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

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]

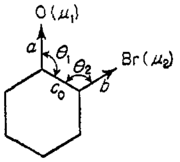

Fig. 1.

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.

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

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

$$\cos\alpha_1 = \frac{a^2 + r^2 - c_0^2 - b^2 + 2c_0b\cos\theta_2}{2ar} \qquad (4)$$

$$\cos\alpha_2 = \frac{b^2 + r^2 - c_0^2 - a^2 + 2c_0a\cos\theta_1}{2br} \qquad (5)$$

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 $U_{\mathrm{IIIB}} - U_{\mathrm{IIB}}$. 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 $U_{\mathrm{IIIB}} - U_{\mathrm{IIB}}$.[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, $\Delta U = (E^{\mathrm{E}}_{\mathrm{III}} - E^{\mathrm{E}}_{\mathrm{II}})$ = 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]

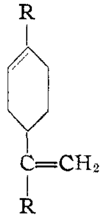
BY A. T. BLOMQUIST AND JEROME C. WESTFAHL[2]

RECEIVED MAY 8, 1952

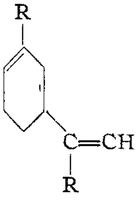
2-Neopentyl-1,3-butadiene is converted to a liquid dimer on heating in the presence of polymerization inhibitors. The dimer is assigned the "dipentene-like" structure, 1-neopentyl-4-(1-methylene-3,3-dimethylbutyl)-1-cyclohexene, from evidence obtained by quantitative hydrogenation, isomerization, pyrolysis, 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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(1) The work reported here was done as part of a research project at the Baker Laboratory of Chemistry, Cornell University, sponsored by the B. F. Goodrich Company.

(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).

of optical activity with hydrogen absorption, that the rapid absorption involved the preferential hydrogenation of the isopropenyl double bond.

The catalytic addition of one mole of hydrogen to II gave a hydrocarbon, b.p. 275–278°, which is referred to as the dihydro dimer VII. On heating with sulfur VII was converted to an aromatic hydrocarbon VIII, b.p. 262–266°. Molecular weight determinations on VIII showed that no loss of alkyl groups occurred in the aromatization. VIII gave a bright red color with chloroform and anhydrous aluminum chloride, indicating the presence of a benzene ring.[5] In this test II and VII gave pale yellow colors.

The ultraviolet absorption spectra of ethanolic solutions of I, II, VII and VIII were determined. They showed the dimer II and dihydro dimer VII to be transparent above 235 mμ. The spectrum of I showed an absorption maximum ($\epsilon_{\max}^{227.5}$ 15,400) characteristic of a 2-alkyl-1,3-butadiene while that of the aromatic hydrocarbon VIII showed low intensity absorption in the neighborhood of 250–270 mμ typical of a dialkylbenzene.[6] The presence of a benzene ring in VIII is thus indicated and a six-membered ring must be present in II.

VIII was unaffected when refluxed with aqueous alkaline potassium permanganate and was only slowly attacked by refluxing with potassium dichromate and aqueous sulfuric acid. Oxidation with chromic anhydride and 65% sulfuric acid gave a vigorous oxidation which produced terephthalic acid and the intermediate oxidation product pivalophenone-*p*-carboxylic acid. Pivalophenone-*p*-carboxylic acid (XII) was characterized by conversion to its 2,4-dinitrophenylhydrazone which was shown to be identical with the 2,4-dinitrophenylhydrazone prepared by the synthesis given in Chart I.

CHART I

$$\underset{\text{IX}}{p\text{-ClCH}_2\text{—C}_6\text{H}_4\text{—Br}} \longrightarrow \underset{\text{X}}{p\text{-(CH}_3)_3\text{CCH}_2\text{—C}_6\text{H}_4\text{—Br}} \longrightarrow$$

$$\underset{\text{XI}}{p\text{-(CH}_3)_3\text{CCH}_2\text{—C}_6\text{H}_4\text{—CO}_2\text{H}} \longrightarrow$$

$$\underset{\text{XII}}{p\text{-(CH}_3)_3\text{C—CO—C}_6\text{H}_4\text{—CO}_2\text{H}} \longrightarrow$$

$$\underset{\text{XIII}}{\text{2,4-Dinitrophenylhydrazone}}$$

The formation of terephthalic acid and XII in the oxidation of VIII thus showed that II contains a six-membered ring having alkyl groups attached to the 1- and 4-positions. The pivalyl group of XII very likely was formed by the oxidation of a neopentyl group attached to the ring. The six carbon atoms which were lost in the oxidation of VIII to XII must have been attached to the carboxylic carbon of XII and must have comprised a neopentyl and a methyl group.

The presence of a methylene group in II was established by hydroxylation of II with hydrogen peroxide in formic acid[7] followed by cleavage with lead tetraacetate.[8] The formaldehyde produced was characterized by the preparation of its 2,4-dinitrophenylhydrazone[9] and its condensation product with methone.[10] The large fragment produced in the hydroxylation and cleavage of II was not isolated in a pure condition.

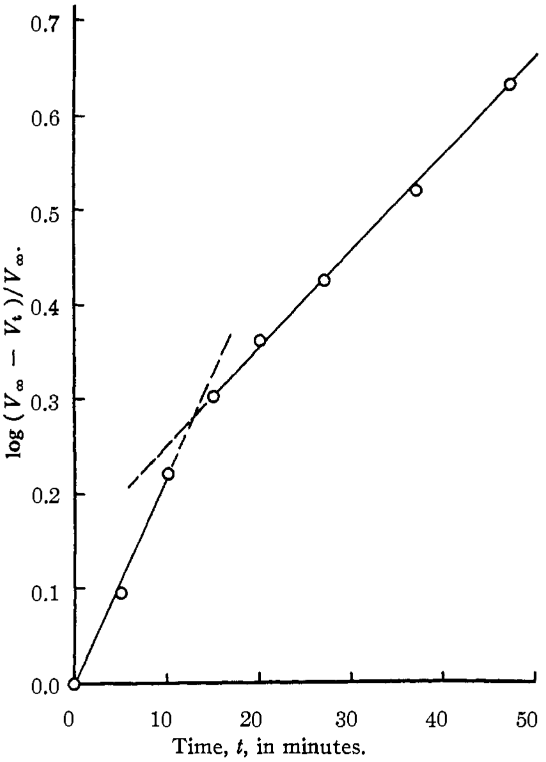
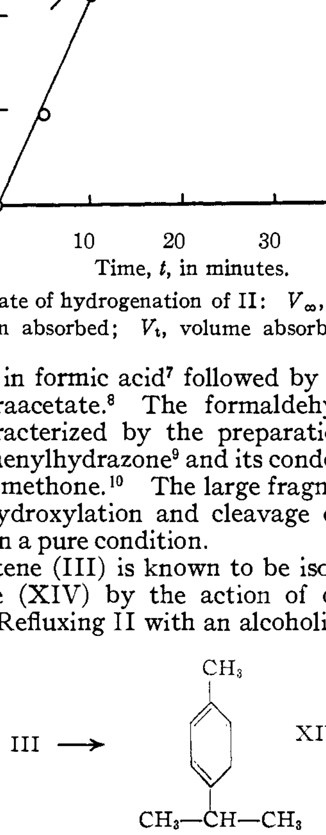


Fig. 1.—Rate of hydrogenation of II: V_∞, total volume of hydrogen absorbed; V_t, volume absorbed at time *t*.

Dipentene (III) is known to be isomerized to α-terpinene (XIV) by the action of dilute sulfuric acid.[11] Refluxing II with an alcoholic sulfuric acid solution produced an isomerized dimer XV whose ultraviolet absorption spectrum showed an absorption maximum ($\epsilon_{\max}^{258}$ 937) whose position is in agreement with the reported maxima of 1,3-cyclohexadiene and various substituted 1,3-cyclohexadienes.[12]



XIV

Pyrolysis of II resulted in considerable decomposition but gave a liquid which was shown to contain I, by the formation of the known adduct with maleic anhydride.[3]

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[5] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd. Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 35.

[6] Compared with the spectra of *o*-, *m*- and *p*-xylene, "International Critical Tables," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 361.

[7] D. Swern, G. N. Billen and J. T. Scanlan, THIS JOURNAL, **68**, 1504 (1946).

[8] J. T. Scanlan and D. Swern, *ibid.*, **62**, 2305 (1940).

[9] Reference 5, p. 65.

[10] Staff of Hopkins and Williams Research Laboratory, "Organic Reagents for Organic Analysis," Chemical Publishing Co., Brooklyn, N. Y., 1946, p. 47.

[11] O. Wallach, *Ann.*, **239**, 15 (1887).

[12] H. Booker, L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 1453, Table VI, 1458 (1940).

The evidence presented is consistent with the "dipentene-like" structure V for 2-neopentyl-1,3-butadiene dimer. The manner of its formation and the regeneration of I on pyrolysis suggests that the dimerization proceeds by the Diels–Alder reaction. This is the accepted mechanism for the formation of dipentene from isoprene.[13]

Experimental Part[14]

2-Neopentyl-1,3-butadiene Dimer (II).—In a 500-ml. flask attached to a reflux condenser which was in turn attached to a trap such as described by Gilman and Hewlett[15] 122.2 g. (0.984 mole) of redistilled 2-neopentyl-1,3-butadiene (I) (b.p. 61–63° (87 mm.), n^{20}_{D} 1.441) and 0.86 g. of hydroquinone was heated by an oil-bath under an atmosphere of carbon dioxide, at slight positive pressure, for 41 hours at 130–135°. Boiling of the hydrocarbon, which occurred at first, ceased within 2 hours. Flash distillation of the mixture at 40° and 0.5 mm. gave 16.5 g. of recovered diene and 100 g. of impure II. The crude II, freed of hydroquinone by washing with aqueous base and dried, was distilled under reduced pressure. The principal fraction (72 g., 68%) showed b.p. 86–89° (0.6 mm.). Redistillation of this fraction gave pure II, b.p. 82.5° (0.4 mm.), 273–276° (739 mm.), n^{20}_{D} 1.4721, d^{20}_{4} 0.844.

Anal. Calcd. for $C_{18}H_{32}$: C, 87.02; H, 12.98; mol. wt., 248.44. Found: C, 87.16, 87.19; H, 12.75, 12.90; mol. wt., 247, 248, 256 (method of Blackman[16]—Blank and Willard[17]).

Dihydro Dimer (VII).—A solution of 25.00 g. (0.1006 mole) of II in 20 ml. of glacial acetic acid and 80 ml. of ethyl acetate was reduced using 100 mg. of platinum oxide catalyst. About 97% of one molar equivalent of hydrogen was absorbed in 20 minutes. The combined filtered solutions from two such reductions were washed to remove acetic acid. The dried ethyl acetate solution was fractionated under reduced pressure to give 41.34 g. of a principal fraction showing b.p. 87–88° (0.4 mm.). This dihydro dimer which probably contained some unreduced dimer and some completely reduced dimer showed the following properties: b.p. 275–278° (739 mm.), n^{20}_{D} 1.4663, d^{20}_{4} 0.839; M_D calcd. for VII (assuming mol. wt., 250.45) 82.69, M_D found 82.72.

***p*-(1,3,3-Trimethylbutyl)-neopentylbenzene (VIII).**—A mixture of 25.00 g. (0.0998 mole) of VII (b.p. 87–88° (0.4 mm.)) and 6.40 g. (0.1996 atom) of sulfur was heated up to 242° within an hour, evolution of hydrogen sulfide beginning at 197° proceeded smoothly as the temperature was raised. The mixture was heated at 242° for 30 minutes, cooled and diluted with an equal volume of petroleum ether (b.p. 40–60°). After washing the solution with dilute sodium hydroxide, drying and distilling there was obtained 10.23 g. of a pale yellow liquid showing b.p. 81–84° (0.6 mm.). This fraction, dissolved in 50 ml. of acetone, was treated with a solution of potassium permanganate until the permanganate color persisted for 15 minutes at room temperature. Excess permanganate was destroyed with a few drops of formalin, the solution filtered, diluted with 300 ml. of water, and extracted with petroleum ether (b.p. 40–60°). Fractional distillation of the petroleum ether solution gave 4.38 g. of a principal colorless fraction, b.p. 82–83° (0.7 mm.), 262–266° (738 mm.), d^{20}_{4} 0.847, n^{20}_{D} 1.4805; M_D calcd. for VIII 81.75, M_D found 82.72 (using mol. wt., 246.42); mol. wt. calcd. for $C_{18}H_{30}$, 246.42; mol. wt. found (Rast), 250, 262, 255. A subsequent larger scale preparation gave a specimen showing b.p. 82° (0.6 mm.), d^{20}_{4} 0.857, n^{20}_{D} 1.4810, M_D 81.82.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.93, 87.90; H, 12.25, 12.22.

Oxidation of VIII.—To a solution of 20 ml. of concentrated sulfuric acid and 20 ml. of water 2.0 g. (0.0081 mole) of VIII derived from II and 12.44 g. (0.1866 equiv. of O_2) of chromium trioxide was added. The agitated mixture was carefully heated with a free flame until the exothermic reaction started. The reaction was moderated by cooling the mixture with a cold bath. After a few minutes heating was continued and finally the mixture was refluxed for 30 minutes. The cooled mixtures from *two* reactions were poured into 300 ml. of cold water and extracted with ether until no white solid acid remained. The ether extracts were washed twice with water and finally with 50 ml. of 1% sodium hydroxide solution. The faintly green alkaline solution, washed with ether, was boiled to remove ether and filtered while hot to remove a small amount of chromium hydroxide. The colorless filtrate was made acid to congo red with hydrochloric acid and placed in the refrigerator overnight. There was obtained after filtering 0.7 g. of solid acidic material. The solid acidic material (0.7 g.) was warmed with 50 ml. of benzene and filtered.

The benzene-insoluble acid, practically insoluble in a large number of solvents, was recrystallized from a large volume of ethanol; m.p. > 355° (fine capillary). The acid was converted to its *p*-bromophenacyl ester; m.p. after three recrystallizations from ethanol was 211.5–218° (uncor.). A mixed m.p. with authentic di-*p*-bromophenacyl terephthalate of m.p. 211.5–218° (uncor.) showed no depression.

The benzene-soluble acid (0.26 g.) after three recrystallizations from water showed m.p. 158.9–161.6°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; neut. equiv., 206. Found: C, 70.28, 70.26; H, 6.98, 7.09; neut. equiv., 207.

The benzene-soluble acid was converted to its 2,4-dinitrophenylhydrazone, m.p. 240.5–242° (uncor.) from benzene. A mixed m.p. with a specimen of the 2,4-dinitrophenylhydrazone prepared from XII synthesized independently (m.p. 241–242.5°) was not depressed.

***p*-Bromobenzyl Chloride (IX).**—Using a modification of the method of Dippy and Williams,[18] from 125 g. of benzyl chloride there was obtained 75 g. (18.5%) of once-recrystallized IX, m.p. 40.2–43.2°; reported m.p.'s range from 38–50°.[18]

***p*-Bromoneopentylbenzene (X).**—A solution of *p*-bromobenzylmagnesium chloride, from 70 g. (0.34 mole) of IX, in 210 ml. of ether was prepared.[19] The cold solution of the Grignard reagent was added dropwise to a stirred refluxing solution of 93.4 g. (0.68 mole) of *t*-butyl bromide in 80 ml. of ether over a period of 3.5 hours. The cooled reaction mixture was hydrolyzed with a cold solution of 35 ml. of concentrated hydrochloric acid in 500 ml. of water. From the washed and dried ether solution and ether extracts of the hydrolyzed mixture there was obtained 69 g. of residue after distilling the ether.

The combined product of two Grignard reactions (147 g.) was distilled and gave 21 g. of a fraction showing b.p. to 50° (0.6 mm.), 177–178° (740 mm.), and m.p. 22°. This was presumably largely *p*-bromotoluene. A following fraction (35 g.) showing b.p. 50–97° (0.6 mm.) consisted of X containing some *p*-bromotoluene and *p*-bromobenzyl alcohol. This fraction, diluted with 50 ml. of petroleum ether, was cooled to 0° and filtered from crystalline *p*-bromobenzyl alcohol. The petroleum ether filtrate was washed three times with 5-ml. portions of concentrated sulfuric acid, with water, with sodium carbonate solution, and finally with water. The dried solution was distilled and after two fractionations there was obtained 14.8 g. of pure X: b.p. 62–63° (0.5 mm.), n^{20}_{D} 1.5318, d^{20}_{4} 1.230.

***p*-Neopentylbenzoic Acid (XI).**—The Grignard reagent prepared from 1.00 g. of X in 5 ml. of ether was poured on 35 g. of powdered Dry Ice. After adding 50 ml. of ether and dilute hydrochloric acid until ether and aqueous layers were clear, the layers were separated. The ether layer was extracted with dilute sodium hydroxide. Acidification of the alkaline extract gave a colorless solid acid, m.p. 190–192.1° from aq. ethanol.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39; neut. equiv., 192. Found: C, 74.82, 75.03; H, 8.55, 8.61; neut. equiv., 192, 192.

Pivalophenone-*p*-carboxylic Acid (XII).—A solution of 93.3 mg. (0.00486 mole) of XI, as its sodium salt, in 20 ml.

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[13] T. Wagner-Jauregg, *Ann.*, **488**, 176 (1931).

[14] All melting points are corrected unless otherwise noted. All boiling points are uncorrected.

[15] H. Gilman and A. P. Hewlett, *Rev. trav. chim.*, **48**, 1124 (1929).

[16] P. Blackman, *J. Chem. Soc.*, **87**, 1474 (1905).

[17] E. W. Blank and M. L. Willard, *J. Chem. Education*, **9**, 1819 (1932).

[18] J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 164 (1934).

[19] This Grignard reagent has been prepared in 60% yield by R. Quelet, *Compt. rend.*, **184**, 888 (1927).

of water and 0.1020 g. (0.000968 equiv. of O_2) of potassium pemanganate was refluxed 3.5 hours. After adding a small amount of sodium bisulfite solution to discharge the faint permanganate color, the mixture was boiled and filtered. The cooled filtrate was acidified and gave an impure acid showing m.p. 143.8–151.4° with previous softening.

This crude acid was converted to its 2,4-dinitrophenylhydrazone, m.p. 241–242.5° (uncor.) from benzene.

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: N, 14.51. Found: N, 14.25, 14.18.

Hydroxylation of II.—Following the procedure of Swern, Billen and Scanlan[7] 5 g. of II was treated with 32 ml. of 98% formic acid and 4.77 g. of 30% hydrogen peroxide. After saponification with alcoholic potassium hydroxide there was obtained 4.62 g. of a brown, viscous liquid having a menthol-like odor. This liquid was assumed to be the crude tetraol derived from II.

Lead Tetraacetate Cleavage of Hydroxylated II.—Following the procedure of Scanlan and Swern[8] the crude tetraol in 75 ml. of glacial acetic acid was treated at 55–65° portionwise with 22.02 g. (0.321 mole) of red lead. The odor of formaldehyde was evident after the first few additions of the lead oxide. The reaction mixture, diluted with 400 ml. of water, was extracted with ether and the ether extracts were washed with dilute sodium bicarbonate solution and dried. From the dried ether solution there was obtained 4.09 g. of a brown liquid.

A portion of the aqueous acetic acid solution remaining after the ether extraction was distilled and 20 ml. of the distillate treated with an excess of 2,4-dinitrophenylhydrazine reagent. The phenylhydrazone derivative which separated was recrystallized twice from ethanol; m.p. 154.2–159.5°. A mixed m.p. determination with pure formaldehyde 2,4-dinitrophenylhydrazone (m.p. 165.7–166.2°) showed m.p. 160.5–164.7°. A second portion of the aqueous acetic acid solution, after filtering, was treated with a saturated aqueous dimedone (methone) solution. The crystalline precipitate which separated after one hour at room temperature was recrystallized twice from ethanol; m.p. 191.6–192.1°. The reported m.p. for the methone derivative of formaldehyde is 189°.

The brown liquid from the ether extract (4.09 g.) was oxidized with alkaline hydrogen peroxide at 65–70°.[20] The major portion of the liquid remained insoluble in the dilute basic solution and was removed by ether extraction. From the ether extract of the acidified solution 0.7 g. of a crude liquid acid was obtained. This gave only a small amount of an insoluble calcium salt, presumably the salt of a diketo-C_{17}-monobasic acid. Acidification of this salt gave a light tan greasy solid acid which could not be recrystallized.

Isomerization of II.—A solution of 18.22 g. of II, 364 g. of 95% ethanol and 36.44 g. of concentrated sulfuric acid was refluxed for 16 hours. The reaction mixture, diluted with an equal volume of water, was extracted with petroleum ether. From the petroleum ether extracts, after washing and drying, there was obtained 17.37 g. of crude isomerized dimer. After two fractional distillations from a Claisen flask there was obtained 8.09 g. of isomerized dimer showing b.p. 84–85.5° (0.4 mm.), $n^{20}D$ 1.4748, d^{20}_4 0.847. The ultraviolet absorption spectrum in 95% ethanol was determined and showed an absorption maximum ($\epsilon_{\max}^{258\ m\mu}$ 937) expected for a 1,3-cyclohexadiene. Assuming that the pure isomerized dimer has a molar extinction coefficient (ϵ) comparable to known alkyl 1,3-cyclohexadienes,[14] the extent of isomerization was probably less than 20%.

Pyrolysis of II.—The pyrolysis apparatus consisted of a vertical glass tube containing an 8-inch long helix, wound from 5 feet of number 20 nichrome alloy wire. The helix was suspended from heavy copper wire which passed through a rubber stopper closing the upper end of the tube. The lower end of the tube was attached to a boiling flask. Above the helix there was attached a tube to remove distilling dimer and pyrolysis products, leading to a small downward water-cooled condenser. The condensate was returned to the boiling flask through a U-liquid seal. At a point below the condenser and above the U-seal the apparatus was attached to a Dry Ice trap and a vacuum system.

In this boiling flask (50 ml.) 10 g. of II was heated to reflux under 0.6 mm. pressure. The helix was heated to redness whereupon the pressure rose to 7.0 mm. and it was necessary to raise the temperature of the heating bath to 165° in order to maintain boiling. After operation for 1 hour 4.8 g. of dimer remained in the flask and 2 g. of "product" collected in the Dry Ice trap. The 3.2 g. loss of dimer was presumably due to "cracking" of the dimer and/or diene to hydrocarbon fragments not condensed at Dry Ice temperature.

Evaporative distillation of the "product" at room temperature and 0.6 mm. pressure gave 1.2 g. of volatile material and 0.8 g. of residue, probably dimer. Treatment of the volatile fraction (1.2 g.) with maleic anhydride (0.95 g.) gave a crystalline adduct which was dissolved in dilute sodium hydroxide. Acidification of the basic solution gave a tan crystalline acid. After recrystallization from water–acetic acid it showed m.p. 150.1–151.1°. A mixed m.p. with authentic 4-neopentyl-4-cyclohexene-1,2-dicarboxylic acid,[3] m.p. 150.4–151.5°, was not depressed. The acid was characterized as its N-phenylimide, m.p. 129.1–130.1° from aqueous ethanol. A mixed m.p. with authentic 4-neopentyl-4-cyclohexene-1,2-dicarboxylic-N-phenylimide,[3] m.p. 129.1–130.1°, was not depressed.

Ithaca, N. Y.

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[20] Reference 5, proc. 9B, p. 142.