230°. The infrared spectrum of the product and that of *o*-dimesitoylbenzene were superimposable.

Hydrogenation of 1,6-Dimesitoyl-1-cyclohexene.—A solution of 374 mg. (0.00100 mole) of the ketone in 60 ml. of absolute ethanol was treated with hydrogen in the presence of a catalyst prepared from 60 mg. of platinum oxide in 15 ml. of absolute ethanol in an Adams micro-hydrogenation apparatus. The volume of hydrogen taken up was 22.4 ml. (0.00100 mole). The reaction vessel was opened to the air with the catalyst still present. When the solution was concentrated, a quantitative amount of the starting material was recovered as a colorless solid.

1,6-Dimesitoyl-1-cyclohexene Oxide.—To a solution of 2.00 g. (0.00535 mole) of 1,6-dimesitoyl-1-cyclohexene and 1 l. of absolute ethanol was added 10.0 ml. (0.0835 mole) of 30% hydrogen peroxide and 12 ml. (0.0300 mole) of 10% sodium hydroxide, with stirring. The addition of hydrogen peroxide caused the solution to develop an orange color and to deposit a colorless solid. The reaction mixture was stirred at room temperature for 48 hr., a portion of 5 ml. of 30% hydrogen peroxide being added every 12 hr. A colorless precipitate was removed by filtration, and an equal volume of water was added to the clear, colorless filtrate; a solid precipitated (700 mg., m.p. 213–225°). Two recrystallizations of this solid from high-boiling petroleum ether–methylene chloride followed by two recrystallizations from chloroform–ethanol yielded 162 mg. (7.9%) of colorless crystals, m.p. 248–251°. The infrared spectrum of this product has one carbonyl band (1685 cm.$^{-1}$), two unsymmetrical epoxide peaks (1100 and 900 cm.$^{-1}$) and a weak band (1310 cm.$^{-1}$) for a tertiary hydrogen atom. The ultraviolet spectrum in ethanol (λ_{max} 235 mμ, log ε, 4.10) exhibits no appreciable shift from the peak in the spectrum of *trans*-1,2-dimesitoylcyclohexane.

Anal. Calcd. for $C_{26}H_{30}O_3$: C, 79.96; H, 7.74. Found: C, 80.23; H, 7.89.

Ethyl Hexahydrophthalate.—A solution of 100 g. (0.650 mole) of *cis*-hexahydrophthalic anhydride, 100 ml. (21.8 moles) of absolute ethanol, 300 ml. of anhydrous benzene and 1 ml. of concentrated sulfuric acid was heated at vigorous reflux under conditions that permitted removal of the water as it formed. At the end of 12 hr., water ceased to come over; the ester, purified by conventional procedures, was a clear, colorless oil, yield 94%. The infrared spectrum indicated that the product was contaminated with a small amount of the anhydride used as a starting material. This procedure was found to be superior to the one previously described.[4]

***trans*-1,2-Dimesitoylcyclohexane.**—The ethyl hexahydrophthalate was converted by hydrolysis under conditions known to isomerize the *cis*- acid to the *trans* form. The *trans*-hexahydrophthalic acid (79% yield) was transformed into the acid chloride (97% yield) by use of phosphorus pentachloride.[4] A mixture of 67.3 g. (0.560 mole) of mesitylene and 29.3 g. (0.140 mole) of the acid chloride was allowed to react in the presence of aluminum chloride. From the crude solid 28.1 g. (53%) of pure diketone was isolated after four extractions with boiling benzene; m.p. 241–242°. A mixture melting point (238–239°) with an authentic sample (m.p. 234–235°)[4] was not depressed; the infrared spectrum of the product and that of *trans*-1,2-dimesitoylcyclohexane were superimposable. A hindered aroyl carbonyl band (1695 cm.$^{-1}$) and a peak for tertiary hydrogen (1315 cm.$^{-1}$) are also consistent with the structure. Peaks for the α,α'-tertiary hydrogen atoms in the 1,4-diketone appeared at + 2.2 p.p.m. in the nuclear magnetic resonance spectrum. When the area under the + 2.2 p.p.m. curve was compared to that under the + 3.45 p.p.m. peak (methylene hydrogen), the ratio was found to be 1:4. Evidence for the validity of this assignment was obtained from the spectrum of benzoylcyclohexane. Tertiary hydrogen and methylene hydrogen adsorb at + 1.95 and + 3.5 p.p.m., respectively; the ratio of the areas under these curves is 1:10. In addition, the ultraviolet spectrum of *trans*-1,2-dimesitoylcyclohexane is characteristic of hindered aroyl ketones; λ_{max} 243 mμ, log ε 4.02.

The *trans*-diketone remained unchanged after being heated with an equivalent amount of selenium dioxide for 96 hr. in acetic acid and in the presence of an equivalent amount of sodium acetate.

Cyclohexyl Mesityl Ketone.—A Grignard reagent prepared from 4.25 g. (0.175 g. atom) of magnesium, 2.94 g. (0.180 mole) of cyclohexyl bromide and 100 ml. of ether was added during 30 min., with stirring, to a solution of 34.5 g. (0.188 mole) of mesitoyl chloride in 50 ml. of ether and 50 ml. of benzene. The reaction mixture was heated under reflux for 90 min. and decomposed with a mixture of ice and hydrochloric acid. The cyclohexyl mesityl ketone, recrystallized from low-boiling petroleum ether at −50°, melted at 41.0–41.5°. The infrared spectrum has bands at 1695 and 850 cm.$^{-1}$, assignable, respectively, to a carbonyl group and a mesityl nucleus.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 6.93. Found: C, 83.57; H, 6.97.

Other products isolated were mesitoic acid and mesitil. An attempt to form an epoxy derivative of cyclohexyl mesityl ketone was not successful.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Photochemical Reactions. IX.[1] Isomerization of Eucarvone

BY G. BÜCHI AND EDWARD M. BURGESS

RECEIVED JANUARY 25, 1960

Irradiation of eucarvone in alcoholic solution gave mainly 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one which on pyrolysis at 320° was reconverted to eucarvone. Further irradiation of the first photoproduct produced 4,4,6-trimethylbicyclo-[3.2.0]hept-6-en-2-one by a novel photochemical rearrangement whose mechanism is discussed. The structure of the second photoisomer was established by pyrolysis at 380° to 3,3,5-trimethylcyclohepta-4,6-dien-1-one and reduction to 3,3,5-trimethylcycloheptanone. The striking acid-catalyzed isomerization of the first to the second photoproduct can be rationalized in terms of a non-classical cationic intermediate.

Substituted cyclobutanes can be prepared conveniently by photochemical dimerization of appropriately activated olefins.[2] Ring formation becomes especially facile in intramolecular cyclizations, provided the two unsaturated systems involved in the bond-forming process are in spatial proximity. To exemplify we may cite the intramolecular cyclizations leading to carvonecamphor,[3] the photopyrocalciferols,[4] the lumicolchicins,[5]

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(1) Part of a program of research supported by a grant from the Godfrey L. Cabot Fund, Publication No. 68, M. I. T. Solar Energy Conversion Project. Paper VIII, D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957).

(2) A. Mustafa, *Chem. Revs.*, **51**, 1 (1952).

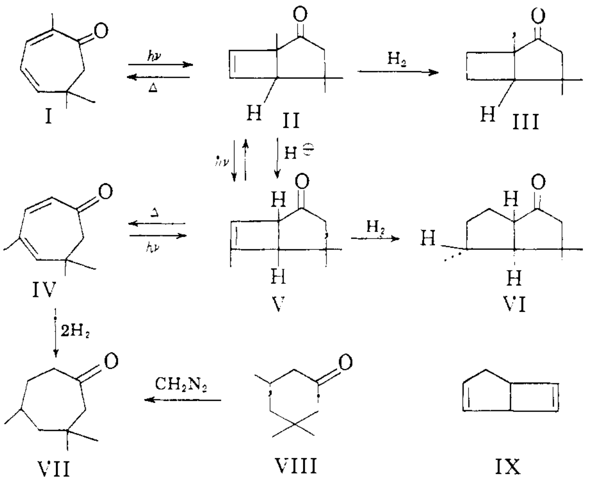
(3) (a) G. Ciamician and P. Silber, *Ber.*, **41**, 1928 (1908); (b) E. Sernagiotto, *Gazz. chim. ital.*, **48**, 52 (1918); **47**, 153 (1917); (c) G. Büchi and I. M. Goldman, THIS JOURNAL, **79**, 4741 (1957).

(4) (a) A. Windaus, K. Dimroth and W. Breywisch, *Ann.*, **543**, 240 (1940); (b) W. G. Dauben and G. J. Fonken, THIS JOURNAL, **81**, 4060 (1959).

(5) (a) R. Grewe and W. Wulf, *Chem. Ber.*, **84**, 621 (1951); (b) E. J. Forbes, *J. Chem. Soc.*, 3864 (1955).

photo-γ-tropolone methyl ether,[6] photodrin[7] and other "bird-cage molecules."[8]

We have studied the photoisomerization of eucarvone (I) and wish to present our findings in this paper. Irradiation of I in alcoholic solution with a "Labortauchlampe S81" (Quarzlampengesellschaft Hanau) during eight days gave an isomer (II) in 15% yield readily separable from starting material by fractional distillation. Further irradiation of the recovered eucarvone for fourteen days produced an additional quantity of II and raised the total yield to 36%. In agreement with the anticipated structure II, this photoisomer exhibited infrared bands (in CCl_4) at 1730 (cyclopentanone); 3020, 1640 and 725 cm.$^{-1}$ (*cis*-disubstituted double bond in strained ring). The ultraviolet spectrum, λ^{EtOH} 219 mμ (ε 820), λ_{max}^{EtOH} 303 mμ (ε 174), is that of non-planar β,γ-unsaturated ketones in which the n-π*-transition is strengthened, apparently by overlap of the non-bonding p-orbital of the carbonyl oxygen with the π-orbitals of the double bond.[9] A 60 mc./sec. nuclear magnetic resonance spectrum[10] showed three singlet peaks of equal intensity at 9.16, 9.02 and 8.88 p.p.m. which we assign to the three methyl groups. The two vinyl hydrogens appear at low field (characteristic of cyclobutenes[4b]). Spin-spin coupling with the second vinyl hydrogen is responsible for the doubling of the signal centered at 3.77 p.p.m. while the quartet at 3.97 p.p.m. indicates additional coupling presumably with the angular hydrogen. A poorly resolved doublet at 7.44 p.p.m. with an integrated intensity corresponding to two protons may be due to the methylene protons adjacent to the carbonyl group. The remainder of the spectrum was not well enough defined to warrant analysis.



It follows that the photoisomer II is bicyclic and the presence of only one double bond was ascertained by catalytic reduction to the saturated ketone III, λ_{max}^{EtOH} 296 mμ, ε 33, showing an infrared band (in CCl_4) at 1740 cm.$^{-1}$. Base-catalyzed hydrogen-deuterium exchange resulted in the introduction of two D atoms.[11] That II is simply a valence tautomer of the starting material is also substantiated by its pyrolysis to eucarvone (I). Precisely analogous thermal rearrangements have been observed with the photopyrocalciferols[4a,b] and with the more closely related compound IX which is converted to cycloheptatriene.[12]

Careful analysis of the products formed on irradiation of eucarvone (I) by gas-liquid partition chromatography revealed the presence of another product. Assuming that it originated from II rather than from eucarvone (I) we investigated the photolysis of the valence tautomer II. Indeed, a facile isomerization was observed and a second photoisomer, which we have shown to be V, could be isolated by fractional distillation. It possessed infrared bands at 1730 (cyclopentanone); 820, 1630 and 3020 cm.$^{-1}$ (trisubstituted double bond in strained ring) and the ultraviolet spectrum, λ_{max}^{EtOH} 219, 303 mμ (ε 1730, 230), was again typical of non-planar β,γ-unsaturated ketones. In consonance with the proposed structure V, the nuclear magnetic resonance spectrum showed sharp peaks at 9.03 and 8.80 p.p.m. for the geminal dimethyl system. The third methyl appeared as a three proton singlet at 8.15 p.p.m., while a one proton peak at 4.12 p.p.m. must be attributed to the vinyl hydrogen. This proton shows small but unresolved coupling with one or both of the angular protons.

Catalytic reduction of V proceeded smoothly and the dihydroketone VI, tentatively assigned the *endo*-methyl configuration, had λ_{max}^{EtOH} 296 mμ, ε 31, and $\nu_{max}^{CCl_4}$ 1735 cm.$^{-1}$, in full agreement with the assigned structure. The substitution pattern in the neighborhood of the carbonyl group was established again by deuteration which was complete after the introduction of three deuterium atoms. It was desirable to prove the carbon skeleton of V by a chemical method and this was accomplished as follows: Pyrolysis of the second photoisomer V at 380° produced a dienone IV which was reconverted to V by irradiation. It was clearly different from eucarvone (I) and exhibited absorption bands at 304 mμ, ε 4900, 1660 (carbonyl) and 1645, 1590, 820 and 760 cm.$^{-1}$ (*cis*-di- and trisubstituted double bonds). Catalytic reduction produced a saturated tetrahydroketone whose semicarbazone was identical in every respect with the corresponding derivative of 3,3,5-trimethylcycloheptanone (VII). A sample of this ketone of established structure[13] was prepared by Demjanow ring expansion from dihydroisophorone (VIII).[14]

We shall now discuss the mechanism of the photochemical transformation of II to V which to our

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[6] O. L. Chapman and D. J. Pasto, This Journal, **80**, 6685 (1958).

[7] R. C. Cookson and E. Crundwell, *Chemistry & Industry*, 1004 (1958).

[8] R. C. Cookson, E. Crundwell and J. Hudec, *ibid.*, 1003 (1958).

[9] (a) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); (b) H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).

[10] N.m.r. spectra were measured on a Varian Associates instrument in carbon tetrachloride with tetramethylsilane as internal reference. Peak positions are in τ-values; G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958). We are indebted to Mr. J. Atkinson for these measurements.

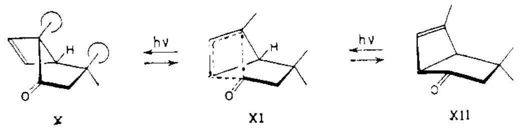
[11] We are much indebted to Prof. K. Biemann and Dr. J. Seibl, M. I. T., for the deuterium analyses by the mass spectrometric method. The spectra were taken on a CEC 21-103C mass spectrometer equipped with a heated inlet system (135°) using an ionization potential of 70 v. The mass peaks observed confirmed the monomeric nature of III and VI.

[12] E. Vogel, *Angew. Chem.*, **68**, 189 (1956); M. V. Evans, Jr., Ph.D. thesis, M. I. T., 1958.

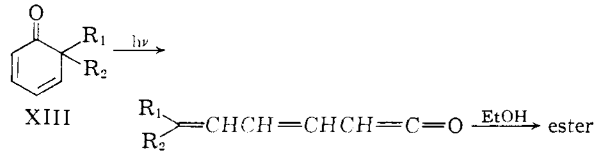
[13] L. Ruzicka, H. Schinz and C. F. Seidel, *Helv. Chim. Acta*, **23**, 935 (1940).

[14] M. Stoll and W. Scherrer, *ibid.*, **23**, 941 (1940).

knowledge is the first of its kind described. Formally, the change corresponds to a 1,3-methyl migration, but we rather doubt that such a scheme has much in common with reality. It seems more likely that the bond adjacent to the carbonyl group is cleaved and reconstituted. We propose that the ketone II assumes conformation X and that the transformation passes through a stage XI in which one of the bonds indicated by dotted lines is broken while the other is being formed. The geometry of the molecular site undergoing transformation is essentially that of cyclobutane and therefore similar to that of the transition state between I and II. The interconversion of the two photoketones is an equilibrium reaction and we were able to isomerize either ketone photochemically into an equilibrium mixture containing approximately four parts of II and one part of V. This composition does *not* reflect on the relative thermodynamic stabilities of the two isomers but represents the stationary state of the two photochemical reactions (neglecting thermal isomerization) and depends on the wave length of the light used because the two ketones have different ultraviolet spectra.[15] Since the transformation also occurs in Pyrex vessels, the carbonyl group is the light-absorbing chromophore in the two ketones and we predict that the equilibrium should lie in favor of the ketone which exhibits less intense light absorption in the 300 mμ region and this is in agreement with our findings. The same argument furthermore demands that the photochemical equilibrium between eucarvone (I) and the first photoisomer II lie very much in favor of the non-conjugated ketone and we have in fact been unable to detect eucarvone (I) among the photoisomerization products of II. It must also be emphasized that the cycloheptadieneone I itself is not a β,γ-unsaturated ketone and therefore unable to undergo the cleavage reaction (XIII → XIV → XV) of cyclohexadienones on irradiation in alcoholic solution.[16]



X XI XII

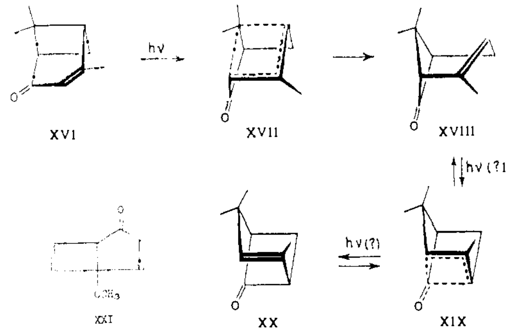


XIII

$$\underset{R_2}{\overset{R_1}{>}}C{=}CHCH{=}CHCH{=}C{=}O \xrightarrow{EtOH} \text{ester}$$

XIV XV

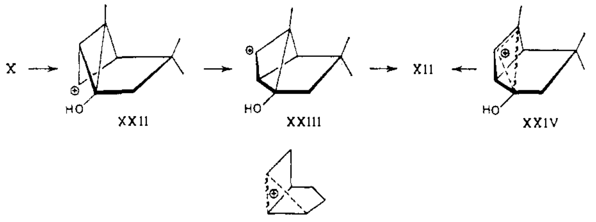
Whether or not our second photoisomerization represents a general reaction of non-planar β,γ-unsaturated ketones awaits further investigation, but two comments may be in order at this time. It obviously could not have been detected with photo-γ-tropolone methyl ether (XXI) because the rearrangement leads to the same product. It may be related to the exceedingly elegant synthesis of chrysanthenone (XVIII)[17] by photoisomerization[18] of verbenone (XVI) which may proceed through the hypothetical intermediate XVII. In addition to XVIII, one might have anticipated XX, formed by a second photochemical process (XVIII → XIX → XX), although this transformation has not been reported yet.



XVI XVII XVIII

XXI XX XIX

In conclusion, we wish to discuss the remarkable acid-catalyzed isomerization of II to V. When the first photoproduct II was heated in benzene solution in the presence of a trace of toluenesulfonic acid, but carefully shielded from light, a nearly quantitative conversion to the second photoisomer V was observed. Similar treatment of V produced no change and both compounds were recovered unchanged after refluxing in benzene solution in the absence of daylight. That the previously discussed transformation of II to V was indeed photochemical was demonstrated by irradiation in the presence of triethylamine. The acid-induced transformation demonstrates the higher thermodynamic stability of V/XII in which a destabilizing 1:3-methyl–methyl and an essentially eclipsed 1:2-methyl–hydrogen interaction present in II/X have been eliminated. Whether the rearrangement proceeds through the classical cyclopropylcarbinyl (XXII) and cyclobutylcarbonium ions (XXIII) or an unsymmetrical bicyclobutonium ion XXIV[19] is unknown, but the proposed intermediates are sterically feasible and the cyclopropylcarbinyl cation XXII has essentially the geometry of the bridged tricycloheptonium ion[20] XXV. The acid-catalyzed rearrangement observed provides the only evidence for a *cis* ring juncture in the two photoproducts.



XXII XXIII XXIV

XXV

Acknowledgment.—We are much indebted to the National Science Foundation (Research Grant G7424) for financial support.

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[15] For an excellent discussion of this topic see G. Zimmerman, L.-Y. Chow and U.-J. Paik, THIS JOURNAL, **80**, 3528 (1958).

[16] D. H. R. Barton and G. Quinkert, *Proc. Chem. Soc.*, 197 (1958); *J. Chem. Soc.*, 1 (1960).

[17] M. Kotake and H. Nonaka, *Ann.*, **607**, 153 (1957); E. P. Blanchard, Jr., *Chemistry & Industry*, 293 (1958).

[18] J. J. Hurst and G. H. Whitham, *Proc. Chem. Soc.*, 160 (1959).

[19] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, THIS JOURNAL, **81**, 4390 (1959); S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959).

[20] S. Winstein, F. Gadient, E. T. Stafford and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

Experimental[21]

Eucarvone (I).—Eucarvone (b.p. 58.5–59°, 14 mm.) was prepared from D-(+)-carvone in a 60% yield by the procedure of Corey and Burke.[22]

1,4,4-Trimethylbicyclo[3.2.0]hept-6-en-2-one (II).—A solution of eucarvone (100 g., 0.666 mole) in 100 ml. of 95% ethanol was irradiated with an immersible quartz mercury arc lamp (Hanau) for 8 days. The solution was agitated by a slow stream of nitrogen and the entire irradiation vessel was cooled in a circulating water-bath. The ethanol was removed by distillation through a 20-cm. column and the residual oil fractionated through a 40-cm. spinning band column at 45 mm. pressure. A fraction, b.p. 94–96°, was collected and after redistillation through the same column afforded 15.0 g. (15.0%) of 1,4,4-trimethylbicyclo-(3.2.0)hept-6-en-2-one, b.p. 95–96° (45 mm.), n^{25}D 1.4562. Irradiation of the recovered eucarvone (70.0 g.) for 14 days afforded an additional 21.7 g. (36.7% over-all) of the bicyclic ketone II; $\nu_{\max}^{CCl_4}$: 725 (CS_2). 1102, 1280, 1375, 1418, 1455, 1730(s), 2850(sh), 2930(s) and 3020(wk) cm.$^{-1}$; λ^{EtOH} 219 mμ, ϵ 820; $\lambda_{\max}^{EtOH}$ 303 mμ, ϵ 174.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.24; H, 9.50.

Treatment with 2,4-dinitrophenylhydrazine in methanol containing a trace of HCl at room temperature gave yellow needles of the 2,4-dinitrophenylhydrazone which was recrystallized twice from methanol, m.p. 161.5–162.5°; $\lambda_{\max}^{EtOH}$ 361 mμ, ϵ 23,400.

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.20; H, 5.45. Found: C, 58.17; H, 5.53.

1,4,4 - Trimethylbicyclo(3.2.0)heptane - 2 - one (III).—1,4,4-Trimethylbicyclo-(3.2.0)hept-6-en-2-one (2.0 g., 0.01335 mole) was hydrogenated over 100 mg. of prereduced 20% palladized charcoal in 50 ml. of absolute ethanol at 26° and 1 atm. pressure. After 90 min., 0.98 equivalent of hydrogen had been consumed and uptake ceased. The mixture was filtered, the ethanol removed by distillation through a 20-cm. column, and the residual clear oil distilled in a Claisen flask yielding 1.136 g. (56%) of 1,4,4-trimethylbicyclo(3.2.0)heptan-2-one (III), b.p. 110–111° (45 mm.), n^{25}D 1.4556; $\nu_{\max}^{CCl_4}$: 1125, 1375, 1470(broad), 1735(s), 2880(sh) and 2960(s) cm.$^{-1}$; $\lambda_{\max}^{EtOH}$ 296 mμ, ϵ 33.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.94; H, 10.53. Found: C, 78.78; H, 10.71.

Treatment with 2,4-dinitrophenylhydrazine in methanol containing a trace of HCl gave long yellow-orange needles of the 2,4 dinitrophenylhydrazone which was recrystallized twice from methanol, m.p. 147.5–148°; $\lambda_{\max}^{EtOH}$ 363 mμ, ϵ 22,600.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.80; H, 6.02. Found: C, 58.06; H, 6.09.

Pyrolysis of 1,4,4 - Trimethylbicyclo(3.2.0)hept - 6-en-2-one (II).—The pyrolysis apparatus consisted of a vertical Pyrex tube (18 × 1 cm., filled two-thirds full with $^3/_{16}$-inch diameter Pyrex helices) equipped with a nitrogen and sample inlet capillary at the top and a removable collection tube immersed in a Dry Ice–acetone-bath at the bottom. A thin wire in the inlet capillary permitted control of the rate of addition of the sample. Heating was accomplished with an external electrical heating jacket fitted with a thermocouple.

1,4,4 - Trimethylbicyclo(3.2.0)hept - 6 - en - 2 - one (300 mg., 0.2 millimole) was pyrolyzed at the rate of 4 mg./min. at 320–330° with a nitrogen flow of 10 ml./min. The light yellow pyrolysate collected (237 mg., 91%) was homogeneous to gas–liquid partition chromatography over Dow–Corning Silicone oil (no. 550) at 170° and had an infrared spectrum superimposable on that of eucarvone.

4,4,6-Trimethylbicyclo(3.2.0)hept-6-en-2-one (V).—1,4,4-Trimethylbicyclo(3.2.0)hept-6-en-2-one (25.0 g., 0.166 mole) in 150 ml. of *n*-hexane was irradiated for 10 days under conditions described previously for eucarvone. The *n*-hexane was removed by evaporation and the residue distilled at 1 mm. The clear oil obtained was fractionated through a 40-cm. spinning band column at 30 mm. pressure. A fraction, b.p. 82–83° (7.267 g.), consisted of starting ketone and the fraction, b.p. 101–103° (7.886 g., 31.5%), was 4,4,6-trimethylbicylco(3.2.0)hept-6-en-2-one, n^{25}D 1.4705; $\nu_{\max}^{CCl_4}$: 775 (CS_2), 815 (CS_2), 1145, 1520(s), 1705(sh). 1730-(s), 2930(s), 2850(sh), and 3020(wk) cm.$^{-1}$; $\lambda_{\max}^{EtOH}$ 303 mμ, ϵ 230; 219 mμ, ϵ 1730.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.75; H, 9.24.

Treatment with 2,4-dinitrophenylhydrazine in methanol containing a trace of HCl gave yellow needles which were recrystallized twice from methanol, m.p. 149–150°; $\lambda_{\max}^{EtOH}$ 362 mμ, ϵ 24,200.

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.20; H, 5.45. Found: C, 57.95; H, 5.38.

4,4,6-Trimethylbicyclo(3.2.0)heptan-2-one (VI).—4,4,6-Trimethylbicyclo(3.2.0)hept-6-en-2-one (V) (1.0 g., 0.0066 mole) was hydrogenated over 50 mg. of 20% palladized charcoal in 25 ml. of absolute ethanol at 25° and 1 atm. pressure. After 40 min., 0.98 equivalent of hydrogen had been consumed. The product was isolated in the manner described previously for 1,4,4-trimethylbicyclo(3.2.0)heptan-2-one. There was obtained 0.663 g. (66.0%) of 4,4,6-trimethylbicyclo(3.2.0)heptan-2-one, b.p. 120–121° (40 mm.), n^{25}D 1.4662; $\nu_{\max}^{CCl_4}$: 1155, 1465, 1735(s), 2850(sh) and 2930(s) cm.$^{-1}$; $\lambda_{\max}^{EtOH}$ 296 mμ, ϵ 31.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.94; H, 10.53. Found: C, 78.83; H, 10.34.

Treatment with 2,4-dinitrophenylhydrazine in methanol as above gave yellow needles which were recrystallized twice from methanol, m.p. 134–135°; $\lambda_{\max}^{EtOH}$ 362 mμ, ϵ 22,900.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.80; H, 6.02. Found: C, 57.78; H, 6.15.

Acid Isomerization of II.—1,4,4-Trimethylbicyclo(3.2.0)-hept-6-en-2-one (II) (200 mg., 1.33 millimoles) and *p*-toluenesulfonic acid (50 mg.) were added to 10 ml. of benzene and refluxed for 2 hr. in the dark. The resulting solution was washed once with 50 ml. of 5% aqueous sodium hydroxide and three times with 25-ml. portions of water. The benzene layer was dried over magnesium sulfate and the benzene removed under reduced pressure at room temperature. Chromatography in the vapor phase at 150° over tricyanoethoxypropane and collection followed by infrared spectra comparison of the resulting two components indicated 92.5% 4,4,6-trimethylbicyclo(3.2.0)hept-6-en-2-one (V) and 7.5% starting material. A sample of 1,4,4-trimethylbicyclo(3.2.0)hept-6-en-2-one (II) subjected to the same experimental conditions but without acid gave no conversion. Treatment of 4,4,6-trimethylbicyclo(3.2.0)-hept-6-en-2-one (V) with *p*-toluenesulfonic acid in benzene in the same fashion gave starting material.

3,3,5-Trimethylcycloheptadien-1-one (IV).—4,4,6-Trimethylbicyclo(3.2.0)hept-6-en-2-one (V) (2.724 g., 0.018 mole) was pyrolyzed at 380–390° in the manner described previously for 1,4,4-trimethylbicyclo(3.2.0)hept-6-en-2-one. The light yellow pyrolysate (2.582 g.) when chromatographed in the vapor phase over Dow–Corning Silicone oil (no. 550) at 170° was separated into two components in the ratio of 9:1 which were subsequently collected in small traps cooled in a Dry Ice–acetone-bath. The minor component on infrared analysis proved to be starting material and the major component after distillation from a Claisen flask at reduced pressure gave 1.462 g. (53.5%) of 3,3,5-trimethylcycloheptadien-1-one, b.p. 115–116° (25 mm.), n^{25}D 1.5060; $\nu_{\max}^{CCl_4}$: 765 (CS_2), 825 (wk, CS_2), 1270, 1310, 1640(sh), 1660(s), 2900(sh), 2930(s), and 2980-(sh) cm.$^{-1}$; $\lambda_{\max}^{EtOH}$ 304 mμ, ϵ 4900.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.46; H, 9.29.

In a preliminary experiment, pyrolysis at 320–330° gave only 50% conversion to the monocyclic dieneone. Repyrolysis of this mixture at 360–370° increased the total

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[21] Microanalyses are by Dr. S. M. Nagy and associates, Massachusetts Institute of Technology Microanalytical Laboratory. Melting points were taken on a Kofler hot-stage microscope and are corrected. Boiling points are uncorrected. Ultraviolet spectra were measured on a Cary recording spectrophotometer, model 11, and infrared spectra were measured on a Perkin–Elmer recording spectrophotometer, model 21, with a sodium chloride prism. The listings of infrared bands include those bands which are relevant to the structural argument and other medium and strong bands. Helium was used as the eluent gas for all vapor phase chromatograms, and the specified liquid phases (30%) were supported by 60–80 mesh fire-brick packed in 8 mm. × 200 cm. columns.

[22] E. J. Corey and H. J. Burke, This Journal, **78**, 174 (1956).

conversion to 70%. At 380–390°, 90% conversion was obtained and recyclization of the pyrolysate failed to increase this yield.

Treatment with 2,4-dinitrophenylhydrazine in methanol as above gave the deep red 2,4-dinitrophenylhydrazone which was recrystallized three times from methanol, m.p. 143–144°; λ_{max}^{EtOH} 381 mμ, ϵ 29,500.

Anal. Calcd. for $C_{16}H_{18}N_4O_4$: C, 58.20; H, 5.45. Found: C, 58.30; H, 5.29.

Deuterium Exchange of 1,4,4-Trimethylbicyclo(3.2.0)heptan-2-one (III) and 4,4,6-Trimethylbicyclo(3.2.0)heptan-2-one (VI).—Sodium (20 mg.) was added to 1 ml. of deuterioethanol followed by 0.5 ml. of deuterium oxide. 1,4,4-Trimethylbicyclo(3.2.0)heptan-2-one (60 mg.) was added and the solution refluxed under nitrogen for 10 min. and the product distilled *in vacuo*. The distillate was diluted with 2 ml. of deuterium oxide and extracted with three 5-ml. portions of petroleum ether and the extracts were dried over magnesium sulfate. Evaporation of the petroleum ether on a steam-bath followed by distillation of the residue in a micro Hickman still at 45 mm. gave a clear oil which had a mass spectrum indicating 81% of the dideuterioketone and 17.3% of the monodeuterioketone.

Treatment of 4,4,6-trimethylbicyclo(3.2.0)heptan-2-one in the same manner gave a mixture of 41% trideuterioketone, 35.2% dideuterioketone and 18.1% monodeuterioketone.

Interconversion of 4,4,6-Trimethylbicyclo(3.2.0)hept-6-en-2-one (V) and 1,4,4-Trimethylbicyclo(3.2.0)hept-6-en-2-one (II).—To a small quartz flask equipped with a reflux condenser and a nitrogen inlet was added 200 mg. of 4,4,6-trimethylbicyclo(3.2.0)hept-6-en-2-one, 2 drops of triethylamine and 5 ml. of *n*-hexane. The solution was agitated by a slow stream of nitrogen and illuminated by an external quartz mercury arc (Hanau) for 25 hr. Both the lamp and the flask were cooled by a circulating water-bath. The *n*-hexane was removed under reduced pressure and the residual oil chromatographed in the vapor phase over tricyanoethoxypropane at 150°. The two major components present in a ratio of *ca.* 1:5 were collected and comparison of their infrared spectra indicated the major component to be starting ketone and the minor component to be 1,4,4-trimethylbicyclo(3.2.0)hept-6-en-2-one. Irradiation of 1,4,-4-trimethylbicyclo(3.2.0)hept-6-en-2-one under the above conditions gave the same mixture in a ratio of 1:4.

Conversion of 3,3,5-Trimethylcycloheptadien-1-one (IV) to 4,4,6-Trimethylbicyclo(3.2.0)hept-6-en-2-one (V).—3,3,-5-Trimethylcycloheptadien-1-one (100 mg.) in 5 ml. of *n*-hexane contained in a small quartz flask was illuminated under nitrogen with a quartz mercury arc (Hanau) for 5 hr. After removal of the *n*-hexane under reduced pressure at room temperature, a small sample of the residual oil was chromatographed in the vapor phase over tricyanoethoxypropane at 150°. Collection followed by infrared spectra comparison of the two primary components indicated 72% of starting ketone and 25% of 4,4,6-trimethylbicyclo-(3.2.0)hept-6-en-2-one.

3,3,5 - Trimethylcycloheptanone - 1 (VII).—3,3,5 - Trimethylcycloheptadienone (70.0 mg., 0.466 millimole) was hydrogenated over 10 mg. of 20% palladized charcoal in 10 ml. of absolute ethanol at 28° and 1 atm. pressure. After 10 min., 2.3 equivalents of hydrogen had been consumed and uptake ceased. The mixture was filtered, the ethanol removed under reduced pressure at room temperature, the residue distilled in a micro Hickman still at 15 mm. to give 35 mg. (49.0%) of 3,3,5-trimethylcycloheptanone-1.

The semicarbazone after three recrystallizations from methanol and water had m.p. 186–186.5° (lit. 196–197°,[23] 189°[14]) pure and mixed with a synthetic sample described below. Both samples had identical infrared spectra in KBr.

In a three-necked flask equipped with a magnetic stirrer and thermometer was placed 5.35 g. (0.04 mole) of dihydroisophorone and 4.5 g. (0.08 mole) of potassium hydroxide in 100 ml. of methanol. N,N'-Dimethyl-N,N'-dinitrosoterphthalamide (du Pont EXR-101, 6.57 g., 0.4 mole) was washed three times with 50-ml. portions of *n*-hexane to remove the mineral oil stabilizer. Small portions of the nitroso compound were added to the dihydroisophorone solution maintained at 5–10° with external cooling. After one-third of the product had been added, the solution was allowed to warm to room temperature and the addition continued (3 hr.). After each addition the solution was allowed to decolorize. Excess diazomethane was destroyed by acidifications and the methanol was removed by distillation. Filtration of the residue followed by distillation through a Holtzman column at 20 mm. afforded 0.643 g. of a fraction, b.p. 107–110°. Chromatography of a small sample of this fraction in the vapor phase over nitromethylpimelonitrile at 100° indicated three components in the ratio of *ca.* 1:2:4 which were subsequently collected. The infrared spectrum of the major component was identical with that of dihydroisophorone (VIII).

The semicarbazones of the two minor components were prepared in the usual manner and after three recrystallizations from methanol and water both had m.p. 185–186° (lit. for 3,3,5-trimethylcycloheptanone, m.p. 196–197°[23] and m.p. 189°[14]; for 3,5,5-trimethylcycloheptanone, m.p. 192–193°[23] and m.p. 194°[14]). The semicarbazones of the reduction product of IV gave no melting point depression when mixed with the corresponding derivative of 3,3,5-trimethylcycloheptanone but, on admixture of the derivative of 3,5,5-trimethylcycloheptanone, the melting point was depressed to 175°.

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[23] B. Tchoubar, *Bull. soc. chim. France*, 164 (1949).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Terpenoids. XLIV.[1] Synthetic Confirmation of the Structure and Absolute Configuration of Petasin[2]

BY DAVID HERBST[3] AND CARL DJERASSI

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The total synthesis of (−)-*trans*-1,9-dimethyldecalin-2,6-dione (VIII) from an intermediate of known absolute configuration is described. The same diketone could also be obtained from the sesquiterpene petasin (I), thus confirming the earlier structural and absolute configurational assignments.

Petasin,[4,5] the angelate ester of petasol (II),[6] has recently been assigned[5] structure I (without any stereochemical implications). The main arguments in the structure proof[5] of petasin (I) have already been reviewed[7] and it was pointed out that

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[1] Paper XLIII, E. J. Eisenbraun, T. George, B. Riniker and C. Djerassi, THIS JOURNAL, **82**, 3648 (1960).

[2] Supported by the Division of Research Grants (grant No. RG-6840) of the National Institutes of Health, U. S. Public Health Service.

[3] From part II of the Ph.D. dissertation of David Herbst.

[4] A. Aebi, J. Büchi, T. Waaler, E. Eichenberger and J. Schmutz, *Pharm. Acta Helv.*, **30**, 277 (1955); A. Stoll, R. Morf, A. Rheiner and J. Renz, *Experientia*, **12**, 360 (1956).

[5] A. Aebi and T. Waaler, "Uber die Inhaltstoffe von *Petasites hybridus* (L.) Fl. Wett." Verlag Helbing und Lichtenhahn, Basel, 1958. A preliminary note of these studies has been published by A. Aebi, T. Waaler and J. Büchi, *Pharm. Weekblad*, **93**, 397 (1958).

[6] Petasol (II) itself has never been isolated, because during the saponification of the angelate ester the double bond of the isopropenyl group migrates into conjugation to afford directly isopetasol (III).

[7] A. Aebi and C. Djerassi, *Helv. Chim. Acta*, **42**, 1785 (1959).