An approximate solution to 1, 2 and 3 based on perturbation methods is

$$\lambda\ (\mathrm{C{=}C}) = f_3 + \frac{[(k_{12} - d_1 - d_2)\cos^2\beta + (d_1 + d_2)]^2}{m_1 m_2\ (f_3 - f_2)} + \frac{(k_{12} - d_1 - d_2)^2}{m_1 m_2 (f_3 - f_1)}\left(1 + \frac{m_2}{m_1}\right)\sin^2\beta\cos^2\beta \qquad (4)$$

where

$$f_3 = \frac{(k_{12} - d_1 - d_2)\cos^2\beta + 2k_{22} + d_1 + d_2}{m_2}$$

$$f_2 = \frac{(k_{12} - d_1 - d_2)\cos^2\beta + 2k_{11} + d_1 + d_2}{m_1}$$

$$f_1 = \frac{[(k_{12} - d_1 - d_2)\sin^2\beta + d_1 + d_2][1 + m_2/m_1]}{m_2}$$

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, AMERICAN OIL CO., WHITING, IND.]

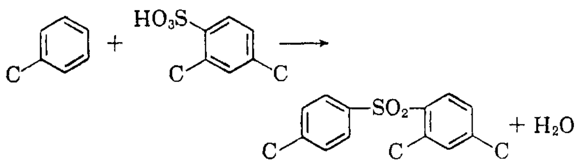
Transsulfonation in Preparing Aromatic Sulfones

BY HARALD DREWS, SEYMOUR MEYERSON AND ELLIS K. FIELDS

RECEIVED APRIL 12, 1961

The reaction of an arenesulfonic acid with an arene has generally been assumed to give the sulfone derived from both reactants. However, treating *p*-toluenesulfonic acid with *o*-xylene gives considerable dixylyl sulfone in addition to tolyl xylyl sulfone. Likewise, *p*-xylenesulfonic acid with toluene gives ditolyl and dixylyl sulfones in a total yield almost as great as that of the expected tolyl xylyl species. Further, the product mixture contains also *p*-xylene and *p*-toluenesulfonic acid. Because the over-all reaction involves the transfer of a sulfonic acid group from one hydrocarbon to another, it is referred to as "transsulfonation." It is a new addition to the class of reactions—such as transcarbonylation and transbenzylation—in which functional groups are transferred from one aromatic nucleus to another.

A general method for preparing diaryl sulfones was described by Meyer[1] nearly forty years ago. He claimed that symmetrical diaryl sulfones result from reaction of sulfuric acid with an arene, and that unsymmetrical sulfones result from reaction of an arenesulfonic acid with another arene. For example, he reported that *m*-xylenesulfonic acid with toluene gives *p*-tolyl *m*-xylyl sulfone



However, the reaction of *p*-xylenesulfonic acid with toluene actually gives ditolyl and dixylyl sulfones, besides the expected *p*-tolyl xylyl sulfone and its *o*-tolyl isomer.[2]

This unexpected result appears to involve "transsulfonation," that is, the transfer of a sulfonic acid group from one aromatic nucleus to another. The scope of transsulfonation has therefore been explored by treating three arenesulfonic acids separately with four different arenes, treating an arenesulfonic acid with a sulfone, and pyrolyzing two arenesulfonic acids. In three further experiments, one essential feature of the Meyer procedure was altered—in two cases, by using a lower temperature; in the third, by not removing the water formed in the reaction—and the reaction mixture was examined for evidence of transsulfonation. Identification of reaction products was made possible by new analytical tools not available to Meyer.

Experimental

The transsulfonation studies were carried out in a reaction flask in which hydrocarbon vapor was passed through a molten sulfonic acid.[1] Excess hydrocarbon together with entrained water from the reaction was continuously condensed, dried over calcium chloride, vaporized, and recycled to the sulfonic acid.

All reasonable efforts were made to ensure high purity of starting materials. Toluene and benzene, Mallinckrodt analytical reagent grade, and Phillips Pure grade *o*-xylene were found by gas chromatography to be free of the other homologs and were used without further treatment. Eastman *p*-toluenesulfonic acid was recrystallized from dilute hydrochloric acid to remove benzenesulfonic acid. Eastman benzenesulfonic acid contained traces of *p*-toluenesulfonic acid not removable by fractional recrystallization. *p*-Xylenesulfonic acid was prepared by sulfonation of *p*-xylene, Matheson Coleman & Bell, found by gas chromatography to be free of toluene and benzene. The acid was recrystallized twice from dilute hydrochloric acid; it contained two moles of water, melted at 83°, and had an acid number of 250. Toluenesulfonyl chloride and the xylenesulfonyl chlorides, Eastman white label grade, were used as purchased for synthesis of authentic sulfones.

Products were analyzed by appropriate physical methods: hydrocarbons by gas chromatography; sulfonic acids by infrared absorption; and sulfones by mass spectrometry. The last method was found to be highly sensitive, not only to differences in molecular weight, but also to structural differences among isomeric sulfones.

To calibrate the mass spectrometer, seven authentic sulfones were synthesized by the Friedel-Crafts reaction of a sulfonyl chloride with an aromatic hydrocarbon,[3,4] as summarized in Table I. In a typical synthesis, 100 g. of 2,5-dimethylbenzenesulfonyl chloride dissolved in 120 ml. of *p*-xylene was dropped into a 1-liter four-necked flask containing 200 ml. of *p*-xylene and 30 g. aluminum chloride, maintained as a slurry by rapid stirring, at 35° over 1 hour. During addition of the sulfonyl chloride, 50 g. more of aluminum chloride was added in two portions. The reaction mixture was then heated for 2 hours at 65° and poured onto crushed ice. The sulfone was collected on a filter; crystallization from alcohol gave 78.6 g. of product melting at 138°. After two more crystallizations from alcohol, it melted at 144°. The mass spectrum revealed no components other than dixylyl sulfone.

Six sulfones not reported in Table I were also used in calibration. Diphenyl and di-*p*-tolyl sulfones were Eastman products, recrystallized. Synthesis of the others—di-*o*-tolyl, *o*-tolyl *p*-tolyl, *p*-xylyl *o*-tolyl and *m*-xylyl *p*-tolyl sulfones—will be reported in a subsequent publication.

Meyer's procedure[1] was employed in preparing sulfones by the reaction of an arenesulfonic acid with an arene. In a typical experiment, 225 g. of *p*-xylenesulfonic acid dihydrate was heated for 6 hours at 100° at about 130 mm. to dehydrate the acid. The anhydrous acid was put in the recycle apparatus and toluene was circulated through the

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(1) H. Meyer, *Ann.*, **433**, 327 (1923).

(2) H. Drews, S. Meyerson and E. K. Fields, *Angew. Chem.*, **72**, 493 1960).

(3) S. C. J. Olivier, *Rec. trav. chim.*, **33**, 91 (1914); **35**, 109 (1915).

(4) G. Holt and B. Pagdin, *J. Chem. Soc.*, 2508 (1960).

TABLE I

FRIEDEL-CRAFTS SYNTHESIS OF AUTHENTIC SULFONES

Diphenyl sulfone	Benzenesulfonyl chloride, g.	Hydrocarbon, ml.	Mole ratio	AlCl$_3$, g.	Temp., °C. Start/end	Yield		M.p., °C.[a]		Carbon, % Calcd. Found	Hydrogen, % Calcd. Found	Sulfur, % Calcd. Found
						Wt., g.	Mole, %	This work	Lit.			
2,5,2',5'-Me$_4$	2,5-Dimethyl, 100	*p*-Xylene, 300	1:5	80	35/65	62	45	144	[b]	70.0 69.8	6.6 6.8	11.7 11.3
2,4,2',4'-Me$_4$	2,4-Dimethyl, 100	*m*-Xylene, 300	1:5	80	35/55	60	45	122	121[c]	70.0 70.1	6.6 6.8	11.7 11.6
3,4,3',4'-Me$_4$	3,4-Dimethyl, 30	*o*-Xylene, 200	1:11	24	35/65	12	30	162	[d]	70.0 70.2	6.6 6.8	11.7 11.6
2,5,3',4'-Me$_4$	2,5-Dimethyl, 100	*o*-Xylene, 310	1:5	80	45/70	80	59	133	[d]	70.0 69.7	6.6 6.8	11.7 11.6
2,5,4'-Me$_3$	2,5-Dimethyl, 100	Toluene, 300	1:6	80	35/65	72	57	105	108–110[e]	69.2 69.7	6.2 6.6	12.3 12.3
3,4,4'-Me$_3$	4-Methyl, 100	*o*-Xylene, 165	1:3	80	55/55	73	54	130	131[e]	69.2 69.3	6.2 6.3	12.3 12.3
2,5-Me$_2$	2,5-Dimethyl, 50	Benzene, 200	1:9	40	35/50	26	40	106	111–112[e]	68.3 67.7	5.7 5.9	13.0 13.0

[a] Recrystallized from alcohol or acetic acid. [b] A. Tohl and O. Eberhard, *Ber.*, **26**, 2943 (1893), have prepared this compound but give no melting point. [c] See ref. 1. [d] New compound. [e] H. Burton and P. F. G. Praill, *J. Chem. Soc.*, 887 (1955).

TABLE II

SULFONES FROM ARENESULFONIC ACIDS AND ARENES

Reactants		Yield of crude sulfone, mole %	Diphenyl sulfones, vol. %	
Sulfonic acid	Hydrocarbon		Normal	Transsulfonation
p-Xylenesulfonic acid dihydrate	Toluene	31	2,5,4'-Me$_3$, 45 2,5,2'-Me$_3$, 8	2,5,2',5'-Me$_4$, 7 4,4'-Me$_2$, 29 2,4'-Me$_2$, 11
Benzenesulfonic acid	*p*-Xylene	37	2,5-Me$_2$, 98	2,5,2',5'-Me$_4$, 2 Unsubstituted, 1
p-Xylenesulfonic acid	Benzene	37	2,5-Me$_2$, 56	2,5,2',5'-Me$_4$, 15 Unsubstituted, 29
p-Toluenesulfonic acid	*o*-Xylene	47	3,4,4'-Me$_3$, 73 2,3,4'-Me$_3$, 7	3,4,3',4'-Me$_4$, 20 4,4'-Me$_2$, 0.3
p-Xylenesulfonic acid	*o*-Xylene	41	2,5,3',4'-Me$_4$, 41[a]	2,5,2',5'-Me$_4$, 1[a] 3,4,3',4'-Me$_4$, 38[a]

[a] Rough analysis, ignoring isomers other than those listed.

system at 135°. After 3 hours, the temperature was raised to 175° and kept at 175 to 180° for 4 hours. The cooled reaction mixture was extracted with 1500 ml. of water; evaporation of the water extract gave 135 g. of sulfonic acid. The water-insoluble portion was recrystallized twice from alcohol and gave 37 g. of sulfone melting at 95°. The alcoholic mother liquors were evaporated under vacuum and gave 45 g. of residue. This residue and the crystallized end-product were subjected to mass-spectral analysis. The over-all yield of sulfone in this run, 82 g., corresponded to 31 mole % conversion.

Table II shows product yields and compositions. The latter are reported in terms of liquid volume per cent. This is the form in which quantitative results are most conveniently obtained, because samples and calibrating materials to be introduced to the spectrometer are measured simply by charging a fixed liquid volume.[5] Concentrations found totaled 100 ± 3% and have been normalized to total 100% for all the product mixtures except that from *p*-xylenesulfonic acid and *o*-xylene. In this case, other possible tetramethyldiphenyl sulfones—the 2,5,2',3'-, 3,4,-2',3'-, and 2,3,2',3'-isomers—were ignored because reference materials for calibrations were not available. The large discrepancy between total sulfones found and 100%, as well as poor balances on peaks used for internal checks, showed that other isomers were in fact present. Thus, the analysis reported is no more than a crude approximation to the actual composition. In one other case—2,3,4'-trimethyldiphenyl sulfone from the reaction of *p*-toluenesulfonic acid and *o*-xylene—no reference material was available to calibrate the spectrometer. Analysis of the product mixture was made by substituting the spectrum of the 2,4,4'-isomer, because examination of the spectra of available diaryl sulfones suggested that the two compounds should give rather similar spectra. Good internal checks may be taken as indications that no gross error resulted from the approximation.

To see if a sulfonic acid can transsulfonate with a sulfone, a mixture of 65 g. of dehydrated *p*-toluenesulfonic acid and 30 g. of di-*p*-xylyl sulfone was stirred at 180° for 5 hours. During this period, 9.8 g. of hydrocarbon was distilled overhead; gas chromatography showed it to be 91.5% toluene and 8.5% *p*-xylene. The water-insoluble part of the reaction mixture, recrystallized from alcohol, gave 11 g. of original di-*p*-xylyl sulfone, m.p. 142°. The alcoholic mother liquor was evaporated under vacuum. Analysis of the residue showed it to be a mixture of three newly formed diphenyl sulfones: 2,5,4'-Me$_3$, 55 vol. %; 4,4'-Me$_2$, 34 vol. %; and 2,4'-Me$_2$, 11 vol. %. Clearly, transsulfonation had taken place.

Meyer's procedure calls for a rather high reaction temperature—about 180°. To determine whether transsulfonation products might be due in part to pyrolysis, 30 g. of *p*-xylenesulfonic acid was held for 4 hours at 180°. No volatile products were detected, although the color darkened somewhat. After 2 hours at 210°, the acid gave 7 g. of *p*-xylene. Water extraction of the decomposition product left 4.3 g. of insoluble material, m.p. 135°. Recrystallization from alcohol gave white crystals, m.p. 140°. The substance showed no melting-point depression when mixed with di-*p*-xylyl sulfone; identity of the material was confirmed by infrared and mass spectrometry.

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[5] H. M. Grubb, C. H. Ehrhardt, R. W. Van der Haar and W. H. Moeller, 7th Annual Meeting of ASTM Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May, 1959.

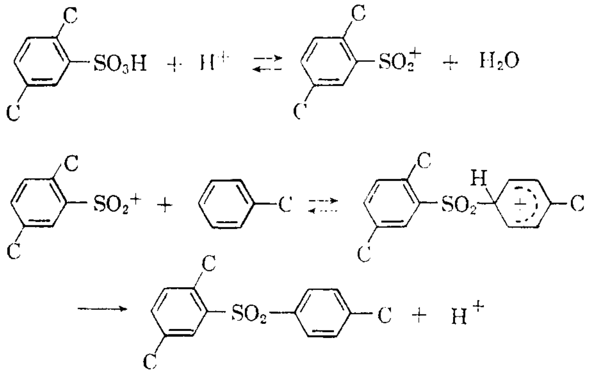
Pyrolyzing 30 g. of dehydrated *p*-toluenesulfonic acid for 5 hours at 190 to 220° gave 3.4 g. of toluene. An insoluble coke-like material remained. Mass spectrometry indicated di-*p*-tolyl sulfone and a small amount of *o*-tolyl *p*-tolyl sulfone, comprising together about 1% of the decomposition product.

To determine whether transsulfonation occurs at lower temperature, 48 g. of anhydrous *p*-xylenesulfonic acid suspended in 500 ml. of toluene was refluxed at 110° for 26 hours. No free *p*-xylene could be found in the recovered hydrocarbon. The recovered acid was solely *p*-xylenesulfonic acid. A similar experiment in which 50 g. of *p*-toluenesulfonic acid was refluxed with an 18-mole excess of *o*-xylene for 6.5 hours also showed no reaction.

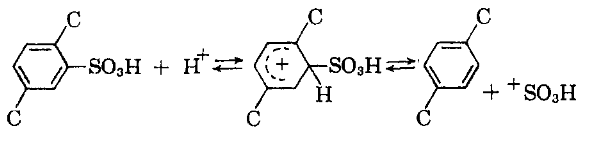
To determine whether transsulfonation takes place if water is not removed and sulfones not formed, 149 g. of dehydrated *p*-xylenesulfonic acid was treated with 500 ml. of toluene for 7.5 hours at 180° in the Meyer apparatus but without calcium chloride. The water produced was thus returned to the reaction flask. The sulfonic acid (141 g.) obtained by water-extraction proved to be a mixture of *p*-xylenesulfonic acid and *p*-toluenesulfonic acid of roughly 45:55 composition. Recrystallization from alcohol of the water-insoluble part of the reaction mixture yielded 0.5 g. of di-*p*-tolyl sulfone, m.p. 150°. Of the 390 g. of hydrocarbon recovered, 59.7 g. was *p*-xylene.

Discussion

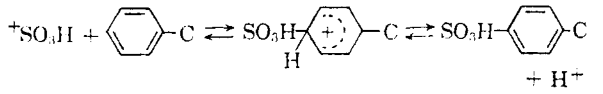
Both normal sulfone formation and transsulfonation can be explained in terms of proton and sulfonium-ion reactions. Arenesulfonium ions have been shown to exist in the reaction of benzenesulfonyl chloride with silver perchlorate to give benzenesulfonium perchlorate, and in subsequent reactions with arenes to give sulfones.[6] Thus the tolyl xylyl sulfones expected—according to Meyer—from the reaction of *p*-xylenesulfonic acid and toluene may result from reaction of the xylenesulfonic acid and a proton to give xylenesulfonium ion, followed by attack on toluene and loss of a proton



Transsulfonation apparently involves attack of a proton on xylenesulfonic acid, followed by collapse to *p*-xylene and sulfonium ion



The sulfonium ion sulfonates the toluene to give toluenesulfonic acid

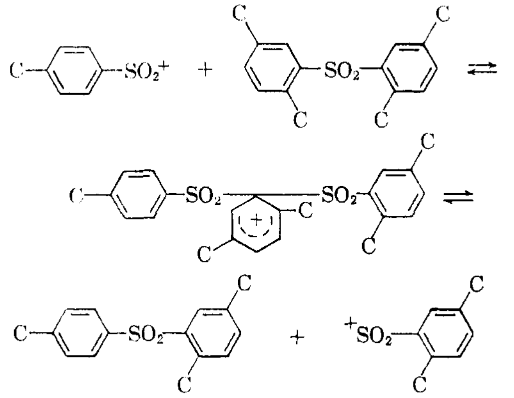


The products then are formed by reaction of *p*-xylene and toluene with the mixture of arenesulfonic acids

$$\mathrm{ArH} + \mathrm{HO_3S\text{-}Ar'} \longrightarrow \mathrm{Ar\text{-}SO_2\text{-}Ar'} + \mathrm{H_2O}$$

where Ar and Ar′ are tolyl or xylyl. *Ortho* and perhaps *meta* isomers are formed both in the sulfonation of toluene and in the reaction of the toluenesulfonic acid with more toluene.

The reaction of *p*-toluenesulfonic acid with di-*p*-xylyl sulfone to give xylyl tolyl and—by subsequent attack on the primary product—ditolyl sulfones can also be viewed in terms of attack by a toluenesulfonium ion on a sulfone



Such secondary reactions may well contribute to formation of transsulfonation products in the Meyer synthesis.

Another contributing reaction may be pyrolysis of the arenesulfonic acid. Pyrolysis of *p*-xylenesulfonic acid at 210° is appreciable and leads to formation of di-*p*-xylyl sulfone and *p*-xylene. However, little change occurs at the 180° temperature used in the Meyer reaction. Thus, pyrolysis can account for no more than a small contribution to the total reaction products.

The temperature range of transsulfonation is narrow. No appreciable reaction occurs at 145°, and temperatures high enough to cause pyrolysis lead to charring and formation of unidentified products. Water does not interfere with transsulfonation. Cycling toluene through *p*-xylenesulfonic acid without drying resulted in an insignificant yield of sulfone, but about half the xylenesulfonic acid transsulfonated to form toluenesulfonic acid and xylene.

Conclusion

Sulfone formation by the reaction of an aromatic sulfonic acid and an arene is not simple. Diaryl sulfones, known to be attacked by such strong bases as sodamide,[7] are susceptible also to electrophilic attack by sulfonium ions and protons. Such attack on both reactants and primary products gives rise to transsulfonation, leading to a variety of additional sulfones. Thus, in general, no single sulfone can be obtained in high yield or purity at the high temperatures required.

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(6) H. Burton and H. B. Hopkins, *J. Chem. Soc.*, 4457 (1952).

(7) W. Bradley, *ibid.*, 458 (1938).

(8) R. C. Fuson, G. R. Bakker and B. Vittimberga, *J. Am. Chem. Soc.*, **81**, 4858 (1959).

Transsulfonation resembles transcarbonylation[8] and transbenzylation.[9] In the former, symmetrical diaryl ketones are formed by transfer of a carbonyl group from duroic acid or duryl aryl ketones to arenes,[8] just as symmetrical sulfones are formed by transfer of a sulfone group to arenes. Transbenzylation leads to symmetrical diarylmethanes by transfer of a methylene group from a benzyl halide or an unsymmetrical diarylmethane to an arene.[9] Transsulfonation is thus part of an important larger class of functional-group transfers, operating through an electrophilic substitution mechanism.

[9] C. Serres, Jr., and E. K. Fields, *J. Am. Chem. Soc.*, **82**, 4085 (1960).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

The Hydrogenation of Cycloalkenes over Supported Palladium Catalysts

BY JAMES-FREDERICK SAUVAGE,[1] ROBERT H. BAKER AND ALLEN S. HUSSEY

RECEIVED MARCH 8, 1961

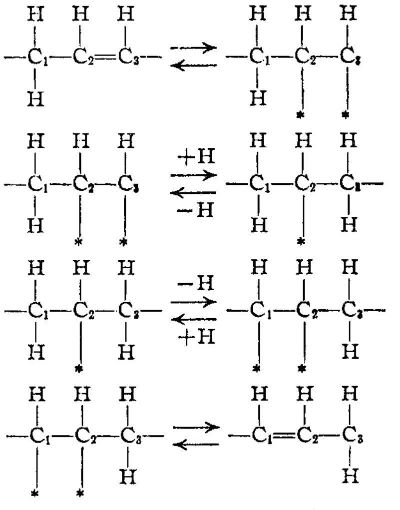
The hydrogenation of several 1,4-disubstituted cyclohexenes and $\Delta^{1,9}$- and $\Delta^{9,10}$-octalin in acetic acid solution over supported palladium catalysts has been carried out. Extensive isomerization of the unhydrogenated cycloalkenes has been observed except with $\Delta^{9,10}$-octalin. All of the cycloalkenes have furnished cycloalkane mixtures in which the more stable of the two isomers predominates. These results stand in contradistinction to the results observed when reduced platinum oxide was the catalyst.[2] A "stereochemically symmetrical intermediate" is postulated to explain the results observed.

Previously[2] we have reported the results of the hydrogenation of a number of disubstituted cyclohexenes and of $\Delta^{9,10}$-octalin in acetic acid solution over reduced platinum oxide at one atmosphere of hydrogen and room temperature. Considerable steric selectivity was observed and isomerization of the unhydrogenated cycloalkenes was observed to be very slight. Consequently, the *cis-trans* isomer ratio in the product mixtures was viewed to correspond to a steric selectivity in the adsorption of the substrate on the catalyst surface. At the same time,[3] other workers reported a similar steric selectivity on platinum catalysts, likewise with limited or insignificant isomerization of the unhydrogenated olefin. These workers offered an alternative explanation for the stereoselectivity observed with this catalyst.

We report here the hydrogenations of many of the same cycloalkenes[2] over supported palladium catalysts. The results are quite different from those observed when a platinum catalyst is used and are in agreement with those reported by Siegel and Smith[4]: hydrogenation over palladium catalysts induces extensive isomerization of the cycloalkenes and yields product mixtures in which the more stable of the two possible isomers predominates. These results are summarized in Table I as averages of replicate analyses of duplicate or triplicate hydrogenations and are reproducible to ±1%.

Discussion.—The data included in Table I show clearly that hydrogenation over supported palladium catalysts in acetic acid solution is not a straightforward addition of two hydrogen atoms to the same side of the chemisorbed substrate. That adsorption–isomerization–desorption steps may intervene before the hydrogenation process is complete seems clearly established by these data. These results are quite in accord with those reported by Siegel and Smith to result from the use of this catalyst,[4] as well as those of earlier workers.[5] The incorporation of excess deuterium and tritium atoms[6] may be the result of similar intervening isomerization, as may also be the racemization of optically active 3-phenyl-1-butene during hydrogenation.[7]

The intervention of isomerization pathways is one of the characteristic properties of a palladium catalyst which differentiates it from reduced platinum oxide. The simplest picture of such isomerizations involves four steps (in which steps 2 and 3 may be simultaneous or not, to the same result).



(1)

(2)

(3)

(4)

Another characteristic of palladium catalysts is to produce cycloalkane product mixtures in which the thermodynamically more stable isomer predominates. It has been proposed that the predom-

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[1] Abstracted in part from the Ph.D. thesis of J-F. S., September, 1959. Monsanto Co. Fellow, 1955–1957; United States Rubber Co. Fellow, 1957–1958.

[2] J-F. Sauvage, R. H. Baker and A. S. Hussey, *J. Am. Chem. Soc.*, **82**, 6090 (1960).

[3] S. Siegel and G. V. Smith, *ibid.*, 82, 6082 (1960).

[4] S. Siegel and G. V. Smith, *ibid.*, 82, 6087 (1960).

[5] H. E. Stavely and G. N. Bollenback, *ibid.*, **65**, 1600 (1943); W. G. Young, *et al.*, *ibid.*, **69**, 2046 (1947); W. M. Hamilton and R. L. Burwell, Jr., "Proceedings of the Second International Congress on Catalysis," Paris, 1960, Paper Number 44.

[6] T. F. Gallagher, *et al.*, *J. Am. Chem. Soc.*, **74**, 5280 (1952); **77**, 139 (1955); M. Gut and M. Uskokovic, *J. Org. Chem.*, **25**, 792 (1960).

[7] D. J. Cram, *J. Am. Chem. Soc.*, **74**, 5518 (1952).