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. Trans-

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

benzylation 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.

[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

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).

$$(1)$$

$$(2)$$

$$(3)$$

$$(4)$$
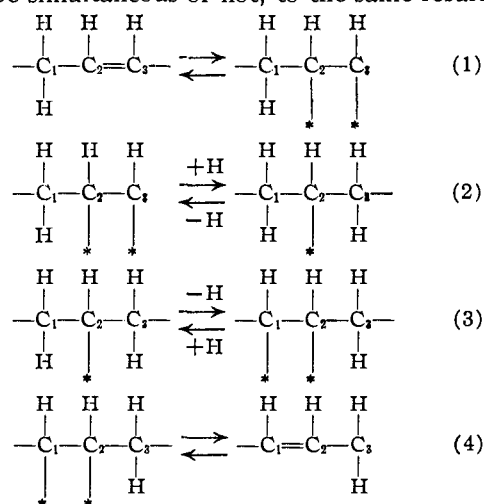
Another characteristic of palladium catalysts is to produce cycloalkane product mixtures in which the thermodynamically more stable isomer predominates. It has been proposed that the predom-

(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).

TABLE I

HYDROGENATIONS OVER CARBON-SUPPORTED PALLADIUM

	Cycloalkene	Complete hydrogenation % trans isomer[a]	% trans Isomer	Part hydrogenation[e] Cycloalkene composition
1	4-Methylmethylenecyclohexane (I)	71	71	Trace I, 99+% III
2	4-Isopropylmethylenecyclohexane (II)	76 (79)	80	Trace II, 23% IV, 77% V
3	1,4-Dimethylcyclohexene (III)	72	69	100% III
4	1-Isopropyl-4-methylcyclohexene (IV)	79	f	75% IV, 22% V, 3% IX[g]
5	1-Methyl-4-isopropylcyclohexene (V)	74 (75)[b]	79	19% IV, 81% V
6	4-Methylisopropylidenecyclohexane (VI)	82 (86)	f	75% IV, 22% VI, 3% IX[g]
7	$\Delta^{9,10}$-Octalin (VII)	90 (93)[c]	90	100% VII
8	$\Delta^{1,9}$-Octalin (VIII)	79[d]	77	100% VII[h]

[a] Hydrogenations in 95% ethyl alcohol in parentheses, all others in purified glacial acetic acid. [b] Over Pd–BaSO$_4$ in acetic acid, 73%. [c] Over Pd–BaSO$_4$ in acetic acid, 88%. [d] Over Pd–BaSO$_4$ in acetic acid, 77%. [e] Interrupted at 25 to 50% hydrogenation. [f] Analysis difficult because of overlapping peaks. [g] IX is trans-1-isopropenyl-4-methylcyclohexane. [h] At 80% hydrogenation.

inance of the more stable product isomer when palladium catalysts are used is a result of the approach to equilibrium between the several "half-hydrogenated" states corresponding to all of the isomers of a given cycloalkene.[4] This mechanism requires desorption of initially chemisorbed 1,2-dimethylcyclohexene[4] or of $\Delta^{9,10}$-octalin (VII, Table I) as 2,3-dimethylcyclohexene or $\Delta^{1,9}$-octalin (VIII), respectively, in order to accommodate the formation of the trans products which predominate.

We offer an alternative explanation for the results observed with palladium catalysts, as follows:
1. Steric factors control the geometry of the adsorption step of the original alkene on palladium catalysts very much to the same degree as on platinum.[2]
2. A fraction of the original chemisorbed alkene completes the hydrogenation process in the same geometrical conformation in which it was originally adsorbed (i.e., without an intervention of step 4 above).
3. Isomerization proceeds to a much greater degree on palladium catalysts than on platinum. However, desorption of the isomerized alkene (step 4 above) is not an important pathway when the isomer produced on the catalyst is more efficiently bound to the catalyst surface than is the original alkene: isomerized alkene appears in the bulk of the solution only when it is equally or less efficiently chemisorbed.
4. Steric factors control the geometry of the re-adsorption of isomerized alkenes and a certain fraction of such re-adsorbed, isomerized alkene completes the hydrogenation process in the same geometrical conformation in which it is re-adsorbed, as in 2 above.
5. The major part of the chemisorbed alkene, from 1 and 4 above, completes the hydrogenation process by way of a "stereochemically symmetrical intermediate" which leads to a product mixture having an equilibrium composition. This pathway to product becomes more important than direct hydrogenation (2 and 4 above) to a greater degree the less efficiently the alkene is diadsorbed on the catalyst.

While features of this mechanism are essentially in agreement with that of Siegel and Smith,[3,4] the inclusion of a "stereochemically symmetrical intermediate" in our mechanism constitutes a fundamental difference. Further, it is implicit in our

mechanism that the difference in character of palladium and platinum catalysts is one of degree and not of kind. Thus a palladium catalyst is merely more prone to isomerize alkenes and to enhance the pathway to product via a "stereochemically symmetrical intermediate" than is platinum. With the latter catalyst only the most unstable alkenes are observably isomerized and only those most weakly chemisorbed proceed to product to an appreciable extent by way of such a "stereochemically symmetrical intermediate."[2] In our view, it is not necessary to postulate a shift of rate-controlling step from formation of the "half-hydrogenated" state on platinum catalysts to passage of the "half-hydrogenated" state to product on palladium.[3,4] The effect of an increased hydrogen pressure on the ratios of cis- to trans-1,2-dimethylcyclohexane observed by Siegel and Smith,[3] accordingly, reflects merely an enhancement of the rate at which cis diadsorbed cycloalkene is converted to cis-cycloalkane (and trans diadsorbed to trans-cycloalkane) relative to the rate at which those steps not involving hydrogen proceed. Those steps not involving hydrogen are isomerization steps 2, 3 and 4, and, more important, those processes from diadsorbed alkene to the symmetrical intermediate. This mechanism is represented schematically in Fig. 1 in which cis-A represents alkene diadsorbed in a geometry which leads to cis-cycloalkane (cis-AH$_2$), etc. The trans-A** state is, of course, not possible with cycloalkenes such as VII or 1,2-dimethylcyclohexene nor is symm. intermediate A. Likewise, the

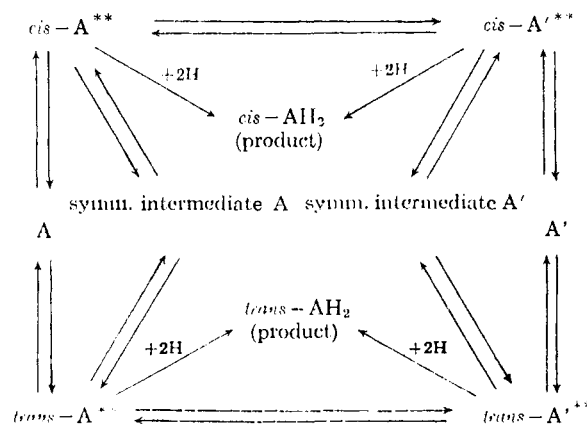Fig. 1.

pathway trans-A** ⇌ trans-A'** cannot be followed by disubstituted endocyclic alkenes although it is a suitable pathway for semicyclic alkenes.

Concerning the details of such "stereochemically symmetrical intermediates," we point once again[2] to the "dissociatively adsorbed olefin," which was proposed some time ago by Burwell,[8] as one possibility (Fig. 2).
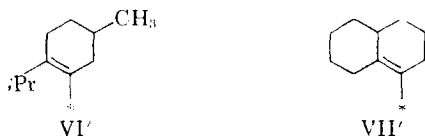

Fig. 2.

The intermediates of Fig. 2 correspond to symm. intermediate A' formed from VI and VII, respectively, via the pathways of Fig. 1. The preference of VI and VII (as compared to IV and VIII, respectively) for such a pathway to product may be the consequence of the relatively weak chemisorption, hence low surface coverage, of these tetrasubstituted alkenes. Thus while both VI and VII are considered to proceed through species which correspond to chemisorbed IV and VIII, respectively, such chemisorbed species undoubtedly are present on the catalyst surface under entirely different circumstances than those which exist when IV and VIII, respectively, are themselves the cycloalkenes diffusing to the catalyst surface. If, for example, vacant sites are required for the promotion of the pathway to the symmetrical intermediate, such sites are much more likely to be available in the presence of VI or VII than in the presence of IV or VIII.[9]

As evidence for a preferred geometry in the adsorption step on palladium catalysts quite to the same degree as on platinum catalysts, we point to the data of Siegel and Smith[4] concerning the isomerization of 2-methylmethylenecyclohexane. On platinum catalysts this semicyclic alkene gives 70% of cis-cycloalkane with only a modest amount of isomerization.[3] During the early stages of hydrogenation over palladium this relatively unstable alkene isomerizes to give more 2,3- than 1,2-dimethylcyclohexene. If one assumes a geometry of initial adsorption of this alkene on palladium to have the same preference as on platinum, then 70% would be adsorbed in the form of A, 30% in the form of B (Fig. 3).
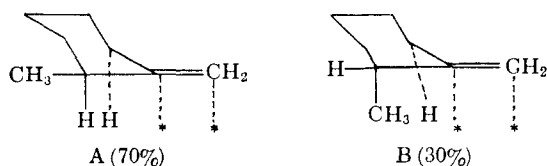

Fig. 3.

Isomerization (steps 2, 3 and 4) would lead from A to both 1,2- and 2,3-dimethylcyclohexene, but only

(8) R. L. Burwell, Jr., B. K. Shim and H. C. Rowlinson, J. Am. Chem. Soc., 79, 5142 (1957).

(9) This possibility was suggested by Professor R. L. Burwell, Jr., in a discussion of possible pathways from VII to trans-decalin. It is a fact that VIII hydrogenates almost exclusively in the presence of VII on platinum catalysts (A. S. H. and R. H. B., unpublished observations).

the latter can arise from B. Assuming that A proceeds to 1,2- or 2,3-dimethylcyclohexene with equal probability, then the composition of the mixture of the two isomers at the very beginning of the hydrogenation should be 35% the former, 65% the latter. At 8% hydrogenation, according to the data of Siegel and Smith,[4] the isomerized cycloalkene consists of 39% the former, 61% the latter. Thus the isomerization of this semicyclic alkene, preferentially to furnish 2,3-dimethylcyclohexene, supports the view that there is a preferred geometry of adsorption on palladium catalysts about to the same degree as on platinum catalysts.

As evidence in support of the intervention of a "stereochemically symmetrical intermediate" we point to the formation of more trans-decalin from $\Delta^{9,10}$-octalin (VII) than from $\Delta^{1,9}$-octalin (VIII) (90% vs. 79%). Actually, VIII is observed to isomerize to VII. Therefore, the VIII which hydrogenates directly without intervening isomerization-desorption must produce rather less trans-decalin than the 79% observed on complete hydrogenation of VIII. These results are not consistent with a pathway which requires VII to isomerize to VIII, desorb, flip over and re-adsorb in a conformation leading to trans-decalin.[8,4] Additionally, but not so strikingly, the formation of more trans-p-menthane (82%) from VI than is produced by the hydrogenation of II, IV and V (74 to 79%) supports our explanation. Furthermore, Siegel and Smith's data[4] for the hydrogenation of 2-methylmethylene-cyclohexane also support the intervention of a "stereochemically symmetrical intermediate." The composition of the 1,2-dimethylcyclohexane product does not correspond, even initially, to the preferred geometry of adsorption of this semicyclic alkene which its isomerization requires. At the beginning, product can be derived only from the original alkene, yet extrapolation of Siegel and Smith's data indicates that less than 40% of cis-1,2-dimethylcyclohexane is formed at zero time. An intermediate which remains on the catalyst must be involved.

We wish also to report that repetitions of the hydrogenation of $\Delta^{9,10}$-octalin (VII) over platinum catalysts, originally reported to give 51% of cis-decalin in a single experiment,[2] have shown that 63% of this isomer is actually formed. Likewise, we can now report that $\Delta^{1,9}$-octalin similarly treated generates only 58% of cis-decalin. These facts are consistent with a pathway from VII to hydrogenation product which involves passage through desorbed VIII by way of isomerization steps 1 to 4. However, in view of the greater trans-decalin from VII than from VIII when a palladium catalyst is used, we regard these facts to reflect merely the greater tendency for a straight-forward addition of two hydrogens to the substrate chemisorbed on platinum as compared to palladium. The lesser tendency of a platinum catalyst to promote such a symmetrical intermediate as VII' has been demonstrated in hydrogen–deuterium exchange reactions with cycloalkanes.[8,10] The fraction of cyclohexane and cyclopentane molecules which suffer exchange of more than half of their hydrogens dur-

(10) J. R. Anderson and C. Kemball, Proc. Roy. Soc. (London), 226A, 472 (1954).

ing a single residence on the catalyst is much larger on palladium than on platinum.

Experimental

Cycloalkenes.—The preparations and purifications of all of the cycloalkenes except $\Delta^{1,9}$-octalin have been described earlier.[2] $\Delta^{1,9}$-Octalin was prepared as follows: the mixture of isomeric 1-decalols, obtained in 75% yield from 1-naphthol in acetic acid over reduced platinum oxide at 3–4 atmospheres of hydrogen, was oxidized by reverse addition of chromic acid[11] to give 92% of 1-decalone, b.p. 125–130° at 23 mm., n^{27}D 1.4848. This product was reduced with sodium in absolute ethanol[12] to give 75% of trans-trans-1-decalol, m.p. 58–60°. The acetate distilled at 117–118° at 10 mm., n^{24}D 1.4706. Pyrolysis of the acetate at 516° furnished 91% of octalins composed of 56% $\Delta^{1,9}$-octalin and 44% $\Delta^{1,2}$-trans-octalin. This mixture was hydrogenated in acetic acid with Adams catalyst at 40 p.s.i. until 70% of the theoretical hydrogen has been adsorbed. Chromatography

on silica, using petroleum hexane as eluent, furnished $\Delta^{1,9}$-octalin in the trailing fractions, b.p. 99° at 45 mm. This contained less than 0.5% $\Delta^{9,10}$-octalin as indicated by analysis through a 6-foot column of saturated silver nitrate–triethylene glycol on 60–80 mesh fire brick.

Hydrogenation and Analysis.—The cycloalkenes were hydrogenated in purified glacial acetic acid, or ethyl alcohol, in a micro-hydrogenation apparatus as described earlier.[2] Analyses of the product mixtures were by vapor–liquid partition chromatography as before.[2] Part hydrogenations were interrupted at 25 to 50% uptake of theoretical hydrogen.

Catalysts.—Three different samples of commercial palladium-on-charcoal (10%)[13] and palladium-on-barium sulfate (5%)[14] were used in these studies. The latter catalyst appeared to furnish a slightly lesser amount (ca. 2%) of the more stable of the two isomers (see footnotes b, c, d, Table I).

(11) A. S. Hussey and R. H. Baker, J. Org. Chem., 25, 1434 (1960).

(12) W. G. Dauben, et al., J. Am. Chem. Soc., 76, 4420 (1954).

(13) The American Platinum Works, Newark, N. J.

(14) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 685.


Positive Halogen Compounds. III. Allylic Chlorination with t-Butyl Hypochlorite. The Stereochemistry of Allylic Radicals[1]
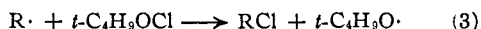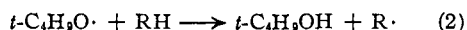
BY CHEVES WALLING AND WARREN THALER

A variety of olefins have been shown to react with t-butyl hypochlorite by a photoinduced radical chain process to give good yields of allylic chlorides. Relative reactivities of allylic C–H bonds have been shown to lie in the order primary < secondary < tertiary with further differentiation in each class. A small amount of addition to give β-chloroalkyl t-butyl ethers accompanies substitution, and the factors determining the competition are discussed. It is shown that substitution products arising without double-bond shift retain their cis-trans stereochemistry, so that *allylic radicals are configurationally stable in this reaction*. The stereochemistry of substitution products which have undergone allylic rearrangement also has been elucidated and is explained in terms of olefin conformation at the moment of reaction. The ratio of allylic isomers from a given allylic radical favors the more substituted olefin, although less so when it is necessarily a cis isomer.

Previous work in this Laboratory has shown that t-butyl hypochlorite is an efficient free radical chlorinating agent for a variety of hydrocarbons and derivatives.[2] The over-all reaction is effected in non-polar solvents using light or free radical

$$t\text{-}C_4H_9OCl + RH \longrightarrow t\text{-}C_4H_9OH + RCl \quad (1)$$
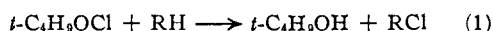
sources as initiators, and proceeds via the radical chain sequence

$$t\text{-}C_4H_9O\cdot + RH \longrightarrow t\text{-}C_4H_9OH + R\cdot \quad (2)$$

$$R\cdot + t\text{-}C_4H_9OCl \longrightarrow RCl + t\text{-}C_4H_9O\cdot \quad (3)$$

Preliminary experiments indicating that the reaction of cyclohexene under these conditions gives 3-chlorocyclohexene in high yield[3] suggested the utility of t-butyl hypochlorite as an allylic halogenating agent. This paper describes a study of such allylic halogenations, showing that allylic substitution rather than addition is indeed the preferred reaction of t-butoxy radicals with many olefins, and also that allylic radicals may retain their cis or trans stereochemistry during the reaction.

Results

Reactions of t-butyl hypochlorite with a variety of olefins were carried out in sealed evacuated tubes employing in general 10–20-fold excesses of olefin in order to avoid possible polychlorination and using an incandescent light for photoinitiation. Whenever possible, products were separated and analyzed by gas–liquid chromatography (g.l.c.). Details for particular systems are given in the Experimental Part.

Butenes.—Results on the chlorination of the four isomeric butenes are listed in Table I and

TABLE I

CHLORINATION OF BUTENES WITH t-BUTYL HYPOCHLORITE

Butene	T, °C.	Composition of allylic chlorides, % 1-Chloro-2-butene	3-Chloro-1-butene	% Addition product[d]
trans-2-	−78.5	83.1 ± 0.2[a]	16.9 ± 0.2	Trace
Butene	40	73.2 ± .3[a]	26.8 ± .3	3–4
cis-2-	−78.5	65.0 ± .0[b]	35.0 ± .0	16.4 ± 0.2
Butene	40	63.2 ± 1.1[b]	36.8 ± 1.1	16.9 ± 0.9
1-Butene	−78.5	73.9 ± 0.1[c]	26.1 ± 0.1	Trace
	40	69.1 ± 0.3[c]	30.9 ± 0.3	3.3
Isobu-	−78.5	Methallyl chloride		11.8 ± 0.1
tylene	40			17.1 ± 0.9

[a] Solely trans isomer. [b] Solely cis isomer. [c] Mixed cis and trans, 65 + 5% trans at 40°. [d] For structure, see text.

show allylic chlorides to be the major product in every case. The radical chain nature of the re-