[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of α-Haloketones. I. The Molecular Configurations of Some Monocyclic α-Halocyclanones

BY ELIAS J. COREY

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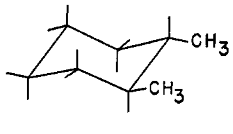
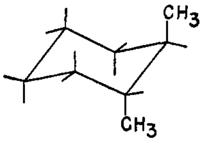
The molecular configurations of several monocyclic α-haloketones have been determined by means of infrared spectroscopy. The most stable conformation of α-chlorocyclohexanone and of α-bromocyclohexanone is that chair form in which the halogen substituent is *polar*, while the most stable conformation of 2-bromo-4,4-dimethylcyclohexanone and of 7-bromo-spiro[4.5]decane-6-one is that chair form in which the halogen substituent is *equatorial*. The results with α-chlorocyclohexanone and α-bromocyclohexanone are in agreement with calculations which clearly show that with these substances dipole–dipole interaction is more important than steric interaction between substituents in determining molecular configuration. The results with 2-bromo-4,4-dimethylcyclohexanone and 7-bromo-spiro[4.5]decane-6-one indicate the magnitude of the steric interaction needed to overcome the opposing electrical interaction. Information is also provided concerning the molecular configurations of α-chlorocycloheptanone and α-bromocycloheptanone.

Recent work has shown that the "chair" conformation of cyclohexane derivatives is of considerably lower energy than the "boat" conformation.[1,2,3] The energy of the chair form of cyclohexane itself, for example, is *ca.* 5.6 kcal./mole less than that of the boat form.[3] Furthermore, an appreciable energy difference usually exists between the two chair forms which are possible for *substituted* cyclohexanes.[3] The more stable chair form, *sterically*, is that in which the substituents of high steric requirement occupy equatorial[3] positions and those of low steric requirements occupy polar positions. Thus, the stable form of *trans*-1,2-dimethylcyclohexane is IA and not IB.



IA



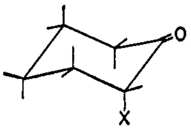
IB

In general, the foregoing considerations suffice for the prediction of the relative stability of cyclic rotational isomers such as IA and IB, if the only important interactions between substituents are steric repulsions. The occurrence of strong electrostatic interactions between groups, which is obviously possible with certain substituted cyclohexanes, might result in considerable destabilization of the sterically less strained form, and one might even expect to find cases where the stable form is that which is sterically more strained.

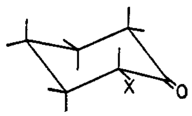
This paper concerns the study of various systems in which opposing steric and electrostatic interactions are operative and the nature of the equilibria in such systems. In particular, we have investigated the molecular configurations of several α-halocyclanones using infrared spectroscopy as the analytical tool.

The study of α-halocyclanones is advantageous for two reasons: first, these compounds contain two strong dipoles, in close proximity, which are mutually repulsive to the greatest extent when steric strains are at a minimum and second, the approximate relative orientations of the two dipoles can be determined by infrared spectroscopy. It has been demonstrated[4] that in ketosteroids the introduction of an α-bromo substituent shifts the carbonyl (ketone) absorption to higher frequencies ($\Delta = 13$ to 25 cm.$^{-1}$) if the carbon–bromine and carbon–oxygen bonds are approximately in the same plane, but has relatively little effect if the carbon–bromine and carbon–oxygen bonds are far from coplanar. Thus, while ketone absorption occurs at 1710 cm.$^{-1}$ in pregnanone-12, methyl 11-α-bromo-12-keto-3-acetoxycholanate and the corresponding 11-β-bromo compound exhibit ketone absorption at 1736 and 1706 cm.$^{-1}$, respectively.[4]

The α-Halocyclohexanones.—We wish first to advance the theoretical arguments which lead to the conclusion that α-bromo- and α-chlorocyclohexanone should exist almost completely at room temperature as the chair form in which the halogen occupies a *polar* position (II). Considering the bromoketone, the difference in energy between the chair forms, IIIB and IIB, may be formulated as



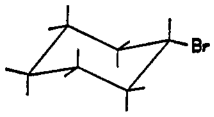
IIA, X = Cl
IIB, X = Br



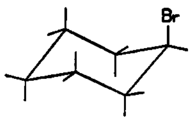
IIIA, X = Cl
IIIB, X = Br

$$E_{\mathrm{III}} - E_{\mathrm{II}} = (E^{\mathrm{S}}_{\mathrm{III}} - E^{\mathrm{S}}_{\mathrm{II}}) + (E^{\mathrm{E}}_{\mathrm{III}} - E^{\mathrm{E}}_{\mathrm{II}})$$

where $(E^{\mathrm{S}}_{\mathrm{III}} - E^{\mathrm{S}}_{\mathrm{II}})$ is the difference in energy between IIIB and IIB due to steric repulsion and $(E^{\mathrm{E}}_{\mathrm{III}} - E^{\mathrm{E}}_{\mathrm{II}})$ is the difference in energy between IIIB and IIB due to CO dipole–CBr dipole repulsion. The quantity $(E^{\mathrm{S}}_{\mathrm{III}} - E^{\mathrm{S}}_{\mathrm{II}})$ may be taken as $(x + y)$, where x is the energy corresponding to the steric repulsion between bromine and oxygen in III, and y is the difference in energy, between the Br-equatorial (IV) and Br-polar (V) forms of bromocyclohexane.



IV



V

The value of y can be calculated from published data. Bastianson and Hassel have reported that

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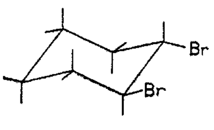
[1] O. Hassel, *Tids. Kjemi, Bergvesen Met.*, **3**, 32 (1943).

[2] O. Bastianson and O. Hassel, *Nature*, **157**, 765 (1946).

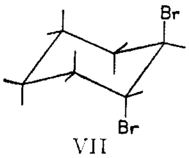
[3] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

[4] R. N. Jones, D. A. Ramsay, F. Herling and Konrad Dobriner, *ibid.*, **74**, 2828 (1952).

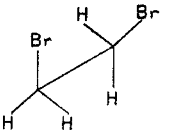
trans-1,2-dibromocyclohexane in the gas phase exists as an equilibrium mixture containing *ca.* 50% of the Br(e), Br(e) form (VI) and 50% of the Br(p), Br(p) form (VII) and, consequently, the energy difference between VI and VII must be small.[5] This energy difference, which is effectively zero, can be equated to the energy difference (1.4 kcal./mole)[6] between the *gauche*- and *trans*-forms of ethylene dibromide (VIII and IX) plus $2y$. Thus, y is -0.7 kcal./mole.[7]



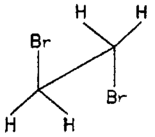
VI



VII



VIII



IX

Assuming a value of 0.3 kcal./mole for x, which is probably too low an estimate, and using $y = -0.7$, the lower limit of $(E^{S}_{III} - E^{S}_{II})$ becomes -0.4 kcal./mole.

The lower limit of the quantity $(E^{E}_{III} - E^{E}_{II})$ can be calculated by electrostatics and is found to be 2.7 kcal./mole (see Experimental). The minimum value of $(E_{III} - E_{II})$, therefore, is 2.3 kcal./mole, which corresponds to over 97% of form IIB (as a lower limit) in α-bromocyclohexanone at room temperature. Obviously, there should be a similar predominance of IIA in α-chlorocyclohexanone.

Calculations similar to those above show that the energy of the most stable of the six possible boat forms of α-bromocyclohexanone is at least 5 kcal./mole greater than the energy of IIB.[8]

The infrared spectral data obtained for cyclopentanone, cyclohexanone and their α-bromo and α-chloro derivatives in carbon tetrachloride solution are summarized in Table I. The quantity Δ for each halogenated ketone is the difference between the frequency of its carbonyl absorption and that of the corresponding unhalogenated ketone.

Considering the bromoketones, the Δ-value obtained for α-bromocyclohexanone (4 cm.$^{-1}$) is less than that for α-bromocyclopentanone (8 cm.$^{-1}$) and much less than the Δ-values reported for α-bromoketosteroids in which the CO and CBr dipoles are coplanar (13 to 25 cm.$^{-1}$).[4] This fact indicates strongly that the more stable chair form of α-bromocyclohexanone is that in which the CO and CBr dipoles are not coplanar (IIB). This result is in agreement with the prediction based on the calculations presented above.

TABLE I

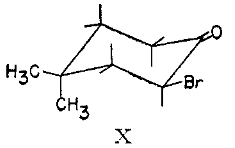
Compound	Position of carbonyl absorption,[d] cm.$^{-1}$	Frequency shift, Δ,[a] due to α-halogen, cm.$^{-1}$
Cyclopentanone	1742	. .
α-Bromocyclopentanone	1750	8
α-Chlorocyclopentanone	1755	13
Cyclohexanone	1712	. .
α-Bromocyclohexanone	1716[b]	4
α-Chlorocyclohexanone	1722[c]	10
4,4-Dimethylcyclohexanone	1712	. .
2-Bromo-4,4-dimethylcyclohexanone	1728	16
Spiro[4.5]decane-6-one	1701	. .
7-Bromo-spiro[4.5]decane-6-one	1723 (strong) 1701 (medium)	22 0
Cycloheptanone	1700	. .
α-Bromocycloheptanone	1708	8
α-Chlorocycloheptanone	1716	16

[a] These values of Δ are ± a maximum of 3 cm.$^{-1}$. [b] Slight shoulder at 1730 cm.$^{-1}$. [c] Slight shoulder at 1740 cm.$^{-1}$. [d] Spectra obtained in carbon tetrachloride using a Perkin–Elmer model 21 double beam spectrophotometer.

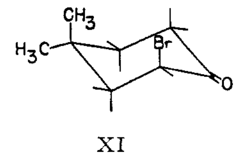
If α-bromocyclohexanone exists almost completely as form IIB, α-chlorocyclohexanone should certainly have the same molecular configuration since $(E_{III} - E_{II})$ is greater for the chloroketone. The observed Δ-value for α-chlorocyclohexanone (10 cm.$^{-1}$), which is less than that for α-chlorocyclopentanone, is in accord with this conclusion. The occurrence of larger Δ-values for α-chloroketones than for the corresponding α-bromoketones is only to be expected and has already been anticipated by Jones, *et al.*,[4] on the basis of their very plausible interpretation of the observed frequency shifts.

The appearance of slight shoulders on the 1716 and 1722 cm.$^{-1}$ bands of α-bromo- and α-chlorocyclohexanone, respectively, (Table I), is probably an indication of the existence of a small amount of the less stable form (III) in equilibrium with the more stable II. The alternative explanation that some α,α- or α,α′-dihalogenated ketone was present in the samples used seems less likely since the materials used were highly purified.

If indeed the conformation of the stable form of α-bromocyclohexanone is given by IIA (bromine polar), it should be possible to increase the steric repulsions involving polar bromine by the introduction of substituents until the stable form is that in which the α-bromine is equatorial. Such a result has been obtained as is apparent from the data in Table I. The large Δ-value for 2-bromo-4,4-dimethylcyclohexanone clearly indicates that this substance should be formulated as X instead of XI.



X



XI

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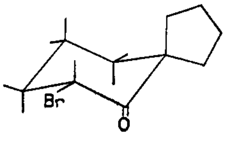
(5) O. Bastianson and O. Hassel, *Tids. Kjemi, Bergvesen Met.*, **6**, 96 (1946).

(6) S. Mizushima, Y. Morino, L. Watanabe and T. Simanouti, *J. Chem. Phys.*, **17**, 663 (1949).

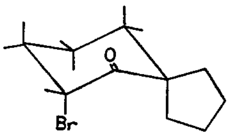
(7) It follows from this value that the energy difference between the *gauche*- and *trans*-forms of *n*-propyl bromide in the gas phase should be approximately 0.35 kcal./mole (*cf.* ref. 3). This figure compares favorably with that reported by J. Goubeau and H. Pajenkamp, *Acta Phys. Austriaca*, **3**, 283 (1949), for the liquid phase, 0.5 ± 0.1 kcal./mole.

(8) All the foregoing calculations apply rigorously only to the gas phase. In view of the rather large energy differences between the forms considered, however, the conclusions drawn from these calculations can be regarded as correct to a first approximation for solutions in non-polar solvents.

Analogously, 7-bromo-spiro[4.5]decane-6-one exhibits strong absorption at 1723 cm.$^{-1}$ (Δ = 22) and a considerably weaker band at 1701 cm.$^{-1}$ (Δ = 0), which indicates that although both possible forms, XII and XIII, are present, the former (bromine equatorial) predominates.



XII

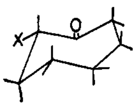


XIII

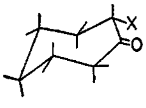
Inspection of Fisher–Hirschfelder–Taylor models reveals that there is strong steric interaction between methyl and bromine in XI, the unstable chair form of 2-bromo-4,4-dimethylcyclohexanone, and considerable, but somewhat less, interaction between methylene and bromine in XIII, the unstable chair form of 7-bromo-spiro[4.5]-decane-6-one.

Application of the above results to the prediction of the stereochemistry of α-bromoketosteroids will appear in a separate communication.

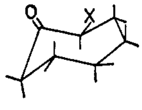
The α-Halocycloheptanones.—The values of Δ observed for α-bromo- and α-chlorocycloheptanone are approximately the same as those for the corresponding cyclopentanones (Table I), which would seem to indicate that the relative orientation of the carbon–oxygen and carbon–halogen bonds is essentially the same in the seven- as in the five-membered series. Since, in the case of the halocyclopentanones the angle between the projections of the carbon–oxygen bond and the carbon–halogen bond on a plane perpendicular to the carbon–carbon bond, ϕ, is constrained to be *ca.* 60°, one would expect a similar value of ϕ for the halocycloheptanones. Excluding structures in which the CO and CBr dipoles are coplanar (ϕ = 0°), which is certainly justified by the infrared data, it appears from the examination of scale models that of the twenty-eight forms which are possible for each epimeric halocycloheptanone by far the least strained sterically are XIV, XV and XVI. The values of ϕ for XIV, XV and XVI are ~30°, 80° and 25°, respectively. Since it is probably more than coincidental that the values of ϕ for XIV, XV and XVI agree approximately with that predicted from the infrared data, it seems reasonable to conclude that α-bromo- and α-chlorocycloheptanone are probably best represented as one or more of these three forms.



XIV



XV



XVI

Experimental[9,10]

Materials.—α-Chlorocyclopentanone was prepared by the method of Kotz, *et al.*,[11] and had b.p. 82–83° (12 mm.), $n^{18.5}_{\rm D}$ 1.4778.

α-Bromocyclopentanone was prepared by the reaction of cyclopentanone with N-bromosuccinimide in carbon tetrachloride with a small amount of benzoyl peroxide present. The product had b.p. 68° (2 mm.) and $n^{16.5}_{\rm D}$ 1.5105 (lit.[11] b.p. 79–82° (15 mm.)).

α-Chlorocyclohexanone[12] was purified by fractional distillation, recrystallization of the fraction, b.p. 78–78.5° (7 mm.), $n^{20}_{\rm D}$ 1.4831, from pentane at −50° and fractional distillation of the material thus obtained. The sample so purified was utilized for infrared analysis and had b.p. 38.5° (0.8 mm.), $n^{20}_{\rm D}$ 1.4830 (lit.[13] b.p. 79° (7 mm.), $n^{20}_{\rm D}$ 1.4825).

α-Bromocyclohexanone was obtained by the method of Schmid and Karrer[14] and had b.p. 74° (3 mm.), $n^{27}_{\rm D}$ 1.5093 (lit.[15] b.p. 112–113° (20 mm.), $n^{25}_{\rm D}$ 1.5085).

α-Chlorocycloheptanone was prepared from α-chlorocyclohexanone and N-nitrosomethylurethan essentially by the method of Steadman[16] and was purified by careful fractional distillation through a "spinning-band" column, b.p. 88–89° (10 mm.), $n^{20}_{\rm D}$ 1.4869.

The other bromoketones used in this study were synthesized as described below.

α-Bromocycloheptanone.—A mixture of 11.2 g. of cycloheptanone (Geigy), 18 g. of N-bromosuccinimide, 0.01 g. of azoisobutyronitrile and 50 ml. of carbon tetrachloride was heated to reflux for 20 minutes after which time the mixture was cooled and filtered. Evaporation of the carbon tetrachloride under reduced pressure, treatment of the residue with 100 ml. of pentane and cooling the resulting solution to −50° afforded two layers. The upper layer (pentane solution) contained α-bromocycloheptanone and the lower sirupy layer consisted of high-boiling material which was extracted again with pentane at −50°. The liquid obtained from the combined pentane extracts afforded pure α-bromocycloheptanone upon distillation, b.p. 72–73° (1.5 mm.), $n^{25}_{\rm D}$ 1.5130.

Anal. Calcd. for $C_7H_{11}OBr$: C, 44.00; H, 5.80. Found: C, 44.07; H, 5.76.

2-Bromo-4,4-dimethylcyclohexanone.—This substance was prepared by heating 4,4-dimethylcyclohexanone[17] with an equivalent quantity of N-bromosuccinimide and a small amount of benzoyl peroxide. The crude bromoketone was purified by three recrystallizations from pentane (at −50°) and evaporative distillation at 90° (0.5 mm.). The colorless solid so obtained had m.p. 61–62.5°.

Anal. Calcd. for $C_8H_{13}OBr$: C, 46.84; H, 6.39. Found: C, 46.56; H, 6.23.

7-Bromo-spiro[4.5]decane-6-one.—A solution of 3.95 g. of bromine in 8 ml. of glacial acetic acid was added dropwise with stirring to a cooled (15°) solution of 3.75 g. of spiro-[4.5]decane-6-one[18] in 10 ml. of acetic acid. Pentane (40 ml.) was added and the pentane solution was washed with water and potassium bicarbonate solution and dried. The product was obtained by crystallization from the pentane solution (20 ml.) at −50° and purified by four recrystallizations from pentane followed by evaporative distillation. The m.p., 51–55°, and infrared spectrum of the product so obtained were unchanged by further recrystallization.

Anal. Calcd. for $C_{10}H_{15}OBr$: C, 51.96; H, 6.54. Found: C, 51.75; H, 6.48.

Reaction of spiro[4.5]decane-6-one with N-bromosuccinimide proceeded extremely slowly and afforded a low yield of an impure product.

Calculation of Dipole–Dipole Interactions.—Electrostatic potential energy, U, due to dipole–dipole interaction was calculated using the expression[19]

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[9] The author is indebted to Mr. Kunizo Osugi for the preparation of α-chloro- and α-bromocyclopentanone and α-bromocyclohexanone, and to Mr. Howard Burke for the purification of α-chlorocycloheptanone.

[10] The infrared spectra were determined by Miss Helen Miklas and Mrs. Rosemary Hill, and the microanalyses were performed by Mrs. Katherine Pih.

[11] A. Kotz, K. Blendermann, E. Karpoti and R. Rosenbusch, *Ann.*, **400**, 47 (1913).

[12] "Organic Syntheses," Vol. 25, John Wiley and Sons, Inc., New York, N. Y., 1945, p. 22.

[13] R. E. Meyer, *Helv. Chim. Acta*, **16**, 1291 (1933).

[14] H. Schmid and P. Karrer, *ibid.*, **29**, 573 (1946).

[15] P. Z. Bedoukian, THIS JOURNAL, **67**, 1430 (1945).

[16] T. R. Steadman, *ibid.*, **62**, 1606 (1940).

[17] R. F. Miller and R. Adams, *ibid.*, **58**, 787 (1936).

[18] N. D. Zelinskii and N. V. Elagina, *Compt. rend. acad. sci. U.R.S.S.*, **49**, 568 (1945).

[19] J. Jeans, "Electricity and Magnetism," Cambridge University Press, Cambridge, 1920, p. 354.

$$U = \frac{\mu_1 \mu_2}{r^3} (\cos \chi - 3 \cos \alpha_1 \cos \alpha_2) \qquad (1)$$

where μ_1 and μ_2 are the moments of dipoles 1 and 2, respectively, r is the distance between one pair of like charged dipole ends, χ is the dihedral angle formed by the intersection of the plane containing dipole 1 and the connecting line between the second pair of like charged dipole ends *with* the plane containing dipole 2 and the same connecting line, and α_1 and α_2 are the angles between r and dipole 1 and between r and dipole 2, respectively.

The quantities r, χ, α_1 and α_2 were related to the known c_0, a, b, θ_1, θ_2 and ϕ (see Fig. 1) by equations (2)–(5) which were derived using the model of Smyth, Dornte and Wilson.[2]

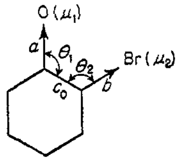

Fig. 1.

For α-bromocyclohexanone, a is the length of the CO dipole, b is the length of the CBr dipole, c_0 is the length of the CC bond between the dipoles, θ_1 is the CCO bond angle, θ_2 is the CCBr bond angle and ϕ, as in the discussion part, is the angle between the projections of the CO and CBr dipoles on a plane perpendicular to the connecting CC bond.

$$r = [a^2 \sin^2 \theta_1 + b^2 \sin^2 \theta_2 - 2ab \sin \theta_1 \sin \theta_2 \cos \phi + (c_0 - a \cos \theta_1 - b \cos \theta_2)^2]^{1/2} \qquad (2)$$

$$\cos \chi = \sin \theta_1 \sin \theta_2 \cos \phi - \cos \theta_1 \cos \theta_2 \qquad (3)$$

$$\cos \alpha_1 = \frac{a^2 + r^2 - c_0^2 - b^2 + 2c_0 b \cos \theta_2}{2ar} \qquad (4)$$

$$\cos \alpha_2 = \frac{b^2 + r^2 - c_0^2 - a^2 + 2c_0 a \cos \theta_1}{2br} \qquad (5)$$

The potential energy difference due to dipole–dipole repulsion between the two chair forms of α-bromocyclohexanone, IIB and IIIB, was calculated using $\phi = 0°$ for IIIB and $\phi = 130°$ for IIB. The CO and CBr dipole moments (μ_1 and μ_2) were assumed to be 2.5 and 1.2 *D*, respectively. These low values were chosen purposely to allow for the decrease in dipole moment of the C=O and C—Br bonds caused by mutual induction and in order to obtain a minimum value of $U_{\text{IIIB}} - U_{\text{IIB}}$. The lengths of the dipoles were taken to be equal to the corresponding internuclear distances, which choice also should lead to the lowest permissible value for $U_{\text{IIIB}} - U_{\text{IIB}}$.[20,21] The bond lengths used were C=O, 1.22 Å.; C—Br, 1.91 A.; C—C, 1.54 Å.; the bond angles used were OCC, 120° and BrCC, 110°. The values calculated for $U(\phi = 0)$ and $U(\phi = 130°)$ are -0.43 kcal./mole and 2.3 kcal./mole, respectively, and, hence, $\Delta U = (E^{\text{E}}_{\text{III}} - E^{\text{E}}_{\text{II}})$ = at least 2.7 kcal./mole.

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(20) C. P. Smyth, R. W. Dornte and E. B. Wilson, Jr. THIS JOURNAL, **53**, 4242 (1931).

(21) *Cf.* G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

URBANA, ILL.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

2-Neopentyl-1,3-butadiene Dimer[1]

BY A. T. BLOMQUIST AND JEROME C. WESTFAHL[2]

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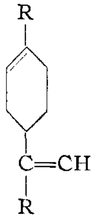
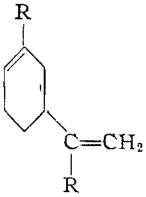
2-Neopentyl-1,3-butadiene is converted to a liquid dimer on heating in the presence of polymerization inhibitors. The dimer is assigned the "dipentene-like" structure, 1-neopentyl-4-(1-methylene-3,3-dimethylbutyl)-1-cyclohexene, from evidence obtained by quantitative hydrogenation, isomerization, pyrolysis, aromatization and oxidation.

Recently the preparation and proof of structure of 2-neopentyl-1,3-butadiene (I) was reported.[3] This paper describes the preparation and structural investigation of the thermal dimer of I.

When I, containing hydroquinone, was heated near its boiling point, 123–125°, in an inert atmosphere, a colorless, odorless hydrocarbon of b.p. 273–276° (739 mm.) was obtained. This hydrocarbon II was shown by analysis and molecular weight determination to be a dimer of I. Of the previously described 2-alkyl-1,3-butadienes, only the dimerization of isoprene appears to have been studied. The two dimers of isoprene whose structures have been established are dipentene or *dl*-limonene (III) and dipren (IV). The dimer of I was assumed to have either of the analogous structures V or VI. Because of its narrow boiling range the possibility of II being a mixture of V and VI did not seem likely.



III, R is $-CH_3$
V, R is $-CH_2C(CH_3)_3$



IV, R is $-CH_3$
VI, R is $-CH_2C(CH_3)_3$

On quantitative catalytic hydrogenation of II using Adams catalyst there was a rapid absorption of approximately half of the total volume of hydrogen in the first 15 minutes followed by slow absorption of the remaining half during the following 212 minutes. The total hydrogen absorption, 1.76 molecular equivalents, indicated the presence of two double bonds in II. The incomplete hydrogenation observed probably resulted from interrupting the hydrogenation when it became very slow but was not complete. The marked change in rate during hydrogenation is shown in Fig. 1. Such a change in rate of hydrogenation was also observed by Vavon on hydrogenating *d*-limonene.[4] Vavon also showed, by measurement of change

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(2) Abstracted from part of the dissertation submitted by Jerome C. Westfahl in September, 1950, to the Graduate Faculty of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) A. T. Blomquist and J. C. Westfahl, THIS JOURNAL, **74**, 4073 (1952).

(4) G. Vavon, *Bull. soc. chim. France*, [iv] **15**, 282 (1914).