crude acid chloride was distilled to give 67%, b.p. 140–145° (5 mm.), of a colorless liquid which turned brown in a few hours, 146–147° (9 mm.).[24])

Phenylmagnesium bromide was prepared from 5.8 g. (0.24 g. atom) of magnesium and 39.3 g. (0.25 mole) of bromobenzene in 125 ml. of ether. The solution was cooled to 10°, 23.8 g. (0.13 mole) of anhydrous cadmium chloride was added and the mixture was refluxed for 45 minutes. The ether was distilled almost to dryness and 170 ml. of benzene was added; 50 ml. was distilled to remove traces of ether. The solution was cooled to 10° and the crude 6-phenylhexanoyl chloride, dissolved in 40 ml. of benzene, was added in 5 minutes with stirring and the reaction mixture was kept at 70–80° for 4 hr. The mixture was decomposed with 20% sulfuric acid and water; the benzene layer was washed with water, 10% sodium hydroxide, water, a saturated salt solution and dried over magnesium sulfate. The residue, 28.8 g. of a dark oil, was distilled to give 10.6 g. (22%), b.p. 169–196° (0.2 mm.), of crude ketone. Redistillation of 5.0 g. gave an analytical sample, 1.9 g., b.p. 160° (0.1 mm.), of a liquid n^{25}_{D} 1.5601, d^{25}_{4} 1.025. The ultraviolet spectrum showed a λ_{max}^{MeOH} 242, log ε 4.11, indicative of a conjugated carbonyl group.

Anal. Calcd. for $C_{13}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.82; H, 8.19.

From 0.5 g. of the ketone, 0.85 g. (99%) of a 2,4-dinitrophenylhydrazone derivative, m.p. 130–135°, was obtained. An analytical sample was obtained by successive recrystallizations from isopropyl alcohol and cyclohexane to give red plates, m.p. 131–132°.

Anal. Calcd. for $C_{24}H_{24}O_4N_4$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.61; H, 5.87; N, 12.68.

From 0.5 g. of the ketone, 0.6 g. (99%) of crude oily semicarbazone, m.p. 126–131°, was obtained. Two recrystallizations from ethanol gave an analytical sample, m.p. 133–135°.

Anal. Calcd. for $C_{19}H_{23}ON_3$: C, 73.75; H, 7.49; N, 13.58. Found: C, 73.51; H, 7.61; N, 13.83.

Preparation of 1,6-Diphenyl-1-hexene and its 2,4-Dinitrobenzenesulfenyl Chloride Derivatives.—The olefin was prepared from the ketone by a procedure essentially the same as that used for the preparation of 1,5-diphenyl-1-pentene.[25]

A solution of 5.6 g. (0.22 mole) of 1,6-diphenyl-1-hexanone in ether was reduced with 1.1 g. (0.03 mole) of lithium aluminum hydride. The crude carbinol was isolated and dehydrated in benzene solution with 2.2 g. (0.015 mole) of phosphorus pentoxide. The dark colored residue, 3.25 g., was distilled to give 1.52 g. (29%) of an oil, b.p. 128–132° (0.15 mm.), n^{25}_{D} 1.5711, d^{25}_{4} 0.974. The infrared spectrum showed the band at 10.35 μ characteristic of this type of olefin.[7] The ultraviolet spectrum showed a λ_{max}^{MeOH} 252 mμ, log ε 4.22, λ_{max}^{MeOH} 283, log ε 3.09, characteristic of a substituted styrene.[26]

Anal. Calcd. for $C_{18}H_{20}O$: C, 91.47; H, 8.53. Found: C, 91.37; H, 8.65.

A solution of 0.35 g. (0.0015 mole) of the olefin and 0.42 g. (0.0018 mole) of 2,4-dinitrobenzenesulfenyl chloride in 2 ml. glacial acetic acid was heated on the steam-bath for 20 minutes. The solution was treated in the manner above for the mixture of decomposition products and chromatographed on 40 g. of alumina. Two oils were collected, the first, 0.30 g. (46%), gave 0.14 g. of yellow feathery crystals, m.p. 98–99°. Further recrystallization gave m.p. 99–100° and a mixture melting point with the first derivative from the decomposition mixture (the adduct without chlorine), m.p. 99–100°, melted at 99–100°. The second oil, 0.15 g. (22%), gave 0.093 g. of yellow needles, m.p. 128–130°, from ethanol. A mixture melting point with the second derivative from the decomposition mixture (the normal adduct), m.p. 129–130°, melted at 128–130°.

Preparation of the *cis*- and *trans*-1,2-Diphenylcyclohexanes. A. The high melting isomer was prepared by a modification of the procedure of Reesor, Smith and Wright.[16] The *trans*-disodium stilbene was rapidly prepared by stirring with sodium dispersion instead of shaking with sodium chunks and after addition of the 1,4-dichlorobutane at −78° the reaction was allowed to warm to room temperature. From 3.6 g. of *trans*-stilbene (0.02 mole) and 5.6 g. (0.044 mole) of 1,4-dichlorobutane there was obtained 2.3 g. (49%) of 1,2-diphenylcyclohexane, m.p. 51–53°. Recrystallization from methanol gave white prisms, m.p. 53–54° (m.p. 54.5–55.5°, 77%).[16] The ultraviolet spectrum showed a λ_{max}^{MeOH} 259 mμ, log ε 1.60.

B. The low melting isomer was prepared according to the procedure described by Parmerter, m.p. 46–47°.[15] The ultraviolet spectrum showed λ_{max}^{MeOH} 259 mμ, log ε 1.58.

When the high and low melting isomers were mixed together for a mixture melting point, an oil resulted whose infrared spectrum was identical to that of the mixture of saturated products obtained from the decomposition of the 8-membered ring azo compound II.

Acknowledgment.—The authors wish to acknowledge the many helpful discussions with Dr. R. G. Hiskey during this investigation.

BROOKLYN, N. Y.

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[24] R. Huisgen, W. Rapp, I. Ugi, H. Walz and I. Glogger, *Ann.*, **586**, 52 (1954).

[25] C. G. Overberger and J. J. Monagle, THIS JOURNAL, **78**, 4470 (1956).

[26] C. G. Overberger, D. Tanner and E. M. Pearce, *ibid.*, **80**, 4566 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

Diels–Alder Reactions with 1-Formylcyclohexene and 1-Formylcyclopentene

BY ERNST D. BERGMANN AND ABRAHAM BECKER

RECEIVED MARCH 5, 1958

1-Formylcyclohexene and 1-formylcyclopentene give with butadiene, 2,3-dimethylbutadiene and 1-vinylcyclohexene normal Diels–Alder adducts. The product from 1-formylcyclohexene and 1-vinylcyclohexene, which gives no carbonyl derivatives, does not have the steroid-like structure III, but is IV; this has been shown by an unambiguous synthesis of the acid IX, obtained by the degradation of IV. The analogous product from 1-formylcyclopentene gives normal carbonyl derivatives. *cis*-9-Methyldecahydronaphthalene (XXIV) and *cis*-8-methylhydrindane (XXV) have been prepared from I and XV, respectively.

Diene reactions with 1-formylcyclohexene and 1-formylcyclopentene have more than systematic interest. These diene reactions may lead to polycyclic compounds containing the aldehyde group in an angular position as it occurs in a number of natural products: strophanthidin,[1] antiarigenin,[1] helleborigenin,[2] scilliglucosidin[3] and aldosterone.[4]

Some experiments on the condensation of 1-formylcyclohexene with dienes have been reported previously by Szmuszkowicz and Bergmann.[5]

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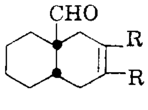
[1] R. Tschesche and W. Haupt, *Ber.*, **69**, 1377 (1936); R. Tschesche and R. Petersen, *ibid.*, **86**, 574 (1953).

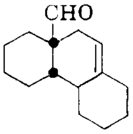
[2] J. Schmutz, *Helv. Chim. Acta*, **32**, 1442 (1949).

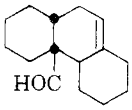
[3] A. Stoll, A. v. Wartburg and J. Renz, *ibid.*, **36**, 1531 (1953); A. Katz, *Experientia*, **12**, 285 (1956).

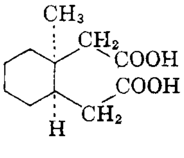
[4] S. A. Simpson, J. F. Tait, A. Wettstein, R. Neher, J. v. Euw, O. Schindler and T. Reichstein, *ibid.*, **10**, 132 (1954).

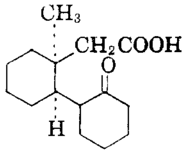
[5] J. Szmuszkowicz and E. D. Bergmann, *Bull. Res. Counc. Israel*,

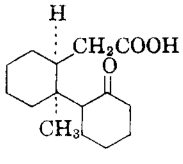

I, R = H
II, R = CH_3

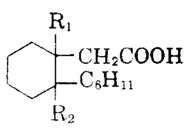

III

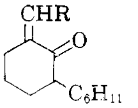

IV

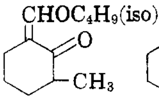

V

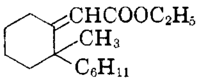

VI

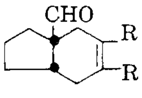

VII

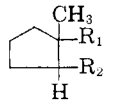

VIII, $R_1 = CH_3$, $R_2 = H$
IX, $R_1 = H$, $R_2 = CH_3$
XIII, $R_1 = OH$, $R_2 = CH_3$

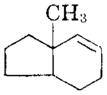

X, R = $NC_6H_5(CH_3)$
XI, R = OC_4H_9(iso)

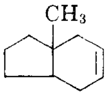

XII

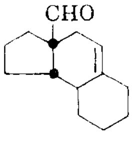

XIV

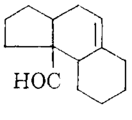

XV, R = H
XVI, R = CH_3

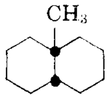

XVII, $R_1 = R_2 = CH_2COOH$
XX, $R_1 = COOH$, $R_2 = CH_2CH_2COOH$
XXI, $R_1 = R_2 = CH_2COCH_3$

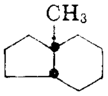

XVIII


XIX


XXII


XXIII


XXIV


XXV

They obtained the condensation products with butadiene (I), 2,3-dimethylbutadiene (II) and 1-vinylcyclohexene (III or IV) in relatively low yields (10, 29, 53%) and proved the structure of I by Huang-Minlon reduction of the aldehyde group and oxidation of the *cis*-9-methyl-1,4,5,6,7,8,9,10-octahydronaphthalene so obtained to the known[6] *cis*-1-methylcyclohexane-1,2-diacetic acid (V).

Under more suitable reaction conditions, the yields of I, II, III (or IV) have been increased to 35, 50 and 59%, respectively.

The elucidation of the structure of the product obtained from 1-vinylcyclohexene and 1-formylcyclohexene led to the aldosterone-*unlike* structure IV: Reduction of the aldehyde group in the adduct to methyl and subsequent oxidation at the double bond gave a keto-acid which could have formula VI or VII. Renewed reduction of the keto group by Huang-Minlon's method led to a well-crystallized acid $C_{15}H_{26}O_2$[5] which should be either VIII or IX; that the latter alternative and, therefore, formula IV was correct, was proved by an unambiguous synthesis. Formula IV explains why the adduct forms neither a semicarbazone nor a 2,4-dinitrophenylhydrazone,[5] since substances like I and II—and therefore also III—give these derivatives normally.

The synthesis of IX started from 2-methylcyclohexanone; its alkylation with cyclohexyl bromide and sodium hydride gave in 30% yield 2-cyclohexyl-2-methylcyclohexanone, free of the isomer. This is in accord with the experience of Haller and Cornubert[7] that alkylation of 2-methylcyclohexanone give exclusively, methylation very preponderantly, the 2,2-disubstituted compounds.

No better method for the preparation of 2-cyclohexyl-2-methylcyclohexanone could be devised. The enolates of 6-(N-methylanilinomethylene)-2-cyclohexylcyclohexanone (X) or the N-isobutoxymethylene derivative XI could be methylated with methyl iodide; however, it proved impossible to achieve complete methylation and to separate, after removal of the protecting group, the desired 2-methyl derivative from unchanged 2-cyclohexylcyclohexanone. Likewise, the reaction of the enolate of 6-isobutoxymethylene-2-methylcyclohexanone (XII) with cyclohexyl bromide converted the latter mostly to cyclohexene and gave only a 15% yield of 2-cyclohexyl-2-methylcyclohexanone, identical with the product obtained by direct cyclohexylation of 2-methylcyclohexanone. This synthesis, although resulting in an unsatisfactory yield, establishes the constitution of the compound unequivocally.

The Reformatzky reaction of 2-cyclohexyl-2-methylcyclohexanone with ethyl bromoacetate gave, even under stringent conditions, only an 8.5% yield of 1-carbethoxymethyl-2-cyclohexyl-2-methylcyclohexanol (XIII), the ethyl ester of which could be smoothly dehydrated with thionyl chloride and pyridine to the unsaturated ester XIV.[8] Hydrogenation of XIV and subsequent hydrolysis gave IX. The synthetic and the degradation product had the same melting point, did not show a depression of the melting point, when mixed, and had identical infrared spectra.

The course of the formation of IV from 1-vinylcyclohexene is analogous to other diene reactions of this hydrocarbon, in which the angular sub-

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3, 93 (1953); L. M. Idelson and E. I. Becker (THIS JOURNAL, **80**, 9081 (1958)) have shown that 1-acetyl-, 1-cyano- and 1-carbethoxycyclohexene do not react with butadiene.

(6) V. C. E. Burnop and R. P. Linstead, *J. Chem. Soc.*, 720 (1940).

(7) A. Haller and R. Cornubert, *Compt. rend.*, **170**, 704, 973 (1920).

(8) The α,β-unsaturated structure follows from the ultraviolet absorption band at 290 mμ (log ε 2.85). Reformatzky reactions with similarly substituted cyclohexanones have been carried out by P. N. Rao and P. Bagchi (*C. A.*, **49**, 10235 (1955)) and D. L. Turner (THIS JOURNAL, **79**, 2271 (1957)).

stituents appear in the most hindered positions,[9,10] and to diene reactions of other vinylcyclohexenes,[11–13] including 1-(α-acetoxyvinyl)-cyclohexene.[14,15]

With 1-formylcyclopentene, butadiene condenses in 40%, 2,3-dimethylbutadiene in 66% and 1-vinylcyclohexene in 80% yield, respectively. The structure of the products XV and XVI in the first two cases was obvious; for XV it has been proved rigidly: reduction of the aldehyde group by the method of Huang-Minlon (to XIX) and oxidation of the double bond with sodium periodate and ruthenium dioxide[16] led to *cis*-1-methylcyclopentane-1,2-diacetic acid (XVII) of m.p. 179°[17]; the *trans*-acid has m.p. 159°.[17] Errington and Linstead[18] have obtained an acid of the same composition $C_{10}H_{16}O_4$ and of m.p. 103° by oxidation of an 8-methyltetrahydroindane for which the position of the double bond was doubtful (XVIII or XIX). It can now be concluded that their acid was β-(2-methyl-2-carboxycyclopentyl)-propionic acid (XX) and their hydrocarbon 8-methyl-4,5,8,9- (XVIII) and not 8-methyl-4,7,8,9-tetrahydroindane (XIX).

Oxidation of XVI with sodium metaperiodate and ruthenium dioxide gave analogously 1-methyl-1,2-diacetonyl-cyclopentane (XXI), which is very likely also the *cis* compound. The structure of the adduct from 1-formylcyclopentene and 1-vinylcyclohexene has not been elucidated; if the reaction takes the same course as with 1-formylcyclohexene, formula XXIII would apply. However, contrary to IV, the adduct gives normal carbonyl derivatives and may therefore be XXXII. If this is so, the difference in behavior of 1-formyl-cyclohexene and -cyclopentene is remarkable.

We have used our results to establish the physical constants of *cis*-9-methyldecahydronaphthalene (XXIV) and *cis*-8-methyl-*cis*-hexahydroindane (XXV) for which the literature contains contradictory data. These two substances were obtained by Huang-Minlon reduction of the adducts I and XV and catalytic hydrogenation of the resulting unsaturated hydrocarbons. The hydrocarbon XXIV had the same refractive index as the 9-methyldecahydronaphthalene described by Linstead and co-workers,[19] which is, therefore, the *cis* compound. The product claimed by Hussey, *et al.*,[20] to be the *cis* form was the impure[21] *trans* compound.[22]

For XXV we found a refractive index of 1.4702, which is in fair accord with the value given by Errington and Linstead[18] for a product of an unproved configuration, and by Kronenthal and Becker[23] for a product which had definitely the *cis* structure.

Experimental

***cis*-9-Formyl-1,4,5,6,7,8,9,10-octahydronaphthalene** (I) was obtained from 1-formylcyclohexene[24] and butadiene according to Szmuszkowicz and Bergmann[5]; however, the heating of the reaction mixture at 140° was continued for 5 days; yield 35%.

***cis*-9-Methyl-1,4,5,6,7,8,9,10-octahydronaphthalene.**[5]—A mixture of 1.7 g. of I and 4.5 ml. of hydrazine hydrate was refluxed for 4 hours. Then a solution of 2.7 g. of potassium hydroxide in 11 ml. of propylene glycol was added and the treatment continued as usual; b.p. 75° (10 mm.), yield 0.8 g. (53%), $n^{25}\text{D}$ 1.4888, $\tilde{\nu}^{\text{liq}}_{\text{max}}$ 2940 cm.$^{-1}$ (methyl).

Anal. Calcd. for $C_{11}H_{18}$: C, 88.0; H, 12.0. Found: C, 88.3; H, 11.9.

***cis*-9-Methyldecahydronaphthalene (XXIV).**—A solution of 0.5 g. of the foregoing compound in 20 ml. of ether was hydrogenated at ordinary temperature and pressure in the presence of 50 mg. of palladium–charcoal (10%); b.p. 81° (10 mm.), $n^{25}\text{D}$ 1.4840.

***cis*-9-Formyl-2,3-dimethyl-1,4,5,6,7,8,9,10-octahydronaphthalene** (II) was prepared as described previously,[5] but at 140° and for 5 days; yield 50%.

4a-Formyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydrophenanthrene (IV) was prepared analogously; the yield was 59%.

2-Cyclohexyl-2-methylcyclohexanone.—The mixture of 72 g. of 2-methylcyclohexanone, 15.1 g. of sodium hydride and 240 ml. of dry xylene was refluxed for 6 hours. Then 109 g. of cyclohexyl bromide was added and the heating continued for 4 days. The product was treated with water, dried and distilled. Apart from cyclohexene and part of the starting materials, 51 g. (30% yield) of the desired ketone was obtained, b.p. 146° (14 mm.).

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.4; H, 11.3. Found: C, 80.3; H, 10.9.

The 2,4-dinitrophenylhydrazone was recrystallized from butyl alcohol, m.p. 183°. (*Anal.* Calcd. for $C_{19}H_{26}N_4O_4$: C, 60.9; H, 6.9. Found: C, 60.5; H, 6.8) and the **semicarbazone** from methyl alcohol, m.p. 178°.

2-Cyclohexylcyclohexanone was prepared according to Rapson[25] by hydrogenation of 2-cyclohexenylcyclohexanone (b.p. 145° (15 mm.)) in ethanol in the presence of palladium–charcoal (10%); b.p. 140° (11 mm.).

6-Hydroxymethylene-2-cyclohexylcyclohexanone was prepared according to Johnson and Posvic[26] from 91 g. of 2-cyclohexylcyclohexanone, 54 g. of sodium methoxide and 74 g. of ethyl formate in 500 ml. of benzene; b.p. 165° (17 mm.), yield 62%, $\lambda^{\text{EtOH}}_{\text{max}}$ 360 mμ (log ϵ 4.19).

The *mono*-2,4-dinitrophenylhydrazone, from butyl alcohol, showed m.p. 173°. *Anal.* Calcd. for $C_{19}H_{24}N_4O_5$: C, 58.7; H, 6.2. Found: C, 58.6; H, 6.4.

6-Isobutoxymethylene-2-cyclohexylcyclohexanone (XI).—Azeotropic distillation of 63 g. of the foregoing compound, 37 g. of isobutyl alcohol and 0.5 g. of *p*-toluenesulfonic acid in 200 ml. of benzene gave the theoretical quantity of water in 6 hours; b.p. 160° (2 mm.), yield 45 g. (60%).

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(9) I. N. Nazarov, *et al.*, *C. A.*, **50**, 1621 (1956).

(10) I. N. Nazarov, *et al.*, *ibid.*, **50**, 1713 (1956). In this case, a mixture of the "hindered" and the "non-hindered" isomers is formed in the ratio of about 2:1.

(11) G. Singh, THIS JOURNAL, **78**, 6109 (1956).

(12) I. N. Nazarov, L. I. Shmonina and I. V. Torgov, *C. A.*, **49**, 2452 (1955).

(13) W. Bockemueller (U. S. Patent 2,179,809; *C. A.*, **34**, 1823 (1940)) claims, but without proof, that the reaction of 6-methoxy-1-vinyl-1,2-dihydronaphthalene with 2-methylcyclopent-2-en-1-one gives a product with steroid-like structure.

(14) F. Winternitz and C. Balmossière, *Bull. soc. chim. France*, 6, 767, 1393 (1955); 108, 625, 988 (1957); I. N. Nazarov, *et al.*, *C. A.*, **50**, 1713, 11304 (1956); **51**, 5742, 14650 (1957); M. Mousseron, F. Winternitz and C. Balmossière, *Compt. rend.*, **243**, 1328 (1950); *cf.* also M. F. Ansell and G. T. Brooks, *J. Chem. Soc.*, 4518 (1956).

(15) We have also condensed this compound with 1-formylcyclohexene and 1-formylcyclopentene; however, the yields were too low (about 5%) to permit an elucidation of the structure of the adducts.

(16) R. Pappo and A. Becker, *Bull. Res. Counc. Israel*, **5**, 300 (1956).

(17) P. Šorm, Z. Šormová and L. Šedivý, *Coll. Czechoslovak Chem. Communs.*, **12**, 554 (1947)(*C. A.*, **42**, 7742 (1948)).

(18) K. D. Errington and R. P. Linstead, *J. Chem. Soc.*, 666 (1938).

(19) R. P. Linstead, A. F. Millidge, S. L. S. Thomas and A. L. Walpole, *J. Chem. Soc.*, 1146 (1937).

(20) A. S. Hussey, H. P. Liao and R. H. Baker, THIS JOURNAL, **75**, 4727 (1957).

(21) W. G. Dauben, R. C. Tweit and R. L. MacLean, *ibid.*, **77**, 48 (1955).

(22) H. S. Dreiding and A. J. Tomasewski, *ibid.*, **77**, 168 (1955); *cf.* also M. Yanagita, K. Yamakawa, A. Tahara and H. Ogura, *J. Org. Chem.*, **20**, 1767 (1955).

(23) R. L. Kronenthal and E. I. Becker, THIS JOURNAL, **79**, 1095 (1957). It should be noted that *cis*- and *trans*-8-methylhydrindane have identical refractive indices and densities.

(24) E. D. Bergmann and A. Becker, *J. Org. Chem.*, **23**, in press (1958).

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(26) W. S. Johnson and H. Posvic, THIS JOURNAL, **69**, 1361 (1947).

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.3; H, 10.6. Found: C, 77.5; H, 10.5.

6-Methylanilinomethylene-2-cyclohexylcyclohexanone (X).—A mixture of 130 g. of 6-hydroxymethylene-2-cyclohexylcyclohexanone and 100 g. of N-methylaniline in 500 ml. of benzene was subjected to azeotropic distillation. The product boiled at 121° (0.03 mm.), yield 170 g. (91%).

6-Hydroxymethylene-2-methylcyclohexanone.—Following the method of Seifert and Schinz,[27] a mixture of 112.5 g. of 2-methylcyclohexanone and 148 g. of ethyl formate was added, with agitation, to a cold suspension of sodium methoxide (freshly prepared from 46 g. of sodium) in 750 ml. of dry benzene. The whole operation was carried out in an atmosphere of nitrogen. After 12 hours at room temperature, ice-water and dilute hydrochloric acid was added and the aqueous layer saturated with sodium chloride and extracted with ether. The combined organic solutions were dried and evaporated; b.p. 87–92° (14 mm.), yield 100.5 g. (72%).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.6; H, 8.6. Found: C, 68.4; H, 9.0.

6-Isobutoxymethylene-2-methylcyclohexanone (XII).—A mixture of 75 g. of the foregoing compound, 74.5 g. of isobutyl alcohol, 50 mg. of *p*-toluenesulfonic acid and 200 ml. of benzene was subjected to azeotropic distillation. When the theoretical quantity of water had separated in the trap (3 hours), the solution was washed with 10% sodium carbonate solution and water, dried and distilled; b.p. 138° (11 mm.), yield 118 g. (80%).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.5; H, 10.2. Found: C, 73.0; H, 10.7.

6-Isobutoxymethylene-2-cyclohexyl-2-methylcyclohexanone.—(a) When 4.4 g. of sodium hydride was added to 45 g. of XI in 100 ml. of toluene, a clear solution resulted. After addition of 30 g. of methyl iodide the solution was refluxed for one hour, after which period it had become neutral. Filtration of the solid phase, which was washed with toluene, treatment of the filtrate with water, drying and distillation gave 35 g. (70%) of b.p. 167° (1.1 mm.).

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 77.7; H, 10.8. Found: C, 77.5; H, 10.7.

When this product, however, was heated with 1 ml. of concentrated hydrochloric acid in 100 ml. of 90% methanol at room temperature for 2 hours, a mixture of 2-cyclohexyl-2-methylcyclohexanone and 2-cyclohexylcyclohexanone resulted which could not be separated. A better product was obtained by method b.

(b) A mixture of 53 g. of 6-isobutoxymethylene-2-methylcyclohexanone (XII), 6 g. of sodium hydride and 100 ml. of toluene was refluxed for 3 hours, after which period a clear solution resulted. After addition of 41 g. of cyclohexyl bromide, the heating was continued for 12 hours and the neutral product treated with water, dried and distilled; yield 6 g. (18%), b.p. 165° (1 mm.), n^{25}D 1.5057, d^{15}_4 0.9800; *MR* calcd. 84.88, *MR* found 84.95; λ^{EtOH}_{max} 277 mμ (3.92).

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 77.7; H, 10.8. Found: C, 77.9; H, 10.9.

2-Methyl-2-cyclohexylcyclohexanone.—Hydrolysis of 6 g. of the foregoing product gave 3.5 g. (83%) of 2-methyl-2-cyclohexylcyclohexanone, b.p. 146 (14 mm.).

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.4; H, 11.3. Found: C, 80.2; H, 11.3.

6-Methylanilinomethylene-2-cyclohexyl-2-methylcyclohexanone.—To a solution of 30 g. of X in 100 ml. of xylene, 2.4 g. of sodium hydride was added and the mixture heated until the evolution of hydrogen ceased. Then 15.6 g. of methyl iodide was added and the heating continued until the mixture became neutral. Water was added and the xylene layer separated. The water was extracted with ether, and the residue of the two organic solutions combined and distilled; b.p. 120–125° (0.03 mm.), yield 30 g. (100%). The substance was not pure, as the hydrolysis yielded a mixture of 2-cyclohexylcyclohexanone and its 2-methyl derivative.

Ethyl (1-Hydroxy-2-methyl-2-cyclohexylcyclohexyl)-acetate (Ester of XIII).—To a boiling mixture of 10 g. of 2-cyclohexyl-2-methylcyclohexanone, 2.3 g. of zinc, 50 ml. of benzene and small quantities of iodine and mercuric chloride, 5 portions each of 1 g. of zinc and 2.5 g. of ethyl bromoacetate were added every 15 minutes. The heating was continued for 5 hours and the product, after filtration of the excess of zinc, treated successively with 50 ml. of dilute acetic acid, 50 ml. of ammonia and water. Distillation gave, apart from unchanged starting material, 1 g. (8.5%) of the ester of XIII, b.p. 104° (0.01 mm.). The product could not be obtained analytically pure, probably because of slight spontaneous dehydration; $\bar{\nu}^{liq}_{max}$ 3448, 2900 and 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{30}O_3$: C, 72.3; H, 10.6. Found: C, 73.5; H, 10.5.

Ethyl (2-Methyl-2-cyclohexylcyclohexylidene)-acetate (XIV).—To a solution of 4 g. of the foregoing ester in 10 ml. of chloroform and 3 ml. of pyridine, 2 ml. of thionyl chloride was added at 0°. After 24 hours, water was added and the product extracted with 20 ml. of benzene. The extract was washed with dilute hydrochloric acid and water; λ^{EtOH}_{max} 290 mμ (2.85) (broad band), b.p. 117° (0.03 mm.), yield 3 g. (78%).

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.3; H, 10.6. Found: C, 77.1; H, 10.8.

(2-Methyl-2-cyclohexylcyclohexyl)-acetic Acid (IX).—A solution of 2.1 g. of XIV in 30 ml. of ethanol was hydrogenated at ordinary temperature and pressure in the presence of 50 mg. of palladium–charcoal (5%). The reaction was very slow, but went to completion. The product (2.1 g., quantitative yield) boiled at 112° (0.03 mm.) and was saponified as follows: The mixture of 1.5 g. of the hydrogenation product, 3.0 g. of potassium hydroxide, 40 ml. of alcohol and 30 ml. of water was refluxed for 12 hours. After addition of concentrated hydrochloric acid, the reaction product was thoroughly extracted with ether and the acid transferred into water by treatment of the ethereal solution with 3 portions of 50 ml. of 10% sodium carbonate solution. Acidification with concentrated hydrochloric acid and renewed extraction with ether gave an oily substance (0.8 g., 40%) which was repeatedly recrystallized from aqueous acetone and melted at 166°. It gave no depression of the melting point with the acid obtained by Szmuszkowicz and Bergmann[5] in the degradation of IV. Also the infrared spectra were completely identical; $\nu_{C=O}$ 1700 cm.$^{-1}$.

1-Formylcyclopentene was obtained only in over-all yield of 9.3% (calculated on cyclopentanone) according to the method of Seifert and Schinz.[27] The best method for its preparation[28] is the cyclization of adipic dialdehyde[29]: From 110 g. of *trans*-cyclohexane-1,2-diol, prepared from cyclohexene and performic acid in 85% yield, one obtains by treatment with 250 g. of sodium metaperiodate and subsequent treatment of the crude product with 2% potassium hydroxide solution, 62 g. (68%) of 1-formylcyclopentene,[30] b.p. 41° (11 mm.), n^{17}D 1.4897; **2,4-dinitrophenylhydrazone**, from butanol, m.p. 200°.

***cis*-8-Formyl-4,7,8,9-tetrahydroindane (XV).**—A mixture of 11.5 g. of 1-formylcyclopentene, 70 g. of butadiene and 1 g. of hydroquinone was heated in an autoclave at 160° for 6 days and at 180° for one further day. The product boiled at 114° (25 mm.), yield 7 g. (40%), $\bar{\nu}^{liq}_{max}$ 1724 cm.$^{-1}$ (carbonyl).

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.0; H, 9.3. Found: C, 80.3; H, 9.5.

The 2,4-dinitrophenylhydrazone, from butanol, showed m.p. 133°, $\lambda^{CHCl_3}_{max}$ 365 mμ (4.24). *Anal.* Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.2; H, 5.5. Found: C, 57.9; H, 5.7.

***cis*-8-Methyl-4,7,8,9-tetrahydroindane (XIX).**—The usual treatment of 5.5 g. of XV with 12 g. of potassium hydroxide, 23 ml. of hydrazine hydrate and 30 ml. of propylene glycol gave 4 g. of XIX, b.p. 165° (690 mm.), $n^{14.5}$D 1.4807, $d^{14.5}_4$ 0.8867; *MR* calcd. 43.94, *MR* found 44.58; $\bar{\nu}^{liq}_{max}$ 3000 cm.$^{-1}$.

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(27) P. Seifert and H. Schinz, *Helv. Chim. Acta*, **34**, 728 (1951).

(28) For other methods, which are not suitable for larger-scale preparations, see E. Urion, *Ann. chim.*, **11**, 1 (1934); E. H. Farmer and A. Sundralingam, *J. Chem. Soc.*, 121 (1942).

(29) J. B. Brown, H. B. Henbest and E. R. H. Jones, *ibid.*, 3634 (1950); *cf.* J. English and G. W. Barber, THIS JOURNAL, **71**, 3310 (1949).

(30) According to R. Pappo, *et al.* (*J. Org. Chem.*, **21**, 478 (1956)), the oxidation of cyclohexene with sodium metaperiodate and osmium tetroxide gives in one step a 77% yield of 1-formylcyclopentene.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 88.3; H, 12.0.

cis-**8-Methylhydrindane (XXV).**—The foregoing product (1 g.) was hydrogenated in 20 ml. of ether in the presence of 50 mg. of palladium–charcoal (10%) at ordinary temperature and pressure. The product boiled at 151° (690 mm.) and had $n^{20}D$ 1.4702.

cis-**1-Methylcyclopentane-1,2-diacetic Acid (XVII).**—To a solution of 2 g. of sodium metaperiodate in 10 ml. of water, 40 mg. of ruthenium dioxide and 0.8 g. of XIX, dissolved in 20 ml. of acetone, were added with stirring.[16] The yellow solution turned black. A second portion of 7.5 g. of solid sodium metaperiodate was added, whereupon the temperature rose to 40°. After one hour, the solution became yellow again. Isopropyl alcohol was added, the inorganic solid filtered and washed with acetone, and the filtrate diluted with 50 ml. of water. Thorough extraction with ether, followed by transfer into 10% sodium carbonate solution, acidification with 10% hydrochloric acid and renewed extraction with ether gave a product which was recrystallized repeatedly from aqueous acetone (1:1); m.p. 197°, yield 0.3 g. (10%).

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.0. Found: C, 60.1; H, 8.0.

cis-**8-Formyl-5,6-dimethyl-4,7,8,9-tetrahydroindane (XVI).**—A mixture of 10 g. of 1-formylcyclopentene, 30 g. of 2,3-dimethylbutadiene and 1 g. of hydroquinone was heated at 200° for 24 hours. The adduct boiled at 80° (0.7 mm.), yield 12 g. (60%).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.9; H, 10.1. Found: C, 80.8; H, 10.2.

The 2,4-dinitrophenylhydrazone was recrystallized from methanol; m.p. 154°, $\lambda_{max}^{CHCl_3}$ 365 mμ (4.23). *Anal.* Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.3; H, 6.2. Found: C, 60.2; H, 6.0.

cis-**5,6,8-Trimethyl-4,7,8,9-tetrahydroindane.**—A mixture of 3 g. of XVI, 8 ml. of hydrazine hydrate. 4.6 g. of potassium hydroxide and 30 ml. of propylene glycol was treated in the usual manner; the reaction mixture was poured into dilute hydrochloric acid and extracted with petroleum ether. The product boiled at 187° (690 mm.), yield 2.5 g. (90%), $n^{25}D$ 1.4965.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.8; H, 12.2. Found: C, 87.4; H, 12.0.

cis-**1-Methyl-1,2-diacetonylcyclopentane (XXI).**—A solution of 1 g. of the foregoing hydrocarbon in 10 ml. of acetone was added slowly to a well-stirred mixture of 9 g. of sodium metaperiodate and 40 mg. of ruthenium dioxide in 20 ml. of 50% aqueous acetone. After 30 minutes, a solution of 30 mg. of ruthenium dioxide and 1.5 g. of sodium metaperiodate in 40 ml. of 50% acetone was added and the stirring continued for 12 hours. Then isopropyl alcohol was added, the solution filtered, diluted with water and extracted thorougly with ether. The ether residue boiled at 140° (0.1 mm.), $\bar{\nu}_{max}^{liq}$ 1710 cm.$^{-1}$ (carbonyl).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.5; H, 10.2. Found: C, 73.2; H, 9.7.

The bis-2,4-dinitrophenylhydrazone, from nitromethane, had m.p. 205°.

1-Vinylcyclohexene.—For the synthesis of this compound, two methods were used: (a) 1-Ethynylcyclohexanol,[31] (b.p. 97° (14 mm.)) was dehydrated with phosphorus oxychloride in pyridine.[32] 1-Ethynylcyclohexene so obtained in 80% yield (b.p. 148°) was hydrogenated with the Lindlar catalyst[33] in pentane solution; yield 95%, b.p. 147°.

(b) A solution of 50 g. of ethynylcyclohexanol in 200 ml. of pyridine (dried over barium oxide) was hydrogenated with 1 mole of hydrogen in the presence of 0.5 g. of palladium–charcoal (10%). The crude 1-vinylcyclohexanol (45 g.), which contained some unchanged starting material and some 1-ethylcyclohexanol, was selectively dehydrated by means of anilinium *p*-toluenesulfonate[34] (5 g.) in 100 ml. of boiling toluene (azeotropic distillation, 6 hours). Thus, 27 g. (6%) of 1-vinylcyclohexene, b.p. 147°, was obtained.

1,2-Cyclopentano-2(or 1)-formyl-1,2,3,5,6,7,8,9-octahydronaphthalene (XXIII or XXII) was obtained from 17 g. of 1-formylcyclopentene, 23 g. of 1-vinylcyclohexene and 1 g. of hydroquinone by heating at 200° for 20 hours; b.p. 114° (1.2 mm.), yield 23 g. (80%), $n^{25}D$ 1.5243 $\bar{\nu}_{max}^{liq}$ 1724 cm.$^{-1}$ (carbonyl).

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.3; H, 9.8. Found: C, 82.1; H, 9.6.

The 2,4-dinitrophenylhydrazone, from ethanol, showed m.p. 175°, $\lambda_{max}^{CHCl_3}$ 365 mμ (4.29). *Anal.* Calcd. for $C_{20}H_{24}N_4O_4$: C, 62.5; H, 6.3. Found: C, 62.6; H, 6.6.

1,2-Cyclopentano-2(or 1)-methyl-1,2,3,5,6,7,8,9-octahydronaphthalene.—A mixture of 4 g. of the foregoing compound, 4 ml. of hydrazine hydrate, 6 g. of potassium hydroxide and 30 ml. of propylene glycol was treated as usual; b.p. 126–128° (14 mm.), yield 3 g. (89%), $n^{15}D$ 1.5163, $\bar{\nu}_{max}^{liq}$ 3000 cm.$^{-1}$ (methyl).

Anal. Calcd. for $C_{14}H_{22}$: C, 88.4; H, 11.6. Found: C, 88.3; H, 11.7.

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(31) E. D. Bergmann, M. Sulzbacher and D. F. Herman, *J. Appl. Chem.*, **3**, 39 (1953).

(32) J. C. Hamlet, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.* 2652 (1951).

(33) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(34) Ch. Weizmann, U. S. Patent 2,381,148 (*C. A.*, **40**, 346 (1946)).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

The Reactions of N,N′-Dicyclohexylcarbodiimide with Benzoyl Peroxide and *t*-Butyl Perbenzoate

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N,N′-Dicyclohexylcarbodiimide reacts with benzoyl peroxide in isopropyl alcohol to give N-benzoyl-N,N′-dicyclohexylurea, acetone, benzene and carbon dioxide. The same reactants in carbon tetrachloride gave N-cyclohexylbenzamide, chlorobenzene, cyclohexyl isocyanate and carbon dioxide.

t-Butyl perbenzoate and N,N′-dicyclohexylcarbodiimide reacted in *n*-butyl alcohol to give N-cyclohexylbenzamide, *n*-butyraldehyde and *n*-butyl N-cyclohexylcarbamate. Mechanisms are suggested for the formation of these compounds.

The reactions of organic peroxides have been the subject of many investigations.[1] They have received continued interest because of their complex character and fundamental value. It is the purpose of this paper to report on the course of the reactions of benzoyl peroxide (I) and *t*-butyl perbenzoate (II) with N,N′-dicyclohexylcarbodiimide (III) in several solvents.

When benzoyl peroxide was allowed to react with N,N′-dicyclohexylcarbodiimide in refluxing chloroform, the 5.60 and 5.68 μ bands of the benzoyl peroxide and the 4.75 μ band of the N,N′-dicyclohexylcarbodiimide steadily diminished in intensity. New strong bands appeared at 4.45 and 6.08 μ.

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(1) (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; (b) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.