene and that only 10% *cis*-β-styryldiphenylphosphine (I) is produced from the commercial *trans*-β-bromostyrene. The latter was shown to contain 10% *cis*-β-bromostyrene.[2]

It can therefore be concluded that substitution of the vinylic bromine in β-bromostyrenes by diphenylphosphorus in tetrahydrofuran proceeds with retention of configuration.

This would indicate that the production of *trans*-vinylenebis(diphenylphosphine) from *trans*-1,2-dichloroethene and *cis*-1,2-vinylenebis(diphenylphosphine) from *cis*-1,2 dichloroethene proceeds *via* two retentions of configuration. The intermediacy of *trans*-β-chlorovinyldiphenylphosphine and *cis*-β-chlorovinyldiphenylphosphine in the *trans*- and *cis*-1,2-dichloroethene reactions, respectively, is a necessary corollary if the replacements are assumed to occur stepwise.

An elimination–addition sequence is excluded as a possible mechanistic explanation for the replacement of vinylic chloride and bromide by diphenylphosphorus in these reactions. This is true since one and only one isomer is obtained in each case, making the postulation of a common intermediate for the reaction of *cis* and *trans* isomers untenable. Halogen–metal interchange is highly unlikely since β-chlorovinyllithium and β-styryllithium would not be expected to be stable in refluxing tetrahydrofuran. A direct displacement involving a transition state in which the vinyl carbon is rehybridized to an sp state, as suggested and dismissed by Bunnett,[8] is untenable in view of the absence of inversion.

A few other cases of vinylic halide substitution with retention of configuration are known, but none involve metalloorganophosphides.[9-12]

At present there is no conclusive evidence to allow a choice between an addition–elimination sequence or a direct displacement in any of the work reported so far.

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[3] S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 2645 (1953).

[4] A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, **27**, 1001 (1962).

[5] Private communication from Professor C. E. Griffin, University of Pittsburgh, Pittsburgh, Pa.

[6] W. A. Anderson, R. Freeman, and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1963).

[7] A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 5354 (1964).

[8] J. Bunnett, *Chem. Rev.*, **49**, 273 (1951); *Quart. Rev.* (London), **12**, 1 (1958).

[9] D. E. Jones and C. A. Vernon, *Nature*, **176**, 791 (1955).

[10] D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 2349 (1960).

[11] F. Montanari, *Tetrahedron Letters*, **No. 18** (1960).

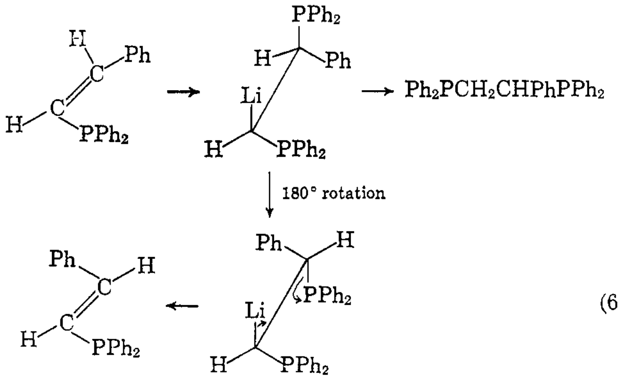
[12] S. I. Miller and P. K. Yonan, *J. Am. Chem. Soc.*, **79**, 5931 (1957).

The production of small amounts of phenylethylenebis(diphenylphosphine) dioxide (IIIa) in the reaction of *trans*-β-bromostyrene, along with its production in higher yields in the reaction of *cis*-β-bromostyrene, especially when the normal mode of addition of reagents is used, merits note. This material apparently arises through an addition of lithium diphenylphosphide to the initially produced β-styryldiphenylphosphine.

$$PhCH{=}CHPPh_2 + LiPPh_2 \longrightarrow PhCH(PPh_2)CH(Li)PPh_2 \longrightarrow \underset{IIIa}{Ph_2P(O)CHPhCH_2P(O)Ph_2} \quad (5)$$

Addition of nucleophiles to the β-carbon of vinylphosphines is known.[13] The *cis*-β-styrylphosphine apparently undergoes addition at a faster rate than the *trans* isomer.

The presence of 9% *trans*-β-styryldiphenylphosphine in the reaction products from a normal addition of reagents, along with the absence of any *trans* phosphine in the reaction mixture of an inverse addition experiment may indicate that the addition of lithium diphenylphosphide to the β-styryldiphenylphosphine is reversible in the absence of a good protonating agent.



(6)

Either a *cis* addition followed by a *trans* elimination, as shown in eq. 6, or the reverse, would lead to isomerization of the *cis*-β-styryldiphenylphosphine.

In separate experiments, the *cis*- and *trans*-β-styryldiphenylphosphine oxides underwent the addition of lithium diphenylphosphide easily.

Experimental Section

Reaction of Lithium Diphenylphosphide with *cis*-β-Bromostyrene. Inverse Addition of Reagents.—To a dilute solution of 14.5 g. (0.0794 mole) of *cis*-β-bromostyrene[8] in tetrahydrofuran was added, under nitrogen, a solution of lithium diphenylphosphide in tetrahydrofuran made from 13.1 g. (0.05 mole) of triphenylphosphine,[4] at room temperature over 1.2 hr. Decolorization of the phosphide was immediate upon contact with the bromostyrene solution. A slight exothermic effect was noted.

Samples of 1 to 2 μl. of this reaction solution were injected into a Microtek Model DSS, dual-column, flame-ionization, gas-liquid partition chromatograph containing $^1/_8$ in. × 4 columns packed with Chromosorb having 3% SE-30 as the liquid phase. The injector block was at 250°, the column oven at 190°, and the detector block at 250°.

Aside from peaks due to solvent, other volatile components such as bromostyrene, and triphenylphosphine and its oxide (from the preparation of lithium diphenylphosphide),[4] only two peaks of long retention time were obtained. These peaks had areas indicating that they represented the major components. The material with the longer retention time was present in less abundance than the material with shorter retention time and was identified as *cis*-β-styryldiphenylphosphine oxide by comparison of retention times with authentic *cis*-β-styryldiphenylphosphine oxide isolated from the reaction mass after oxidation with 3% hydrogen peroxide. The shorter retention time major component is undoubtedly *cis*-β-styryldiphenylphosphine.

Similar analysis of the reaction mixture from commercially obtained *trans*-β-bromostyrene (shown to contain 10% *cis*) and lithium diphenylphosphide showed the same two peaks as the *cis*-β-bromostyrene reaction mixtures, as well as two other, longer retention time peaks identified as *trans* phosphine and oxide. The ratio of *cis* to *trans* peaks was 1 to 9.[2]

Evaporation of solvent and other volatile materials, oxidation of the reaction mixture with 3% hydrogen peroxide, and subsequent extraction with chloroform and trituration with ether, led to the isolation of *cis*-β-styryldiphenylphosphine oxide, m.p. 103–104°, in 25% yield after recrystallization from cyclohexane. The proton magnetic resonance is discussed in the body of this article.

Anal. Calcd. for $C_{20}H_{17}OP$: C, 78.93; H, 5.63; P, 10.17; mol. wt., 304. Found: C, 78.34; H, 5.62; P, 10.83; mol. wt., 275.3.

Acidification of the basic aqueous layer gave diphenylphosphinic acid in 18% yield.

Gas chromatographic analysis of the ether solution showed the presence of 21% more *cis*-β-styryldiphenylphosphine, as well as 12% triphenylphosphine (from the original preparation of lithium diphenylphosphide).

From this ethereal solution was obtained a small amount of solid identified as phenylethylenebis(diphenylphosphine) dioxide. This material did not pass through the column under the conditions employed in the gas chromatographic analysis.

Isomerization of *cis*-β-Styryldiphenylphosphine Oxide to *trans*-β-Styryldiphenylphosphine Oxide.—A small sample of *cis*-β-styryldiphenylphosphine oxide was refluxed with phosphorus pentachloride in dry benzene under nitrogen for 0.5 hr., cooled, and poured into water; the benzene was allowed to evaporate. The water-insoluble solid thus obtained was triturated with cyclohexane and then recrystallized from ethanol and water. This material was found to be identical with *trans*-β-styryldiphenylphosphine oxide by mixture melting point determinations, infrared spectra, and proton magnetic spectral comparison with authentic material.

Reaction of Lithium Diphenylphosphide with *cis*-β-Bromostyrene. Normal Addition of Reagents.—The same procedure as described for the inverse addition of these reagents was used, except that the halide was added to the phosphide. After oxidation with 3% hydrogen peroxide, the aqueous layer was acidified and a 20% yield of diphenylphosphinic acid was obtained. The water-insoluble semisolid was washed with dilute sodium hydroxide and then water until neutral and dried (18 g.). It was recrystallized twice from ethanol and water, then benzene, and finally ethanol and water again to give a solid which was identified as phenylethylenebis(diphenylphosphine) dioxide in 16.0% yield.

All of the remaining solutions and sirups were subjected to gas chromatographic analysis, giving the following yield picture: triphenylphosphine, 3.5%; triphenylphosphine oxide, 5.8%; *cis*-β-styryldiphenylphosphine and oxide, 16.4%; *trans*-β-styryldiphenylphosphine and oxide, 9.1%; total, 34.8%. The approximately 10% of triphenylphosphine and oxide is expected from the preparation of lithium diphenylphosphide.[4] A total material balance of 70–71% may be due to the presence of more low-volatility material such as phenylethylenebis(diphenylphosphine) dioxide which would not pass through the column.

Phenylethylenebis(diphenylphosphine) Dioxide from Lithium Diphenylphosphide and β-Bromo-β-phenylethyldiphenylphosphine Oxide.—A solution of lithium diphenylphosphide in tetrahydrofuran made from 3.2 g. (0.012 mole) of triphenylphosphine was added dropwise to a solution of β-bromo-β-phenylethyldiphenylphosphine oxide,[2] under nitrogen, until no further decolorization occurred. Addition of aqueous peroxide led to an exothermic reaction and finally the precipitation of solid. The 2.7 g. of solid thus obtained had m.p. 277–278°.

Anal. Calcd. for $C_{32}H_{28}O_2P_2$: C, 75.89; H, 5.53; P, 12.25. Found: C, 75.29; H, 5.62; P, 12.75.

The infrared spectrum of a KBr pellet of this material exhibited the usual peaks for a tertiary phenylphosphine oxide.

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[13] M. I. Kabachnik, E. N. Tsvetkov, and C. C. Yu, *Tetrahedron Letters*, 5 (1962).

The 60-Mc. proton n.m.r. spectrum of a trifluoroacetic acid solution showed a phenyl complex extending from $\delta = 7.1$ to 8.3 p.p.m., as well as two other broad bands at $\delta = 4.5$ and 3.5 p.p.m. The latter were in the ratio of 1:2 and were assigned to the methinyl and methylene protons, respectively.

Reaction of Lithium Diphenylphosphide and *trans*-β-Styryldiphenylphosphine Oxide.—To a solution of lithium diphenylphosphide in tetrahydrofuran, made from 1.97 g. (0.0075 mole)[4] of triphenylphosphine, was added 2.0 g. (0.0066 mole) of *trans*-β-styryldiphenylphosphine oxide. After refluxing for 20 min., the solution had decolorized to a light yellow. Addition of 3% peroxide, followed by evaporation of the tetrahydrofuran, led to a precipitate. Filtration and drying of this precipitate gave 2.9 g. of phenylethylenebis(diphenylphosphine) dioxide, as shown by melting point, mixture melting point, infrared spectra, and proton magnetic resonance spectral comparison with authentic material. Acidification of the aqueous filtrate gave little diphenylphosphinic acid.

Reaction of Lithium Diphenylphosphide and *cis*-β-Styryldiphenylphosphine Oxide.—To a solution of lithium diphenylphosphide in tetrahydrofuran produced from 1.97 g. (0.0075 mole) of triphenylphosphine was added a solution of 2.0 g. (0.0066 mole) of *cis*-β-styryldiphenylphosphine oxide, and the reaction mixture was refluxed for 1 hr. The red color was slowly discharged. Addition of water, followed by evaporation of tetrahydrofuran, led to a precipitate which was filtered off. The aqueous filtrate was acidified with dilute hydrochloric acid. Little precipitate was obtained. The water-insoluble solid (2.5 g.) was recrystallized from ethanol and water and found to be phenylethylenebis(diphenylphosphine) dioxide by mixture melting point determination, infrared spectra, and proton magnetic resonance spectral comparison with authentic material.

Acknowledgment.—This work was initiated under Grant 1466-B from the Petroleum Research Fund of the American Chemical Society and continued under National Science Foundation Grant GP-3823. All of the 60-Mc. proton magnetic resonance spectra were obtained by Mr. Gordon Boudreaux of the Cotton Physical Properties Division of U. S. Southern Regional Utilization and Research Laboratories at New Orleans, Louisiana. The 100-Mc. proton magnetic resonance spectra were kindly supplied by Mr. LeRoy F. Johnson, manager of the Spectroscopy Applications Laboratory, Analytical Instrument Division of Varian Associates, Palo Alto, California. We wish to acknowledge the National Aeronautics and Space Administration for supplying the funds for the Micro-Tek Model DSS gas chromatograph used in this work.

Alumina: Catalyst and Support. XXIV.[1] Discussion of the Mechanism of the Aromatization of Alkanes in the Presence of Chromia–Alumina Catalysts[2,3]

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Received June 8, 1965

The mechanism of aromatization of alkanes over chromia–alumina catalysts is reviewed. The experimental results reported by early investigators were re-examined in view of an inadequate description of the nature of alumina they used in the preparation of their catalysts and of the inadequacy of analytical tools. The importance of the nature of aluminas used in the preparation of the catalysts on the formation and the distribution of the reaction product is discussed. The use of C^{14}-labeled alkanes and the distribution of the C^{14} in the aromatics produced assisted in obtaining a clearer picture of the mechanism of aromatization. The participation of six-, seven-, and eight-membered-ring-adsorbed species in the aromatization of C_8 alkanes is discussed. A free-radical mechanism is postulated for methyl-carbon insertion accompanying the dehydrogenation of methylalkanes. The distribution of the cracking products accompanying the aromatization of alkanes is explained by a radical mechanism.

The catalytic aromatization of paraffins over chromia catalysts was discovered independently by Moldavsky and Kamuscher[4] and by Grosse, *et al.*[5,6] At about the same time Kazansky and Plate[7] reported that, at 350°, platinum catalysts are able to aromatize alkanes.

The catalytic aromatization of *n*-heptane over chromia at about 500° yielded large amounts of toluene. The obvious industrial importance of this reaction for converting low-octane-rated hydrocarbons into high-octane-rated aromatics, along with the possible synthesis of individual aromatic compounds, aroused considerable interest and study. Concerning the many aspects of this reaction, much study has been given to the mechanism of catalytic aromatization by a number of investigators. The complexity of the reaction will be shown in this and the following papers. However, in order to arrive at a common basis of understanding for this reaction, a condensed survey of the relevant previous work will be given.

The Catalysts. A. General.—The dehydrocyclization of paraffins is thermodynamically unfavorable at moderate temperatures. On the other hand, owing to the high stability of the aromatic ring, this unfavorable equilibrium can be displaced almost quantitatively in favor of the aromatic hydrocarbons at temperatures above 300° providing a suitable catalyst for ring closure is used. Such a catalyst must activate the carbon–hydrogen bond but not the carbon–carbon bond rupture. Taylor and Turkevich[8] have shown that metal dehydrogenation catalysts such as Fe, Ni, and Co would be of little utility owing to their tendency to break carbon–carbon bonds. However, the oxide catalysts, principally chromium oxide, are ideally suited as catalysts in aromatization. It has been shown[9,10] that acti-

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(1) For paper XXIII, see J. Manassen and H. Pines, Proceedings of the 3rd International Congress in Catalysis, Amsterdam, 1964, North-Holland Publishing Co., Amsterdam, 1965, pp. 845–856.

(2) Paper XIII of the series "Aromatization of Hydrocarbons"; for paper XII, see C. T. Goetschel and H. Pines, *J. Org. Chem.*, **29**, 399 (1964).

(3) This work was supported by Atomic Energy Commission Contract AT(11-1)-1096.

(4) B. L. Moldavsky and H. D. Kamuscher, *Compt. rend. Acad. Sci., USSR*, **1**, 355 (1936).

(5) A. V. Grosse and J. C. Morrell, U. S. Patents 2,124,566, 2,124,567, and 2,124,583–2,124,586 (July 1938), applied for Sept.–Oct. 1936.

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(9) J. Turkevich and H. S. Taylor, *J. Am. Chem. Soc.*, **56**, 2254 (1934).

(10) J. Howard and H. S. Taylor, *ibid.*, **56**, 2259 (1934).