fractions no peak correpsonding to 1,2-dimethyl-3-isopropy! cyclopentanes was detected by gas chromatography.[45]

High-Boiling Hydrocarbons from Petroleum Ether.—Commercial petroleum ether (20 kg) of bp 40–60° was fractionated by a 50-cm Vigreux column and 1.58 g of a fraction, bp 158–160°, was obtained. On preparative gas chromatography, a peak corresponding to 1,2-dimethyl-3-isopropylcyclopentane was isolated, n^{20}D 1.4375. The infrared spectrum of this peak was similar to **1**. In the fingerprint region, however, the infrared spectrum was definitely different from those of **1a** through **1d**.

Acknowledgment.—The authors are indebted to Dr. T. Singû, Faculty of Pharmaceutical Sciences, Kyôto University, for nmr spectra.

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[45] In the essential oil of the flowers there were found and identified: γ-decano lactone, α- and β-ionones, *trans*- and *cis*-2,6,6-trimethyl-2-vinyl-5-hydroxytetrahydropyranes, linalool, *trans*- and *cis*-linalool oxides, nonanal, and leaf alcohol (*cis*-γ-hexenol). The details will be published elsewhere.

Stereochemistry and the Mechanism of Catalytic Hydrogenation of Cycloalkenes. VII. Interaction Mechanisms Which Control the Ratio of Stereoisomers[1]

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The ratio of the *cis*- and *trans*-dialkylcyclohexanes obtained on hydrogenating a series of substituted methylenecyclohexanes and disubstituted cyclohexanes, over reduced platinum oxide, is a function of the hydrogen pressure. The results and further argument support previous conclusions that the limiting ratios are characteristic of different product-controlling reactions: the formation of 1,2-diadsorbed alkane at high pressures of hydrogen and the formation of the "half-hydrogenated state" at low pressure. Both inter- and intramolecular interaction mechanisms which may determine the proportion of saturated isomers are considered.

Explanations of the stereochemistry of catalytic hydrogenation have been dominated by ideas concerning the manner in which a given unsaturated compound may best be fitted onto a planar surface from which hydrogen is abstracted;[2] *cis* addition is a consequence. However, detailed studies of the reactions which occur when hydrogen (or deuterium) and unsaturated hydrocarbons interact upon metallic surfaces demonstrate that the net addition is the result of a complex system of reactions.[3] Accordingly, we have sought to interpret our stereochemical studies of the hydrogenation of cycloalkenes[4–8] in terms of the mechanistic proposals of Horiuti and Polanyi[9] and concluded that, on certain platinum catalysts, compounds such as 2,3-dimethylcyclohexene or alkyl-substituted methylenecyclohexanes give limiting ratios of the saturated stereoisomers at high hydrogen pressures which are characteristic of the formation of the 1,2-diadsorbed alkane,[10] while at low pressures the limiting ratio characterizes the formation of the "half-hydrogenated state."[9]

The present study provides additional data to support these views and the factors which determine the particular ratios of isomers are examined further.

Results

The results of this and some previous studies are shown in Tables I and II. Where comparisons are possible, the agreement with results obtained at 1 atm by Sauvage, Baker, and Hussey is satisfactory.[11] Clearly, the fraction of the *cis* isomer which is obtained is not only a function of the structure of the substrate but also of the pressure. However, the effect of changing the pressure differs for the various substances studied not only in magnitude but also in direction.

The alkyl-substituted methylenecyclohexanes yield mainly the axial–equatorial stereoisomer and the proportion, relative to its epimer, drops as the pressure of hydrogen is raised, Table I and Figure 1.

TABLE I

HYDROGENATION OF ALKYL-SUBSTITUTED METHYLENECYCLOHEXANES. VARIATIONS IN THE MOLE PER CENT OF THE *cis* ISOMER WITH THE PRESSURE OF HYDROGEN

	Pressure of hydrogen (atm)					
Substrate	0.25	0.50	1.0	3.0	50	100–200
2-Methyl[a]	70	70	70	69	69	68
3-Methyl	25	25	28	35[b]	43	46
4-Methyl	78	76	73[c]	70[b]	66	67
4-*t*-Butyl[d]	87	86	84	76	62	61

[a] Reference 4. [b] Our earlier report [S. Siegel and M. Dunkel, *Advan. Catalysis*, 9, 15 (1957)] is in error. [c] Sauvage, Baker, and Hussey (ref 11) report that at 1 atm 4-methylmethylenecyclohexane gives 74% *cis*. [d] Reference 6.

The endocyclic alkenes show less regularity in their behavior with respect to both the principal stereoisomer formed at low hydrogen pressures and the direction of change, if any, when the pressure is raised, Table II.

Results that are recorded for pressures of 1 atm or less are obtained from experiments which were carried to less than 50% completion while those data obtained at higher pressures are for complete reductions. For certain of the substrates, the proportion of saturated stereoisomers may depend upon the stage at which the

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[1] (a) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. A grant from the Monsanto Chemical Co., St. Louis, Mo., was also greatly valued. (b) A portion of this work was presented at the American Chemical Society Southwest Regional Meeting, Baton Rouge, La., Dec 3–5, 1959.

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[3] T. I. Taylor, "Catalysis," Vol. V, Chapter V, Reinhold Publishing Corp., New York, N. Y., 1957.

[4] S. Siegel and G. V. Smith, *J. Am. Chem. Soc.*, **82**, 6082 (1960).

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[6] S. Siegel and B. Dmuchovsky, *ibid.*, **84**, 3132 (1962).

[7] S. Siegel and B. Dmuchovsky, *ibid.*, **86**, 2192 (1964).

[8] S. Siegel, P. A. Thomas, and J. T. Holt, *J. Catalysis*, **4**, 73 (1965).

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

[10] R. L. Burwell, Jr., B. K. C. Shim, and C. Rowlinson, *J. Am. Chem. Soc.*, **79**, 5142 (1957).

[11] J. F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **82**, 6090 (1960).

Table II

Hydrogenation of Disubstituted Cyclohexenes. Variation in the Mole Per Cent of the *cis* Isomer with the Pressure of Hydrogen

	Pressure of hydrogen (atm)					
Substrate	0.25	0.50	1.0	3.0	50	100–200
2,3-Dimethyl[a]	81	77	77	71	69	70
1,3-Dimethyl	75	75	76[b]	77	80	78
2,4-Dimethyl	. .	49	49	51	. .	48
1,4-Dimethyl	55	56	56[b]	58	64	65
4-*t*-Butyl-1-methyl[c]	35	35	36	40	47	47

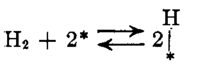
[a] Reference 4. [b] Sauvage, Baker, and Hussey (ref 11), reporting reductions at 1 atm only, give for 1,3-dimethylcyclohexene 74% *cis* and for 1,4-dimethylcyclohexene 57% *cis*. [c] Reference 6.

reaction is interrupted. For example, at 1-atm pressure, 1,3-dimethylcyclohexene yields 76% *cis* 1,3-dimethylcyclohexane at complete reduction and 78% *cis* when only 40% of the theoretical amount of hydrogen has been adsorbed. In addition, 3% of the olefin remaining at this stage of the reaction is 2,4-dimethylcyclohexene which when reduced independently yields a smaller fraction of the *cis* isomer (49%). Although such isomerization is slow relative to hydrogenation on this platinum catalyst,[4,11] it can affect the results, particularly at the lower pressures. The magnitude of this effect is also a function of the difference in the ratios of the stereoisomers which are formed from the initial substrate and its possible products of isomerization.

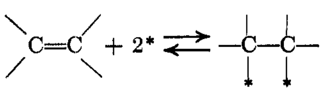
One might expect that isomerization might be a more significant factor in the hydrogenation of the methylenecyclohexanes because the endocyclic isomers are appreciably more stable. ($\Delta G°$ for isomerization of methylenecyclohexane to methylcyclohexene is 3.2 kcal/mole at 25°.)[12,13] However, with the catalyst employed, no isomeric alkenes were detected on hydrogenating 4-methylmethylenecyclohexane even at low pressures (0.11 and 0.25 atm) when the reaction was interrupted at less than 25% completion. Any isomeric olefin so produced would tend to accumulate because in competitive reactions, the exocyclic derivative is reduced selectively.[4,6,11] Sauvage, Baker, and Hussey reported 2% of 1,4-dimethylcyclohexene was present in the unhydrogenated 4-methylmethylenecyclohexane at 75% of complete hydrogenation at a pressure of 1 atm of hydrogen.[11]

Discussion

The Mechanism of Hydrogenation.—In general, the experimental results are in harmony with the Horiuti–Polanyi formulation of the mechanism of hydrogenation of unsaturated hydrocarbons which may be represented by eq 1–4.[9]



$$H_2 + 2* \rightleftarrows 2\overset{H}{\underset{*}{|}} \quad (1)$$



(2)

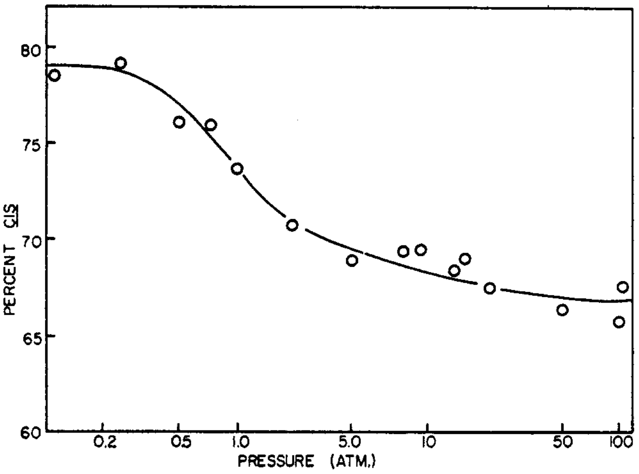
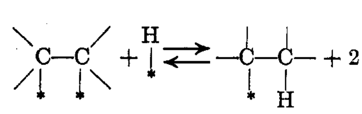
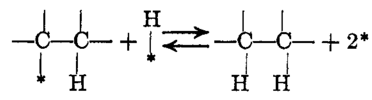


Figure 1.—Per cent *cis*-1,4-dimethylcyclohexane from hydrogenation of 4-methylmethylenecyclohexane as a function of hydrogen pressure (PtO_2).



(3)



(4)

Although the displacements on carbon are assumed to occur with retention of configuration, the proportion of stereoisomeric products will depend upon which of the elementary reactions is product controlling because the geometry and/or composition of the several possible transition states differ from one another.

Since the relative rates of these consecutive reactions are a function of the concentration of adsorbed hydrogen, an independent variable, limiting forms of the mechanism can be realized by varying the pressure of hydrogen. The results of experiments in which this was done have led us to conclude that the ratio of *cis/trans* isomers obtained from the reduction of dialkylcycloalkenes, other than the 1,2-dialkylcycloalkenes, on platinum catalysts at high pressures is determined by the energetics of the alternative transition states for reaction 2, the formation of the diadsorbed species, while the ratio obtained at low pressures is determined at reaction 3, the formation of the "half-hydrogenated state."[4,6] The structures of these transition states differ appreciably; the one retains much of the geometry of the olefin, the other has an essentially saturated structure.

In order that the above analysis be applicable, the isomerization of one olefin to another must be slow relative to the rate of addition of hydrogen. With platinum catalysts, this condition is generally met in hydrogenations of methylenecycloalkanes and dialkylcyclohexenes other than those which may be thought of as tetrasubstituted ethylenes such as 1,2-dimethylcyclohexene.[4,6,11] Isomerization, if unrecognized or improperly evaluated, may obscure the basic stereochemical relationships. A mechanism for isomerization is included in the Horiuti–Polanyi formulation in that the reverse of reaction 3 can produce a diadsorbed state isomeric with the one derived from the original olefin, and the reverse of reaction 2 releases the isomeric

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(12) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, *J. Am. Chem. Soc.* **82**, 1750 (1960).

(13) J. Herling, J. Shabtai, and E. Gil-Av, *ibid.*, **87**, 4107 (1965).

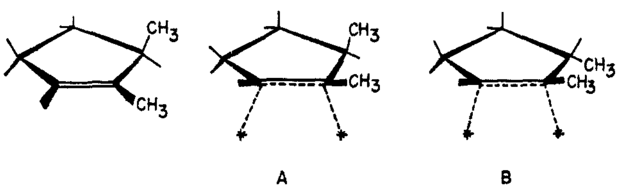

Figure 2.—Potential energy associated with neighboring group interactions (C-2, C-3) is greater in A than in B and opposes interactions with catalytic site.

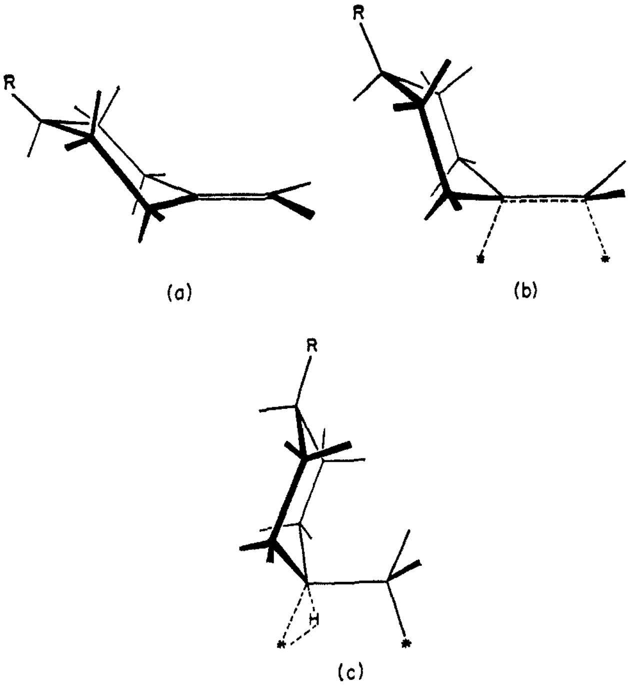

Figure 3.—Variation in geometry of a 4-alkylmethylenecyclohexane (a) on attaining the transition states for chemisorption to α,β-diadsorbed alkane (b) and the formation of the "half-hydrogenated state" (c).

olefin from the surface. However, an alternative mechanism for isomerization is also operable.[14,15]

An additional limiting form of the general mechanism occurs if reaction 4 is rate controlling. Accordingly, the ratio of products should approach the equilibrium value and this result appears to characterize the hydrogenation of cycloalkenes on palladium catalysts.[5,16]

Stereochemistry of Hydrogenation.—The fact that the *cis/trans* ratio of saturated stereoisomers is a function of the pressure of hydrogen, although the competing isomerization of the olefin is negligible, implies that the limiting ratios are characteristic of different product controlling reactions, whose transition states differ in composition by one or more hydrogen atoms.[6] To explain the proportion of saturated stereoisomers which are formed under limiting conditions, models of the pertinent transition states are selected and the relative energies of the geometrical isomeric states are estimated.

In general, the various kinds of interactions which affect the ratio of the geometrical isomeric states may be subdivided into (a) those acting between the organic moiety and the reaction site on the catalyst and (b) the nonbonded interactions between the groups within the organic moiety including torsional and angular deformational strain.

We have assumed that the organic moiety of the transition state which yields the chemisorbed alkene has a structure lying between that of the alkene and an α,β-diadsorbed alkane in which the bonds to the surface are eclipsed.[4,6] Accordingly, if the structure is alkene-like, the unsaturated carbon atoms must lie in a plane perpendicular to a line joining an atom of the surface with the center of the double bond while the groups attached to the unsaturated carbon atoms are displaced outwardly from this plane. This model rests in part on the assumption that the adsorbed species have structures like those to be expected if the hydrocarbon moiety were part of a typical molecular complex of platinum.[17,18] The reactivity of chemisorbed species should be related to the reactivity of similar organometallic compound whose structures may be established by direct means. Similar views have been expressed by others.[19-21]

That the attached groups are displaced appreciably from the planar arrangement in the alkene is suggested by the fact that 2,3-dimethylcyclopentene yields somewhat more *trans*- than *cis*-1,2-dimethylcyclopentane at high pressures on platinum oxide.[7] The contrary result would certainly be expected if the transition state for absorption included the alkene in a slightly perturbed structure. (See Figure 2.)

In contrast, 2,3-dimethylcyclohexene, under the same conditions, yields mainly the *cis* isomer, the larger cycle permitting motions of the neighboring groups, which reduces this intramolecular interaction.[4] However, the fact that in many instances the *cis/trans* ratio is closer to unity at high pressures than at low (Tables I and II) tends to suggest that the geometry lies closer to the alkene than to the saturated structure. We envision the structure of the organic moiety to be quite similar to the description of the transition state for the reduction of alkenes by diimide given recently by Garbisch, Schildcrout, Patterson, and Sprecher,[22] and we will report on some comparative results elsewhere.[23]

The Geometry of the Transition State for the Addition of the First Hydrogen Atom.—The structure of the transition state which determines the limiting *cis/trans* ratios at low hydrogen pressures can be defined as lying between that of an α,β-diadsorbed alkane and the half-hydrogenated state (reaction 3). If one assumes that this transition state is identical with the one implicated in the facile α,β mechanism for the exchange of deuterium for hydrogen in alkanes, then the groups attached to the carbon atoms undergoing changes in bonding are eclipsed.[10,24] In any event, the structure is virtually saturated. Such a structure is clearly in accord with the fact that alkyl-substituted methylenecyclohexanes yield a greater proportion of the axial–

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[14] T. I. Taylor and V. H. Dibeler, *J. Phys. Chem.*, **55**, 1036 (1951).

[15] G. V. Smith and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **84**, 925 (1962).

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[19] D. K. Fukushima and T. F. Gallagher, *J. Am. Chem. Soc.*, **77**, 139 (1955).

[20] J. J. Rooney, *J. Catalysis*, **2**, 53 (1963).

[21] R. L. Burwell, Jr., A. B. Littlewood, M. Cardew, G. Pass, and C. T. H. Stoddart, *J. Am. Chem. Soc.*, **82**, 6272 (1960).

[22] F. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *ibid.*, **87**, 2932 (1965).

[23] S. Siegel and D. Johnson, unpublished work.

[24] R. L. Burwell, Jr., and K. Schrage, *J. Am. Chem. Soc.*, **87**, 5253 (1965).

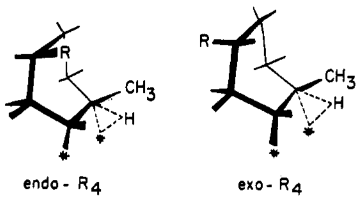
equatorial disubstituted cyclohexane at low than at high hydrogen pressures (Figure 1 and Table I), the reactive site being effectively a much larger group than the emerging methyl group, and the difference in energy of the possible conformations approaches a maximum value. (See Figure 3.)

An Intramolecular Driving Force which Affects the Ratio of Stereoisomers.—The stereochemistry of hydrogenation of disubstituted cycloalkenes calls forth another interaction mechanism. For example, it is difficult to understand why a compound such as 4-*t*-butyl-1-methylcyclohexene should yield mainly the *trans* dialkylcyclohexane at low pressures whereas 1,4-dimethylcyclohexene yields somewhat more *cis*- than *trans*-1,4-dimethylcyclohexane. Sauvage, Baker, and Hussey suggested that this resulted from the adsorption of the cycloalkene in a boat conformation and assumed that a small substituent would tend to adopt an *endo* configuration while a larger group would be free to be *exo*.[11] Although this suggestion was based upon a classical view of the stereochemistry of hydrogenation, it can be adjusted to the present treatment.

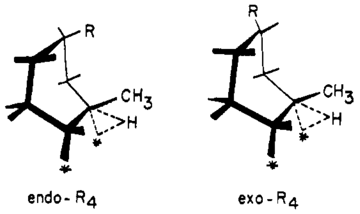
The conformation adopted by a given structure will be a function of both intra- and intermolecular interactions. Molecules which are attracted to a surface experience a lateral force between adjacent molecules which causes them to adopt conformations which will minimize the energy of the adsorbed molecules. Such an effect is demonstrated in measurements of the film pressures of toluene on mercury.[25] As the pressure is increased, the molecules abruptly change their orientation on the surface from a flat to a vertical arrangement. In the present context, the attraction of the surface for the substrate, whether chemical or physical, will cause neighboring molecules to crowd one another so that an adsorbed molecule may adopt a conformation which is different from the conformation of lowest energy in the isolated molecule.

Accordingly, one can rationalize the proportions of epimers obtained from disubstituted cyclohexenes by recognizing this external force which acts to fold the molecule onto itself and increase its extension in a direction away from the surface. The resultant of the interactions produces a boat-like conformation in which substituents at C-3 or C-6 prefer to occupy the bowsprit positions while groups at C-4 and C-5 will be *exo* unless interactions with substituents at carbon 1 and 2 overcome the intramolecular pressure. Thus, at low pressure, 2,3-dimethylcyclohexene yields 80% and 1,3-dimethylcyclohexene yields 75% *cis*-dimethylcyclohexane while 1,4- yields somewhat more *cis* than does 2,4-dimethylcyclohexene (Figure 4). The lesser proportion of *cis* in the latter presumably arises from interactions between the groups at C-2 and C-4 and between those at C-1 and C-5. Apparently, the combination of the one methyl-methyl group (C-2, C-4) and the one hydrogen-hydrogen group interaction (C-1, C-5) in 2,4-dimethylcyclohexene is greater than the two corresponding methyl-hydrogen interactions in 1,4-dimethylcyclohexene.

One might expect that such interactions would be lessened in the transition state for chemisorption, *e.g.*, the product controlling reaction at high pressures, because the distribution of groups about the metal-bonded carbon atoms is closer to the planar trigonal array of the olefin structure, and perhaps this accounts for the somewhat larger proportion of the *cis* isomer formed from 1,4-dimethylcyclohexene at high than at low pressure. However, the lack of any change in the ratio from 2,4-dimethylcyclohexene is unexplained.



4-Substituted 1-methylcyclohexene



4-Substituted 2-methylcyclohexene

Figure 4.—Geometry of transition state leading to the "half-hydrogenated state" of 4-substituted cyclohexenes.

Other Considerations.—In our original analysis of the stereochemistry of hydrogenation of dialkylcyclohexenes, we assumed that the transition states were best represented as distorted chair-like conformations not unlike that represented by Garbisch, *et al.*, for reductions by diimide.[22] However, it was difficult to explain the results from the hydrogenation of 4-*t*-butylmethylcyclohexene on this model.[6] Probably the ultimate analysis will indicate that neither the present nor the previous representation is totally correct, the cycle adopting a twisted conformation in response to the several interaction mechanisms which are operating. However, the present view appears to provide a model which is relatively easy to visualize and thus may encourage further work designed to clarify the stereochemistry of these reactions.

A corollary of the above analysis is that, if the substituents attract one another, the intergroup interactions, which tend to reduce the amount of *cis* isomers in dialkylcyclohexenes, would act in the opposite sense. Perhaps this explains why 2,3-dicarbomethoxycyclohexene yields virtually 100% *cis*-1,2-dicarbomethoxycyclohexane at low pressures and only about 90% at about 100 atm.[26]

Experimental Section

All the compounds used in this study have been previously reported. The procedures employed for their preparation were chosen to yield mainly, if not exclusively, the desired olefin or a mixture from which it could be separated readily. **1,4-Dimethylcyclohexene** was obtained by the iodine-catalyzed dehydration of 1,4-dimethylcyclohexanol according to the procedure of Signaigo and Cramer:[27] bp 125.5–126.0° (727 mm), $n^{25}\text{D}$ 1.4431, $d^{25}{}_4$ 0.7986; lit.[11] bp 126.5°, $n^{20}\text{D}$ 1.4458; lit.[28] bp 127–128°, $d^{19.5}$ 0.8020, $n^{20}\text{D}$ 1.4459.

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[25] C. Kemball and E. K. Rideal, *Proc. Roy. Soc.*, **A187**, 53 (1946).

[26] S. Siegel and G. S. McCaleb, *J. Am. Chem. Soc.*, **81**, 3655 (1959).

[27] F. K. Signaigo and P. L. Cramer, *ibid.*, **55**, 3326 (1933).

[28] O. Wallach, *Ann.*, **396**, 264 (1913).

4-Methylmethylenecyclohexane [bp 124–125° (724 mm), n^{25}_{D} 1.4425, d^{25}_{4} 0.7966; lit.[29] bp 122–123°, n^{22}_{D} 1.4446, d^{22} 0.7925; lit.[11] n^{20}_{D} 1.4447] was prepared from 4-methylcyclohexanone *via* the Wittig reaction,[11,30] or by the pyrolysis of the acetate of 4-methylcyclohexylmethanol as is described in the following procedure for the preparation of 3-methylmethylenecyclohexane.[3]

3-Methylmethylenecyclohexane.—Sodium *m*-toluate (29.5 g of toluic acid, 9.5 g of sodium hydroxide, and 40 ml of water) was reduced catalytically (about 7 g of Raney nickel) in a 300-ml rocking autoclave for 4 hr at 175° with an initial pressure of hydrogen of 2500 psi. The product was obtained as a mixture of *cis* and *trans* isomers of 3-methylcyclohexanecarboxylic acid which distilled at 89–99° (1 mm) (90%).

The acid was reduced with lithium aluminum hydride, as customary for the reduction of ether soluble compounds,[32] to yield the mixed alcohols, bp 101–106° (23 mm), which were converted by gentle heating with acetyl chloride to the mixed acetates, bp 92–97° (13 mm).

The acetate was passed at a rate of 4–5 drops per minute through a heated (475–500°) Pyrex tube (50 cm by 30 mm) packed with Pyrex chips. The crude mixture was dissolved in ether, washed with a saturated solution of sodium bicarbonate and dried. The solvent was removed by distillation through an efficient column and the product distilled at 119–120° (726 mm), n^{20}_{D} 1.4461, n^{25}_{D} 1.4429, d^{25}_{4} 0.7882; lit.[33] bp 123–124°, n^{20}_{D} 1.4461, d^{20} 0.794; see also Smith and Trotter.[34]

1,3-Dimethylcyclohexene.—2,6-Dimethylcyclohexanol, prepared by hydrogenating 2,6-dimethylphenol over Raney nickel according to the directions of Carlin,[35] was converted to the palmitate which was pyrolyzed as suggested by Birch.[36]

Palmitoyl chloride (121 g) was added to 2,6-dimethylcyclohexanol (50 g) in 300 ml of dry dimethylaniline at 20°. The mixture was stirred for 1 hr at 20° and then on a steam bath for 5 hr. Afterwards, it was poured into 1200 ml of iced 2 *M* hydrochloric acid. The ester was extracted with ether. The extract was washed with a saturated solution of sodium bicarbonate, dried over sodium sulfate, and concentrated. The concentrate was heated to 375° (bath temperature); pyrolysis took place. An ether extract of the distillate was washed with a solution of sodium bicarbonate, dried over magnesium sulfate, and distilled to yield 23 g of the crude 1,3-dimethylcyclohexene, bp 115–125°. Careful fractionation of this material (Todd column) yielded 19 g of the pure olefin, bp 123.5–124° (727 mm), n^{25}_{D} 1.4467, d^{25}_{4} 0.7996; lit.[37] bp 124–126°, n^{25}_{D} 1.4480, d^{25} 0.807; lit.[34] bp 130–131° (750 mm), $n^{25.5}_{\mathrm{D}}$ 1.4465, d^{25}_{4} 0.799.

The same product was also obtained by the pyrolysis of the acetate at 470–480°.[31,36]

2,3-Dimethylcyclohexene was separated by preparative chromatography on a 25 ft by 0.5 in. o.d. column of 20% polyethylene glycol 1000 monostearate on 60–80 mesh firebrick at 95° from a mixture of 25% 2,4-dimethylcyclohexene and 75% of 3,5-dimethylcyclohexene which had been obtained from the pyrolysis of 2,4-dimethylcyclohexyl acetate.[31] The compound has been carefully characterized recently by Smith and Trotter.[34]

Procedures for hyrogenation and the analysis of the products have been described previously.[4,6] In each experiment, 0.2 ml of the olefin, 5 ml of acetic acid, and 10–20 mg of platinum oxide were used. Experiments at 1-atm pressure and below were done in a constant-pressure apparatus, those in the intermediate range (2–5 atm) in a Parr low pressure hydrogenation apparatus, and at high pressure in a rocker type high pressure bomb. A 25 ft by 0.25 in. o.d. column containing 20% polyethylene glycol 1000 monostearate on 60–80 mesh firebrick and operated at 90–100° was used for the analysis of mixtures other than those from the hydrogenation of 1,4-dimethylcyclohexene and 4-methylmethylenecyclohexane for which a 15 ft by 0.25 in. o.d. column was adequate. Separations of all products and reactants were satisfactory, the peaks being symmetrical and well separated.

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(31) D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).

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Aliphatic Polynitro Compounds. I. Synthesis of 1,1,1-Trinitrochloroethane and Its Rearrangement to Dipotassium Tetranitroethane[1]

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A general procedure for the conversion of β-polynitro-substituted alcohols to their corresponding halides is described, which consists of the treatment of the alcohol with thionyl chloride containing catalytic amounts of pyridine or pyridine hydrochloride. 1,1,1-Trinitrochloroethane undergoes a novel rearrangement reaction to dipotassium tetranitroethane upon treatment with nitrite ion in basic media. A study of the chemistry of 1,1,1-trinitrochloroethane permits some conclusions regarding possible mechanisms for this rearrangement.

During the course of a program investigating the chemistry of polynitro compounds attention was directed toward studying the little known β-halogen-substituted aliphatic polynitro compounds. Although a few reports of the synthesis of some of these compounds have appeared, the chemistry of these compounds has been largely unexplored. The recent appearance in the literature of a few compounds previously studied in our laboratories prompts the reporting of our results at this time. Novikov and Shvekgheimer[2] have reported the synthesis of 1,1,1-trinitrochloroethane (I) and 2,2-dinitrochloropropane (II) by treating the mixed acetal product of the reaction of corresponding polynitro alcohols and ethyl vinyl ether with phosphorus pentachloride. The yields of chlorides from the mixed acetals were 40 and 57%, respectively. Kissinger and co-workers[3] reported the synthesis of 2,2-dinitro-1,3-dichloropropane (III) and 2,2-dinitrochloropropane (II) from reactions of the corresponding nitro alcohols with sulfuryl chloride and pyridine in yields of 57 and 62%, respectively. Ungnade and Kissinger[4] have recently reported a reaction

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