atmosphere of hydrogen because the several olefins yield somewhat different percentages of the *trans* isomer I (75), II (77) and III (61). As one would expect, increasing the pressure of hydrogen gives a result indicating a further displacement from equilibrium; accordingly 1,2-dimethylcyclohexene (I) yields 62% *trans* at 150 atmospheres of hydrogen on alumina. Conceivably, the fewer the steps required to go from one species to another, the more closely their ratio might approach the equilibrium value. Thus, when starting with the *exo*-olefin, equilibrium may be closely approached with respect to the species immediately derived from it before it is equilibrated with the intermediates derived directly from the isomeric olefins, thus accounting for the small difference in the ratio of *cis/trans* isomer on starting with I, II or III, respectively. Equilibrium among the diadsorbed species is probably reached more quickly and apparently the rate of their desorption under the conditions of the reaction is rapid. However, conformational analysis suggests that the diadsorbed species (a), which alone can yield 1,2-dimethylcyclohexene, is a higher energy intermediate than the other diadsorbed states represented. Consequently, when starting with III and under kinetic control, the reaction mainly follows the path leading to 2,3-dimethylcyclohexene *via* c or e until the *exo* isomer III disappears and no longer supplies e through g. The selectivity in reduction of the olefins suggests that the catalyst's surface is saturated with the intermediates; otherwise one olefin could not prevent another from reacting (as they apparently do), although separately the three olefins react at somewhat comparable rates. Although the kinetic study is incomplete, it indicates an approximate zero order dependence on the concentration of the substrate.

Relative to the behavior on platinum, palladium yields results which suggest that on it hydrogen abstraction reactions are faster than hydrogenation. Consequently, the isomerization of an olefin is readily observed when the latter is used. For example, a platinum catalyst at about one atmosphere of hydrogen yields no 2,3-dimethylcyclohexene (II) when 1,2-dimethylcyclohexene (I) is reduced, although it is posulated that almost all of I goes to II before becoming saturated.[5] Likewise some of I is formed when II is hydrogenated although the ratio is far from the equilibrium value.[5]

**Catalyst Selectivity in the Hydrogenation of Acetylenes.**—An explanation for the generally greater selectivity of palladium over platinum catalysts for the hydrogenation of acetylenes to olefins can be developed from the preceding discussion of the differences in the reaction of hydrogen with olefins on such catalysts.[17] The greater selectivity resides in the catalyst for which the rate-controlling step is the dissappearence of the "half-hydrogenated state" of the olefin. On palladium, this step is slow relative to the establishment of the olefin–adsorbed olefin (1,2-diadsorbed alkane) equilibrium. Consequently, the surface becomes covered with the most strongly adsorbed unsaturated species. Because acetylenes are held more tightly than olefins, a molecule of olefin once desorbed has little chance to return to the surface until all of the acetylene has been consumed. If a catalyst such as platinum is employed, there is less opportunity for the intermediates to become desorbed since the rate-limiting reaction is the *formation* of the "half-hydrogenated" state[5] and, consequently, a mixture of saturated and unsaturated compounds is produced before all of the acetylene has been transformed. Although some palladium catalysts lack the high selectivity in the hydrogenation of acetylene to olefins referred to above, these are generally porous solids[17] and the reduced selectivity may be attributed to the possibility that the diffusion of the acetylene into the pores is the limiting factor.[18] Such catalysts frequently improve with use[9]; in effect, the catalytically active surface which is deep in the pores is deactivated, perhaps through the formation of high polymers which cannot be easily desorbed.

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[17] G. C. Bond, "Catalysis," Vol. 3, Edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1955, p. 143.

[18] A. Wheeler, "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951, pp. 317–322.

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

# The Hydrogenation of Cyclohexenes over Platinum Oxide

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The hydrogenation of nine 1,4-disubstituted cyclohexenes, 1,3-dimethylcyclohexene and $\Delta^{9,10}$-octalin in acetic acid over platinum oxide at 1 atmosphere and room temperature has been carried out. Only one of the compounds studied has been found to show appreciable isomerization in the course of hydrogenation under these conditions. The *cis–trans* isomer compositions of the product mixtures have been determined. An explanation of the stereochemical results is offered.

The present status of knowledge concerning the catalytic addition of hydrogen to carbon–carbon unsaturation can be summarized by the mechanism of steps 1-4, which paraphrases a theory of long standing.[2]

Steps 1 and 2 represent the chemisorption of hydrogen and of alkene on the catalyst surface by reversible processes. The heat liberated in step 2 may be as much as twice that of step 1.[3] Steps 3 and 4 represent the consecutive addition of hydrogen atoms, each also reversible. The reversal of

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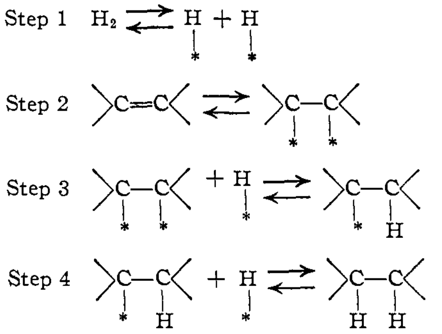
[1] Abstracted in part from the Ph.D. Thesis of J. F. S., September, 1959; Monsanto Co. Fellow, 1955–1957; United States Rubber Co. Fellow, 1957–1958.

[2] I. Horiuti and M. Polyani, *Trans. Faraday Soc.*, **30**, 1164 (1934).

[3] For a discussion of these values see D. D. Eley in "Catalysis," Vol. III, P. H. Emmett, Editor, Reinhold Publishing Corp., New York, N. Y., 1955, pp. 59–63.



step 4 is so slight at room temperature, however, that step 4 can be considered to be irreversible when alkenes are hydrogenating near room temperature or below.[4]

This mechanism, while consistent with much of the experimental data of catalytic hydrogenation, is an over simplification. The gathering evidence suggests that the details of steps 2, 3 and 4 are not so straightforward as this mechanism implies[5] and it is quite possible that one catalytically active surface may produce results quite different from those produced by another. It seems clearly established, however, that steps 3 and 4 correspond to *the addition of two hydrogen atoms to the same side of the chemisorbed alkene*, ("*cis*-addition of hydrogen").[5,6]

We have been interested in the possibility of delineating the more intimate details of steps 2, 3 and 4 by deduction from the stereochemical consequences of the hydrogenation of disubstituted cyclohexenes. Consequently, we have carried out the hydrogenation of carefully purified samples of several such compounds under a variety of conditions. We report here the results of the hydrogenation of these compounds in glacial acetic acid over platinum oxide at room temperature in one atmosphere of hydrogen. These results appear to present a consistent picture of the processes involved and are summarized in Table I as the average of replicate analyses of duplicate or triplicate hydrogenations. The accuracy is ±1% for complete hydrogenations, ±3% or better for partial hydrogenations (except as noted).

**Discussion.**—Examination of the data of Table I shows that isomerization of the olefins is not an important side reaction when hydrogenations are carried out under these conditions,[7] except perhaps in the hydrogenation of the last two cycloalkenes listed. We interpret this to mean that step 2 or step 3 (above) is effectively irreversible under our conditions. Alternatively, both may be irreversible. If reversal of step 3 and desorption by reversal of step 2 were to intervene, extensive isomerization of the first two entries in Table I to the more stable endocyclic alkenes[8] would be observable[9] as it is on palladium catalysts.[7] We therefore propose that the isomer ratios in the products correspond to the steric selectivity in the adsorption of the substrates on the catalyst surface. We will attempt to explain the results from this premise.

TABLE I

HYDROGENATION OVER PLATINUM OXIDE IN ACETIC ACID

| | Cycloalkene | *cis*-Isomer, % Partial hydrogenation | *cis*-Isomer, % Complete hydrogenation |
|---|---|---|---|
| 1 | 4-Methylmethylenecyclohexane | 74[a] | 75 |
| 2 | 4-Isopropylmethylenecyclohexane | 83[b] | 81 |
| 3 | 4-*t*-Butylmethylenecyclohexane | .. | 83[c] |
| 4 | 1,4-Dimethylcyclohexene | 57[b] | 57 |
| 5 | 1-Ethyl-4-methylcyclohexene | 58[b] | 58 |
| 6 | 1-Iso-propyl-4-methylcyclohexene | 50[d] | 58 |
| 7 | 1-Methyl-4-ethylcyclohexene | 47[b] | 48 |
| 8 | 1-Methyl-4-isopropylcyclohexene | 43[b] | 43 |
| 9 | 1-Methyl-4-*t*-butylcyclohexene | .. | 37[c] |
| 10 | 1,3-Dimethylcyclohexene | 74[b] | 74 |
| 11 | 4-Methylisopropylidenecyclohexane | ..[e] | 36 |
| 12 | $\Delta$-9,10-Octalin | ..[f] | 51[g,h] |

[a] 2% 1,4-dimethylcyclohexene in unhydrogenated alkene. [b] No isomerization of unhydrogenated alkene. [c] Professor Samuel Siegel, private communication. [d] Product analysis difficult because of overlapping peaks; 1% of 1-methyl-4-isopropylcyclohexene observed. [e] Product analysis impossible because of overlapping peaks; 13% of 1-isopropyl-4-methylcyclohexene observed. [f] No $\Delta$-1,9-octalin observable at 50% hydrogenation over 5% palladium–charcoal catalyst. [g] Single experiment. [h] 5% $\Delta$-1,9-Octalin impurity in sample hydrogenated.

The selective adsorption of semi-cyclic alkenes to give a higher or lower ratio of *cis* product was proposed several years ago by Siegel.[10] Methylenecyclohexanes with alkyl groups in the 2-, 3- and 4-positions were pictured to approach the catalyst in a chair conformation with ring carbon atoms 3, 4 and 5 inclined away from the surface and with the alkyl group equatorial. In 2- and 4-substituted methylenecyclohexanes, the predominant isomer was predicted to be *cis:* in 3-substituted systems, *trans*. The results observed in the hydrogenation of the first three entries in Table I are in agreement with such an adsorption pathway.

The results observed in the hydrogenation of the endocyclic alkenes show that the group attached to the double bond has no influence on the geometry of the product but rather that the ratio of *cis* to *trans* product is influenced solely by the substituent at a distance (entries 4, 5 and 6). A noteworthy feature of these data is the transition from a slight predominance of *cis* product to an appreciable predominance of *trans* as the 4-substituent increases in steric effect from methyl to *t*-butyl (entries 4, 7, 8 and 9). Further, the influence of the 4-substituent in the endocyclic series is rather less than it is in the corresponding exocyclic compound. The influence of a 3-substituent in 1,3-disubstituted cyclohexenes (entry 10) appears to be somewhat greater than

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(4) Below 50° isotopic exchange in cyclohexane on platinized platinum foil is slow and has an apparent activation energy of 17 kcal.; A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **35**, 917 (1939).

(5) For a critical review see R. L. Burwell, Jr., *Chem. Revs.*, **57**, 895 (1957).

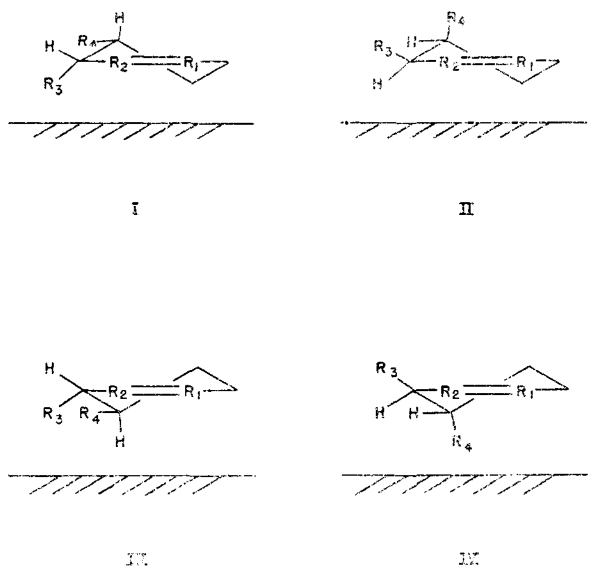
(6) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **33**, 837 (1937); **35**, 906 (1939); R. P. Linstead, *et al.*, THIS JOURNAL, **64**, 1985 (1942); K. N. Campbell and B. K. Campbell, *Chem. Revs.*, **31**, 77 (1942); A. T. Blomquist, L. H. Liu and J. C. Bohrer, THIS JOURNAL, **74**, 3643 (1952).

(7) Samuel Siegel, private communication, reports extensive isomerization over palladium catalysts. We have observed this also.

(8) E. Gil-Av and J. Shabtai, *Chemistry & Industry*, 1630 (1959).

(9) Exocyclic and semi-cyclic double bonds are hydrogenated many times faster than the endocyclics when mixtures of such alkenes compete for the catalyst surface. See Experimental and B. B. Corson, ref. 3, pp. 79–83.

(10) Samuel Siegel, THIS JOURNAL, **75**, 1317 (1953); S. Siegel and M. Dunkel, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 15.



I II III IV

Fig. 1.

that of a 4-substituent. The information on this point is admittedly very incomplete. However, this tendency is exhibited also in the formation of 78% *cis*-1,2-dimethylcyclohexane when 2,3-dimethylcyclohexene is hydrogenated under these conditions.[11]

An examination of molecular models corresponding to the several quasi-chair conformations of these cycloalkenes does not reveal any features of one side of the ring which would make its approach to the catalyst surface appreciably more or less hindered than the other. Of the four pathways by which quasi-chair conformations of dialkyl-cyclohexenes might approach the catalyst surface (Fig. 1), II and IV would appear unfavorable in the 1,4-system (or the 2,4-system), because of the axial arrangement of $R_4$. Because of the added interference of $R_4$ with the catalyst surface, IV would appear to be particularly unfavorable. In the absence of a basis for a choice between I and III, a satisfactory explanation for the trend observed as $R_4$ is changed from methyl to *t*-butyl is not available.

Likewise, in the 1,3- and 2,3-systems there is little discernible difference between the interaction of $R_3$ with the catalyst surface in the several quasi-chair conformations, except that perhaps I and III are slightly more constrained than II and IV. Here again there is no basis for a clear-cut choice of the lowest energy approach of the 1,3- or 2,3-dialkylcyclohexenes to the catalyst surface.

An examination of models of the quasi-boat forms of these endo-cyclic disubstituted cyclohexenes, however, leads one to predictions which are clearly consistent with the data. The energy difference between chair and boat forms of cyclohexene has been estimated to be 2.7 kcal. per mole,[12] considerably less than for the chair–boat cyclohexane system. This lesser energy difference is a consequence of the greater planarity of the cyclohexene conformations (four carbon atoms coplanar in both), and is smaller than the heat of adsorption by perhaps a power of ten.[8] Furthermore, such a conformation would permit the adsorption of the cycloalkene directly in an "eclipsed" conformation. The latter has been shown to be important in the exchange reaction of deuterium for hydrogen in cycloalkane systems[13] and the hydrogenation of cyclopentene and bicycloheptene, which proceed without difficulty, shows that this is a satisfactory pathway.

The interactions present in the two quasi-boat conformations (see Fig. 2) of 1,4-dialkycyclohexenes (and in the 2,4-system) suggest, first, that the substrate must approach so that the catalyst is *exo* to the double bond and, second, that an *exo* 4-substituent has some interaction with the catalyst surface not presented by a substituent in an *endo* configuration. However, the larger the 4-substituent the greater is its constraint in the *endo* conformation. This suggest that the relatively small methyl and ethyl groups can assume an *endo* conformation at some gain or at a very small net cost in energy as the substrate approaches the catalyst surface. Groups larger than ethyl are more restricted to an *exo* conformation. The transition from 58% *cis*-1,4-dimethylcyclohexane to 37% *cis*-1-methyl-4-*t*-butylcyclohexane can thus be rationalized.

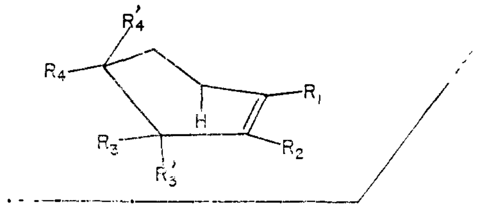


Fig. 2.

In the 1,3- and 2,3-dialkylcyclohexene systems the choice lies between a "bow sprit" and a "mast" 3-substituent. The latter conformation leads to *trans* product. There appears to be serious interaction of the 3-substituent in the latter conformation both with the catalyst surface and the "mast" hydrogen at C–6. Consequently, one predicts that 1,3- and 2,3-disubstituted cyclohexenes would hydrogenate to give a much greater preponderance of *cis* product than is observed with the 1,4- isomers.

To have merit a theory should permit prediction where the facts are unknown. We offer three predictions: First, 2,4-disubstituted cycloalkenes will hydrogenate under these conditions to give the same ratio of *cis* to *trans* product as is furnished by the 1,4-system. Second, in the 1,3- and 2,3- systems, *cis* product will become the exclusive one as the 3-substituent is increased in size. Third, in competitive hydrogenations, the smaller the group at a distance from the double bond, the more successfully will that disubstituted cyclohexene compete for the catalyst surface.

Some comment about the anomalous results observed in the hydrogenation of the last two entries is called for. These are tetrasubstituted alkenes quite analogous to 1,2-dimethylcyclohexene, which also gives anomalous results.[14] The isopropyli-

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(11) S. Siegel and G. V. Smith, private communication.

(12) C. W. Beckett, N. K. Freeman and K. S. Pitzer, THIS JOURNAL, **70**, 4227 (1948).

(13) R. L. Burwell, Jr., B. K. Shim and H. C. Rowlinson, *ibid.*, **79**, 5142 (1957).

denecyclohexane was appreciably isomerized under these conditions, but no isomerization of $\Delta^{9,10}$-octalin was observable even under the more drastic conditions when a palladium catalyst was used. The relatively rapid competitive hydrogenation of $\Delta$-$^{1,9}$ octalin thus formed may have made its detection impossible. Such an explanation has been advanced by Siegel to explain the formation of *trans*-1,2-dimethylcyclohexane from 1,2- dimethylcyclohexene[14] and it is reasonable here also. No data are available concerning the product ratio which results from the hydrogenation of $\Delta^{1,9}$-octalin, however.

An alternative explanation, equally consistent with the facts of the $\Delta^{1,9}$-octalin system, involves the "dissociatively adsorbed olefin" (Fig. 3) proposed by Burwell[13] which would furnish a pathway to the more stable *trans* decalin without an intervening desorption from the catalyst surface. We prefer this alternative because it is a pathway consistent with the formation of only 36% *cis* product from 4 - methylisopropylidenecyclohexane. The most likely (and only observable), isomerization product of this alkene is 1-isopropyl 4-methylcyclohexene which hydrogenates under these conditions to furnish 58% *cis* product. Consequently, there must be another pathway which leads very predominantly to the *trans* product. This pathway is most simply pictured to be the "dissociatively adsorbed olefin," Fig. 4.

If such an intermediate is indeed involved, the subsequent steps must be such that the more stable product is formed preferentially. We are not able to suggest what these steps may be but we do propose that the intervention of "dissociatively adsorbed olefin" on platinum catalysts becomes important only with tetrasubstituted alkenes of the 1,2-dimethylcyclohexene and $\Delta^{9,10}$-octalin type. Steric interactions of four groups attached to the double bond may serve both to interfere with the addition of hydrogen atoms to complete the hydrogenation process and also to put the chemisorbed olefin into a relatively high energy state. In olefins of lower substitution, hydrogenation by steps 3 and 4 is not impeded by such interactions.

## Experimental

**Hydrogenations.**—The micro-hydrogenation apparatus used in this study consisted of a long-neck 30-ml. flask with a side-arm hydrogen inlet for connection to a gas buret and mercury-leveling bulb. The flask was closed with a serum cap fitted with a spring device to hold the sample in its weighing bottle apart from solvent and catalyst during reduction of the catalyst. Agitation was by way of an eccentric cam driven by a 250 r.p.m. motor. Vertical adjustment permitted a stroke variation from 0.5 to 1.0 inch. The system was evacuated and filled with hydrogen several times prior to agitation.

The usual hydrogenation involved 2.5 millimoles of cycloalkene, 5.0 ml. of purified acetic acid[15] and 50 mg. of platinum oxide (Goldsmith Brothers Smelting and Refining Co., Lot no. 12035). The use of one-fifth quantity of catalyst did not change the product ratio, although the rate of hydrogen uptake was considerably retarded. Most hydrogenations carried to completion absorbed slightly more than the calculated amount of hydrogen (103–105% of theory).

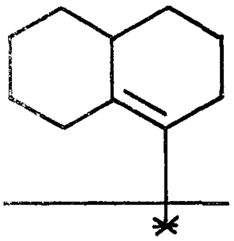

Fig. 3.

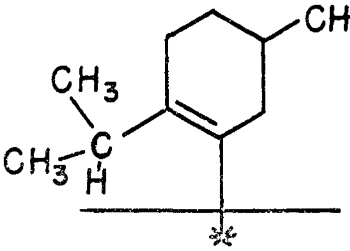

Fig. 4.

Substitution of purified anhydrous ethanol for acetic acid as hydrogenation solvent led to much slower rates of hydrogen up-take and usually to incomplete hydrogenation.

Partial hydrogenations were interrupted after 25–60% of the theoretical hydrogen had been absorbed.

**Analysis.**—Vapor partition chromatographic analyses of the cycloalkene and cycloalkane mixtures were carried out on two types of columns using helium carrier gas and filament thermal conductivity detectors.[16] Particularly effective in the separation of unsaturated components were columns utilizing silver nitrate-saturated triethylene glycol dispersed on 60–80 mesh fire-brick,[17] 1 to 2 or 1 to 3 weight ratio. Tri-*m*-cresyl phosphate on the same support (1 to 5 ratio) was particularly effective in the separation of the several perhydroaromatic isomer mixtures and some of the cycloalkenes.

*m*-Xylene, *p*-xylene, *p*-ethyltoluene, *p*-cymene and naphthalene were hydrogenated in acetic acid over 5% rhodium-on-charcoal catalyst[18] under one atmosphere of hydrogen. Analysis of the resultant perhydroaromatic mixtures on the two types of columns served to identify the appearance time of the *cis* isomer, the predominant product of hydrogenation under these conditions. This assignment was confirmed by hydrogenation over nickel–kieselguhr at 160° under 100 atmospheres of hydrogen for 12–24 hours. Analyses of these mixtures through the two columns served to locate the thermodynamically more stable isomer as the major peak.

The order of appearance of the perhydroaromatic isomers through both columns corresponded to the thermodynamic stability of the two isomers; thus *cis*-1,3- and *trans*-1,4-isomers appeared first. The order of appearance of the cycloalkenes corresponded to the order of complexity of substitution at the double bond: the greater the degree of substitution or the larger the substituent at the double bond, the earlier the appearance of the isomer through the silver nitrate column.[19]

The compositions of the mixtures were estimated by computing peak area from half-peak widths and peak heights.

**4-Methylmethylenecyclohexane.**—Redistilled commercial 4-methylcyclohexanone in 5% excess was added dropwise at 15° to a stirred slurry of triphenylphosphinemethylene[20] in dry ether under nitrogen. After *ca.* 2 hours, the ether was partly replaced by petroleum heptane and the mixture was refluxed for 2 hours at 58°. The addition of water, extraction with heptane and suitable washing was followed by distillation through a short column; yield 9.8 g. (28%), b.p. 122°, $n^{20}$D 1.4421. This was purified by passage through a 4 foot column of activated silica. The 4-methylmethylenecyclohexene exhibited a single peak on the silver nitrate–triethylene glycol column and had $n^{20}$D 1.4447.[21]

**4-Isopropylmethylenecyclohexane.**—4-Isopropylcyclohexanol,[22] from the hydrogenation of 4-isopropylphenol at 165° and 100 atmospheres over nickel–kieselguhr, was oxidized in the usual way[23] to furnish 63% of 4-isopropylcyclohexanone.[22] In 5% excess as above with triphenylphos-

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[14] S. Siegel and G. V. Smith, Abstracts, 135th National Meeting, American Chemical Soicety, Boston, Mass., April, 1959, p. 17-O; S. Siegel and G. V. Smith, private communication.

[15] Purified by 2 hours at reflux over chromic anhydrides followed by distillation from the oxidizing agent.

[16] We acknowledge our gratitude to Podbielniak, Inc., Chicago, Ill., for the gift of a Chromacon Series 9400 which was used in this research.

[17] Wilkens Instrument and Research, Inc., Box 313, Walnut Creek, Calif.

[18] Baker and Co., Inc., Newark 5, N. J., Lot no. 2899.

[19] E. Gil-Av, J. Herling and J. Shabtai, *J. Chromatography*, **1**, 508 (1958).

[20] G. Wittig and U. Schollkopf, *Ber.*, **87**, 1318 (1954).

[21] O. Wallach and E. Evans, *Ann.*, **347**, 345 (1906).

[22] G. Vavon and A. Callier, *Bull. soc. chim.*, **41**, 678 (1927).

[23] L. T. Sandborn, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 340.

phinemethylene,[20] this gave 24% of 4-isopropyl-methylenecyclohexane: b.p. 39.5–40.0° at 4 mm., $n^{20}$D 1.4567.[24] This preparation exhibited a single peak on the silver nitrate-triethylene glycol column.

**1,4-Dimethylcyclohexene.**—1,4-Dimethyl-1-cyclohexanol,[25] from 0.49 mole of 4-methylcyclohexanone and methylmagnesium bromide, was added dropwise over 0.5 hour to a mixture of 20 g. of phosphorus pentoxide and 20 ml. of 86% phosphoric acid maintained at 150° by an external oil-bath and at 100–110 mm. pressure by connection through a partial take-off condenser and an ice-cooled trap to a vacuum pump. The product distilled at 60° at a rate nearly equal to the rate of addition. The total distillate weighed 28 g. and 3.2 g. of polymer was later extracted from the phosphoric acid.

Distillation of this product through a Piros–Glover spinning band column furnished 16.2 g. (30%) of a middle fraction which had b.p. 126.5°, $n^{21.5}$D 1.4452. Passage through 4 ft. of activated silica gave a sample which had a single peak on the silver nitrate column and had $n^{20}$D 1.4458.[26]

**1-Ethyl-4-methylcyclohexene.**—The dropwise addition of 57.7 g. (0.51 mole) of 4-methylcyclohexanone in 100 ml. of anhydrous ether to the Grignard reagent prepared from 60.0 g. (0.55 mole) of ethyl bromide and 13.4 g. (0.55 mole) of magnesium in 200 ml. of ether was followed by 1 hour at reflux; then 100 ml. of water was carefully added. The ether solution was decanted from the solid cake of magnesium salts thus formed and the latter was leached with three 200-ml. portions of ether. The combined ether solution and leachings were distilled to furnish 61.0 g. (86%) of 1-ethyl-4-methylcyclohexanol having b.p. 88–92° (20 mm.), $n^{25}$D 1.4575.

The dehydration of 22.7 g. (0.160 mole) of this alcohol was accomplished by dropwise addition over 10 minutes onto 40 ml. of 100% phosphoric acid at 150° and 105 mm. pressure with vigorous stirring. The product distilled at 90–94° at a rate equal to the rate of addition of the alcohol and was collected in a Dry Ice-cooled receiver. The dried product weighed 19.3 g. (98%). Analysis through the silver nitrate–triethylene glycol column showed the product to consist of 85 ± 3% 1-ethyl-4-methylcyclohexene, 14 ± 3% 4-methylethylidenecyclohexane with traces of 1-methyl-4-ethylcyclohexene and diethylcyclopentenes. The mixture distilled over the range 151–156°.

This mixture was dissolved in purified glacial acetic acid in a low-pressure hydrogenation bottle and 200 mg. of platinum oxide catalyst (Goldsmith Brothers) was added. The mixture was shaken with hydrogen at an initial pressure of 28.5 p.s.i. until 25% of the theoretical hydrogen had been absorbed. The hydrogenation was then interrupted and the product was isolated by dilution with water and extraction with pentane. Removal of the pentane and passage of the residue through 6 ft. of activated silica, using pentane as eluant, gave early fractions rich in *trans*-4-ethylmethylcyclohexane followed by fractions rich in the *cis* isomer. The final fractions contained 1-ethyl-4-methylcyclohexene and had b.p. 153° (752 mm.), $n^{23}$D 1.4504. Analysis through the silver nitrate–triethylene glycol column and through the tri-*m*-cresyl phosphate column showed the latter fractions to contain less than 1% of 1-methyl-4-ethylcyclohexene as impurity and none of the other isomers present in the original product from the dehydration reaction.

**1-Isopropyl-4-methylcyclohexene.**—Pyrolysis of *l*-menthyl acetate at 475° furnished a mixture (60% yield) consisting of 57% 1-isopropyl-4-methylcyclohexene and 43% 3-methyl-6-isopropylcyclohexene ($n^{20}$D 1.4534). This mixture could not be separated by fractional distillation. Refluxing under nitrogen over "benzylsodium" catalyst[27] converted this to a mixture whose composition by analysis through the silver nitrate–triethylene glycol column was 45% 1-methyl-4-isopropylcyclohexene, 45% 1-isopropyl-4-methylcyclohexene, 5% 3-methyl-6-isopropylcyclohexene and 5% 4-isopropenyl-1-methylcyclohexane.[27] Fractional distillation of this mixture in a Piros–Glover still and refractionation of the best cuts gave a middle fraction whose composition was 91% 1-isopropyl-4-methylcyclohexene, 6% 3-methyl-6-isopropylcyclohexene and 3% 4-isopropenyl-1-methylcyclohexane.

The last isomer was removed by percolation of the mixture through 6 ft. of activated silica. The other isomer was removed by a partial hydrogenation in glacial acetic acid over platinum oxide to 30% of theoretical followed by chromatography through 4 ft. of activated silica using absolute ethanol as displacing solvent.

The 1-isopropyl-4-methylcyclohexene so obtained had $n^{20}$D 1.4515[27] and gave a single peak on analysis through the silver nitrate–triethylene glycol column. A less laborious separation of 1-isopropyl-4-methylcyclohexene from the *l*-menthyl acetate pyrolysate can be effected by a low-pressure hydrogenation over platinum oxide to 50% of theoretical, followed by chromatography on activated silica.

**1-Methyl-4-ethylcyclohexene.**—Redistilled *p*-ethylphenol (b.p. 109–110°) was hydrogenated in absolute ethanol over 65% nickel–kieselguhr at 160° and an initial pressure of 2740 p.s.i. to give 4-ethylcyclohexanol in 96% yield, b.p. 118–119° (50 mm.), $n^{23}$D 1.4595.[28]

This was oxidized by the reverse addition of a slight excess of sodium dichromate in one equivalent of 20% sulfuric acid to a stirred slurry of the alcohol and 2 volumes of water: over 0.75 hour, a solution composed of 70.2 ml. of concentrated sulfuric acid (1.33 moles) and 120.0 g. (0.40 mole) of sodium dichromate dehydrate in 500 ml. of water was added without external cooling to a well-stirred slurry of 128.0 g. (1.00 mole) of 4-ethylcyclohexanol and 200 ml. of water. The temperature rose to 66° within 20 minutes, thereafter remained constant until addition was complete. The mixture was stirred an additional 15 minutes as the temperature fell to 50°. The cooled mixture was extracted with benzene. The benzene extracts were washed with water and dilute acid, then distilled. 4-Ethyl-cyclohexanone distilled at 109–112° at 50 mm. and had $n^{25}$D 1.4533,[28] yield 113 g. (90%).

When 63.0 g. (0.500 mole) of this material was added dropwise to the Grignard reagent from 78.1 g. (0.55 mole) of methyl iodide and the reaction mixture worked up as described for 1-ethyl-4-methylcyclo-hexanol, 64.0 g. (91%) of 1-methyl-4-ethylcyclohexanol was obtained. This distilled at 95–98° (20 mm.) and had $n^{25}$D 1.4580.

Dehydration as described above for the isomeric methylethylcyclohexanol with 100% phosphoric acid furnished, from 22.0 g. (0.155 mole) of the alcohol, 18.8 g. (98%) of product which distilled at 95–98° at 105 mm., 154–159° at atmospheric pressure. Analysis through the silver nitrate–triethylene glycol column showed the product to be a mixture of 90 ± 2% 1-methyl-4-ethylcyclohexene and 10 ± 2% of 4-ethylmethylenecyclohexane, with less than 1% of 1-ethyl-4-methylcyclohexene. Pure 1-methyl-4-ethylcyclohexene was obtained by a low-pressure partial hydrogenation (interrupted at 15% absorption of the theoretical hydrogen), followed by percolation through activated silica. It contained less than 1% of 1-ethyl-4-methylcyclohexene.

A second dehydration was performed by dropwise addition of the alcohol onto well-stirred powdered sodium bisulfate at 150° and 105 mm. The product, obtained in 98% yield, was found by analysis through the silver nitrate column to be 95 ± 2% 1-methyl-4-ethylcyclohexene and 5 ± 2% 4-ethylmethylenecyclohexane. A middle fraction obtained by distillation in a Piros–Glover column showed no traces of isomeric impurities and had b.p. 155.0° (742 mm.), $n^{23}$D 1.4512.

**1-Methyl-4-isopropylcyclohexene.**—*d*-Limonene was purified by steam distillation followed by a reduced pressure distillation from sodium; b.p. 104.5–105.5° (78 mm.).[27] This was hydrogenated over platinum oxide (Goldsmith Brothers) in a low-pressure hydrogenation apparatus at an initial pressure of 45 p.s.i. until one mole of hydrogen had been absorbed. Analysis through the silver nitrate–triethylene glycol column showed small amounts of limonene and *cis*- and *trans*- *p*-methane to be present. These impurities were removed by passage through 6 ft. of activated silica using absolute ethanol as displacing agent. The middle 50% of the eluate had $n^{20}$D 1.4569[27] and showed a single peak when analyzed on the silver nitrate–triethylene glycol and the tri-*m*-cresyl phosphate column.

**1-Methyl-4-t-butylcyclohexene.**—This sample was kindly furnished us by Mr. George W. Whitney of these laboratories who prepared it by the addition of 4-*t*-butylcyclohexanone to methylmagnesium bromide, followed by dehydration of the alcohol thus produced using iodine catalyst. The sample had

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[24] R. L. Webb and J. P. Bain, THIS JOURNAL, **75**, 1279 (1953); E. Frainnet and R. Calas, *Compt. rend.*, **240**, 203 (1955).

[25] O. Wallach, *Ann.*, **396**, 266 (1913).

[26] N. Zelinsky and A. Gorsky, *Ber.*, **41**, 2632 (1908).

[27] H. Pines and H. E. Eschinazi, THIS JOURNAL, **77**, 6314 (1955); **78**, 1176. 1178 (1956).

[28] W. Zegenbein, A. Schaffler and R. Kaufhold, *Chem. Ber.*, **88**, 1906 (1955).

$n^{20}$D 1.4599 and contained a trace of 4-*t*-butylcyclohexanone. Analysis through the silver nitrate–triethylene glycol column showed no isomeric cyclohexene to be present, however.

**1,3-Dimethylcyclohexene.**—2,6-Xylenol was hydrogenated in 95% ethyl alcohol over 65% nickel–kieselguhr at an initial pressure of 2680 p.s.i. at 156°. After separation of the catalyst and solvent, 2,6-dimethylcyclohexanol was isolated in 90% yield by distillation; b.p. 173–175° (749 mm.), $n^{23}$D 1.4595.[29]

With 10% excess acetyl chloride in 3 volumes of pyridine this gave 94% of 2,6-dimethylcyclohexyl acetate, b.p. 110–111° (50 mm.), $n^{23}$D 1.4376.[29]

When the acetate was dropped onto a 6-inch column of glass beads in a vertical tube furnace maintained at 500° in a stream of nitrogen adjusted to give a residence time of 1 second, 16% of 1,3-dimethyl-cyclohexene (b.p. 127.5–128.0° at 763 mm., $n^{23}$D 1.4477),[30] was obtained and 75% of the acetate was recovered (b.p. 195° at 761 mm., $n^{23}$D 1.4371). The 1,3-dimethycyclohexene thus obtained showed a single peak when analyzed on the silver nitrate column and on the tri-*m*-cresyl phosphate column.

**4-Methylisopropylidenecyclohexane.**[31]—The Reformatsky reaction of ethyl α-bromoisobutyrate and granular zinc in ether–benzene with 4-methylcyclohexanone by the procedure of Hussey and Newman[32] furnished 86% of 4-methyl-1-(2-carbethoxy-2-propyl)-cyclohexanol (8-carbethoxy-4-p-menthanol) as a mixture of isomers, b.p. 90–97° (14 mm.), $n^{20}$D 1.4402–1.4601.[31] Dehydration was attempted by heating at 145° for 3 hours with 2 parts by weight of anhydrous potassium bisulfate. The distilled product showed hydroxyl bands in its infrared spectrum so the dehydration was repeated by heating with anhydrous potassium bisulfate for 6 hours at 165°. Because of the extra manipulations, the yield of product was only 59%, b.p. 73–78° (1 mm.), $n^{22}$D 1.4550.[31]

Saponification with potassium hydroxide in ethanol followed by acidification furnished 74% of 4-methyl-1-(2-carboxy-2-propyl)-cyclohexene, m.p. 93.5–95.5° (from ether).[31] This acid liberated carbon dioxide at a smooth rate when heated to 195°. Application of a slight vacuum at short intervals during the 8-hour heating period removed product from the heated reaction zone as formed: yield 92%, $n^{22}$D 1.4670. Fractionation furnished 3.4 g. (63%) of 4-methylisopropylidenecyclohexane, b.p. 80.5° (35 mm.), $n^{20}$D 1.4681. This material exhibited a single peak when analyzed through the silver nitrate–triethylene glycol column, but was extensively isomerized by passage through the tri-*m*-cresyl phosphate column. The infrared spectrum (neat) had characteristic bands at 5.62, 10.45 and 10.57 μ.

**$\Delta$-$^{9,10}$-Octalin.**—The $\Delta$-$^{9,10}$-octalin was prepared essentially by the procedure since described by Dauben[33] except that the regeneration of the olefin from its nitroso chloride derivative was effected by careful warming to 70° of 0.10 mole with 30 ml. of N,N-dimethylaniline. The extracted hydrocarbon distilled at 77.5° at 14 mm. and had $n^{20}$D 1.4990.[33] Traces of acids, as on the surface of glassware, or the heat of adsorption on activated silica rapidly cause contamination of purified samples of $\Delta$-$^{9,10}$-octalin by an isomerization to $\Delta$-$^{1,9}$-octalin.

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(29) A. Skita and W. Faust, *Ber.*, **72**, 1128 (1939). See R. Cornubert, *et al.*, *Bull. soc. chim. France*, 631 (1950), for discussion of stereochemistry of the several isomers.

(30) G. Chiurdoglu, *Bull. soc. chim. Belg.*, **47**, 241 (1938).

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(33) W. G. Dauben, *et al.*, *J. Org. Chem.*, **23**, 1205 (1958).

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# I. Mechanism of Solvolysis of Triphenylmethyl Chloride in Hydroxylic Solvents[1–3]

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Rates of solvolysis of triphenylmethyl (trityl) chloride in nine solvents at 25° are reported. Since these rates are very fast, most of them were determined by extrapolation from measurements at low temperatures, but a few were done in a conductimetric flow system at 25°. Although the log $(k/k^0) = mY$ equation gives only a fair correlation of these data, the log $(k/k^0) = c_1d_1 + c_2d_2$ equation gives an excellent correlation using previously determined solvent $(d_1,d_2)$ parameters. The decrease in relative rate of solvolysis in acetic acid in the series *t*-butyl chloride > α-phenylethyl chloride > benzhydryl chloride > trityl chloride suggests that the rate-determining step in acetic acid is nucleophilic attack by acetic acid on the carbonium ion of an ion-pair intermediate.

Table I summarizes new solvolytic data for triphenylmethyl (trityl) chloride in nine solvents, including methanol, ethanol, acetone–water mixtures and acetic acid. The half-lives at 25° range from 5.2 seconds in 95% acetone to 0.0013 sec. in 80% ethanol. The data were obtained by extrapolation from measurements at low temperatures except for 90% and 80% acetone, where a conductimetric flow system at 25° was used, and acetic acid, where a quenching technique at 25° was used. Sodium acetate was added in the solvolyses in acetic acid because they were appreciably reversible without it. Two different concentrations of acetate ion were used to prove that it did not accelerate acetolysis.

TABLE I

RATES OF SOLVOLYSIS OF TRITYL CHLORIDE AT 25°

| Solvent[a] | $k$, sec.$^{-1}$ | $\Delta H^*$, kcal. | log $(k/k^0)$ | $Y$[b] | $d_1$[c] | $d_2$[c] |
|---|---|---|---|---|---|---|
| MeOH, 100 | 159[d] | 13.7 | −0.53 | −1.09 | −0.05 | −0.73 |
| EtOH, 100 | 4.89[d] | 13.9 | −2.04 | −2.03 | − .53 | −1.03 |
| EtOH, 95 | 35.2[d] | 14.0 | −1.18 | −1.29 | .... | .... |
| EtOH, 90 | 81.1[d] | 13.9 | −0.82 | −0.75 | − .01 | − .54 |
| EtOH, 80 | 536[e] | .. | .00 | .00 | .00 | .00 |
| $Me_2CO$, 95 | 0.124[d] | 11.9 | −3.64 | −2.76 | .... | .... |
| $Me_2CO$, 90 | 2.84[d] | 13.7 | −2.28 | −1.86 | − .53 | −1.52 |
| $Me_2CO$, 90 | 1.93[f] | .. | −2.44 | −1.86 | − .53 | −1.52 |
| $Me_2CO$, 80 | 21.9[f] | .. | −1.39 | −0.67 | − .45 | −0.68 |
| AcOH, 100 | 0.24[g] | .. | −3.35 | −1.68 | −4.82 | +3.12 |

[a] Number after solvent is % by volume based on volumes before mixing; the residue is water; Me, Et, Ac = $CH_3$, $C_2H_5$, $CH_3CO$. [b] Based on *t*-butyl chloride.[4] [c] Solvent parameter based on 25 alkyl halides and esters.[6] [d] Extrapolated from lower temperature data in Table IV. [e] Extrapolated from other EtOH mixtures with eq. 1. [f] From flow system at 25°. [g] From quenching technique discussed in Experimental section; sodium acetate was present (0.0015 and 0.0029 *M* in different runs) to prevent the back reaction.

**Comparison of Equations for Correlating Rates of Solvolysis.**—Figure 1 shows the correlation ob-

(1) Supported in part by the research programs of the National Science Foundation and the Atomic Energy Commission and by a National Institutes of Health Research Fellowship to A. M.

(2) For data on triphenylmethyl fluoride and acetate, *cf.* C. G. Swain, T. E. C. Knee and A. MacLachlan, THIS JOURNAL, **82**, 6101 (1960).

(3) For complete experimental data, *cf.* A. MacLachlan, Ph. D. Thesis in Organic Chemistry, M.I.T., August, 1957.