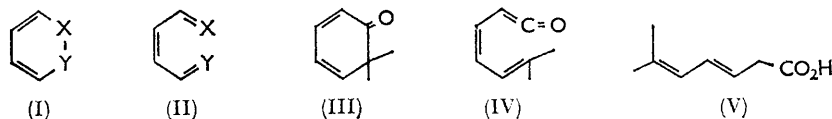


764. *The Photolysis of 3-Methylcar-4-en-2-one.*

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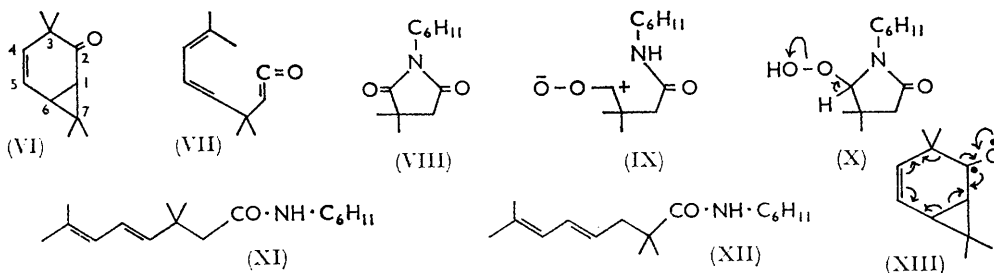
Irradiation of 3-methylcar-4-en-2-one in cyclohexylamine results in photolysis with the formation of *N*-cyclohexyl-3,3,7-trimethylocta-4,6-dienamide.

MANY examples are now known of the photochemical cleavage of six-membered rings containing two conjugated double bonds according to the general scheme (I)  $\longrightarrow$  (II).<sup>1</sup> An important group of such compounds is that of the cyclohexa-2,4-dienones geminally substituted at C-6, *e.g.*, 6,6-dimethylcyclohexa-2,4-dienone (III). Irradiation of the latter in the presence of water results in the formation of 6-methylhepta-3,5-dienoic acid (V). It appears likely that this reaction is initiated by  $n \longrightarrow \pi^*$  excitation of the chromophoric system, followed by electron redistribution in the excited state leading to the keten (IV), which reacts with water to give (V).<sup>2</sup>



An investigation of the irradiation of 3-methylcar-4-en-2-one (VI)<sup>3,4</sup> in nucleophilic solvents seemed, therefore, of interest since excitation followed by electron redistribution might produce the keten (VII) thus leading to derivatives of 3,3,7-trimethylocta-4,6-dienoic acid.

Irradiation of 3-methylcar-4-en-2-one in ether saturated with water or in ethereal ammonia gave, respectively, products of acidic and amidic nature possessing maximal absorption in at 237  $m\mu$ , *i.e.*, consistent with a trisubstituted diene chromophore. In neither case was pure material isolated. From the irradiation of 3-methylcar-4-en-2-one in ether containing cyclohexylamine, however, a crystalline cyclohexylamide was isolated in 55% yield. The latter ( $C_{17}H_{29}NO$ ) had  $\lambda_{max}$ . (in EtOH) 238  $m\mu$  ( $\epsilon$ , 28,600), corresponding to a trisubstituted diene, and the presence of two double bonds was confirmed by catalytic hydrogenation over platinum in acetic acid. Ozonolysis followed by reductive cleavage of the ozonide gave acetone, isolated as the 2,4-dinitrophenylhydrazone, in 50% yield. On the other hand, ozonolysis followed by oxidation with hydrogen peroxide in formic acid



gave a mixture of 2,2-dimethylsuccinic acid and its *N*-cyclohexylimide (VIII). Formation of the latter may be rationalised in terms of a Criegee intermediate,<sup>4</sup> in this case (IX), which could undergo cyclisation to (X) followed by elimination to the imide (VIII). The 2,2-dimethylsuccinic acid may have arisen by hydrolysis of its first-formed half-amide during the isolation procedure.

<sup>1</sup> De Mayo and Reid, *Quart. Rev.*, 1961, **15**, 393.

<sup>2</sup> Barton and Quinkert, *J.*, 1960, 1.

<sup>3</sup> Corey and Burke, *J. Amer. Chem. Soc.*, 1956, **78**, 174.

<sup>4</sup> Bellamy and Whitham, forthcoming publication.

The results of the above degradation coupled with the spectral data led to two possible formulations for the cyclohexylamide, *i.e.*, (XI) or (XII), possibilities of geometrical isomerism being neglected. A decision between these two structures should be possible through the nuclear magnetic resonance spectrum. Thus compound (XI) would be expected to show only a singlet due to the C-2 protons, whereas for (XII) absorption due to the C-3 methylene protons should be split into a doublet by the olefinic proton on C-4. In fact the nuclear magnetic resonance spectrum (40 mc./sec., in  $\text{CHCl}_3$ ) showed a singlet at  $\tau$  8.90 ( $\equiv$  6 protons)—*gem*-dimethyl group at C-3, a singlet at 8.28 ( $\equiv$  6 protons)—*gem*-dimethyl group at C-7, a sharp singlet at 7.95 ( $\equiv$  2 protons)— $\text{CH}_2$  at  $\text{C}_{(2)}$ , and a complex multiplet 3.8—4.7 ( $\equiv$  3 protons) in the olefinic region. This information is only compatible with structure (XI) and serves to confirm the gross structure.

3-Methylcar-4-en-2-one thus undergoes photolysis in the expected sense, and the most reasonable rationalisation for the formation of the derivatives of 3,3,7-trimethylocta-4,6-dienoic acid involves the intermediate keten (VII). Formula (XIII) is a crude representation of the  $n \rightarrow \pi^*$  excited state of (VI) showing schematically the mode of electron redistribution. It is noteworthy that cleavage of the 1,6-bond occurs whereas other cleavage reactions of 3-methylcar-4-en-2-one involve the 1,7-bond.<sup>4</sup> Clearly, however, if continuous electronic redistribution is to occur, only the 1,6-bond can be involved. Presumably the excited state is sufficiently distorted to allow continuous overlap of the developing *p*-orbitals at C-3 and C-6 with the 4,5-double bond and, in particular, the *p*-orbital at C-2 with the developing *p*-orbital at C-1.

#### EXPERIMENTAL

Light petroleum refers to the fraction, b. p. 40—60°.

*Irradiation of 3-Methylcar-4-en-2-one in Ethereal Cyclohexylamine.*—3-Methylcar-4-en-2-one (5.14 g.) in dry ether (1100 ml.) and cyclohexylamine (15 ml.) was irradiated under nitrogen at 15° in a quartz flask with u.v. light (Hanovia U.V.S. 500 mercury arc) for 36 hr. Irradiation was continued until all the ketone had disappeared as judged by thin-layer chromatography. The solution was washed successively with aqueous hydrochloric acid and water and then dried. Evaporation gave a viscous liquid (6.81 g.) which was chromatographed on silica gel (150 g.). Elution with light petroleum-ether (2:1—1:1) gave *N*-cyclohexyl-3,3,7-trimethylocta-4,6-dienamide (4.32 g., 55%), m. p. 74—77° [cryst. from light petroleum (b. p. 100—120°)] (Found: C, 77.8; H, 11.15; N, 5.4.  $\text{C}_{17}\text{H}_{29}\text{NO}$  requires C, 77.5; H, 11.1; N, 5.35%);  $\lambda_{\text{max}}$ . (in EtOH) 238 ( $\epsilon$ , 28,650),  $\lambda_{\text{sh}}$ . 232  $\text{m}\mu$  ( $\epsilon$ , 26,210);  $\nu_{\text{max}}$ . (Nujol) 3300, 3050, 1640, 1550, 1350, 1305, 1250, 1230, 1190, 1160, 1130, 1090, 1040, 995, 985, 960, 940, 895, 870, and 735  $\text{cm}^{-1}$ .

Irradiation in a Pyrex flask led to a slower conversion into the same product. In a control reaction, 3-methylcar-4-en-2-one was recovered unchanged after heating under reflux with ether containing cyclohexylamine in the dark for 15 hr.

*N-Cyclohexyl-3,3,7-trimethyloctanamide.*—Hydrogenation of *N*-cyclohexyl-3,3,7-trimethylocta-4,6-dienamide (38 mg.) in glacial acetic acid (10 ml.) over platinum at atmospheric pressure resulted in the rapid uptake of hydrogen (1.9 mol.). The product was roughly chromatographed on silica gel and elution with light petroleum-ether (1:1) gave the *saturated amide*, m. p. 81—82.5° (after preliminary softening) [from light petroleum (b. p. 100—120°)] (Found: C, 75.9; H, 12.45; N, 4.85.  $\text{C}_{17}\text{H}_{33}\text{NO}$  requires C, 76.35; H, 12.45; N, 5.25%);  $\nu_{\text{max}}$ . (Nujol) 3300, 1640, 1545, 1350, 1250, 1160, and 890  $\text{cm}^{-1}$ .

*Ozonolysis of N-Cyclohexyl-3,3,7-trimethylocta-4,6-dienamide.*—(a) The amide (0.27 g.) in glacial acetic acid (10 ml.) was cooled to 0°, and ozonised oxygen was bubbled through the solution. The outlet tube was connected to a trap, containing water (15 ml.), in turn connected to a trap containing acidified potassium iodide. When iodine was freely liberated in the last trap (2 hr.) the contents of the ozonolysis vessel and the water trap were combined and steam-distilled after the addition of zinc dust (1.0 g.). The distillate (300 ml.) was added to a hot solution of 2,4-dinitrophenylhydrazine reagent. Next morning the precipitate (0.19 g.) was filtered off and chromatographed on alumina (Woelm, neutral). Elution with benzene-chloroform (99:1—1:1) gave acetone 2,4-dinitrophenylhydrazone (0.12 g.; 50%), m. p. 122—127°, identical with an authentic specimen.

(b) The amide (1.81 g.) in dry methanol (70 ml.) was cooled to  $-80^{\circ}$  and ozonised oxygen was bubbled through the solution. When the emergent gases freely liberated iodine from acidified aqueous potassium iodide the gas flow was stopped and the methanol was evaporated at room temperature leaving a crystalline residue. The latter was dissolved in 90% aqueous formic acid (140 ml.), hydrogen peroxide solution (30%; 7 ml.), was added, the mixture was heated under reflux for 1 hr. and then left for 16 hr. at  $20^{\circ}$ . After being poured into brine (2 l.), the product (2.02 g.) was isolated with ether and chromatographed on silica gel (50 g.), giving two main fractions, (A, 0.58 g.) eluted with chloroform, and (B, 0.60 g.).

The oil (A) was further chromatographed on alumina (Woelm, neutral). Elution with benzene-chloroform (1 : 1—1 : 4) gave fairly pure *N*-cyclohexyl-2,2-dimethylsuccinimide (0.36 g.; 25%), b. p. (bath)  $200^{\circ}/2$  mm., which slowly crystallised and was recrystallised (from water), it had m. p.  $49.5-54^{\circ}$ ;  $\nu_{\max.}$  (in  $\text{CCl}_4$ ) 2900, 2850, 1775, 1705, 1470, 1455, 1425, 1395, 1385, 1370, 1350, 1295, 1250, 1230, 1205, 1175, 1125, 1080, 1055, 980, 897, 890, and 865  $\text{cm}^{-1}$ . The m. p. was undepressed on admixture with an authentic sample of *N*-cyclohexyl-2,2-dimethylsuccinimide and the infrared spectra were identical.

The solid (B) was purified by solution in ether and extraction with water. Evaporation of the aqueous extract gave 2,2-dimethylsuccinic acid (0.2 g.; 20%), m. p.  $142-144.5^{\circ}$  (cryst. from light petroleum-ether) (Found: C, 49.5; H, 7.15. Calc. for  $\text{C}_6\text{H}_{10}\text{O}_4$ : C, 49.3; H, 6.9%);  $\nu_{\max.}$  (Nujol) 3500—2250br, 1695, 1345, 1310, 1260, 1220, 1165, 1140, 1030, 995, 940, 880, 797, 770, 725, and 695  $\text{cm}^{-1}$ . It was identical with an authentic sample prepared by the method of Smith and Horwitz.<sup>6</sup>

*N*-Cyclohexyl-2,2-dimethylsuccinimide.—2,2-Dimethylsuccinic anhydride<sup>7</sup> (3.75 g.) and cyclohexylamine (redist., 2.91 g.) were mixed and heated slowly to  $100^{\circ}$ . After 16 hr. at  $20^{\circ}$  the mixture was heated to  $160-170^{\circ}$  for 2 hr. The product was distilled to give the imide (5.4 g., 87%), b. p.  $93-101^{\circ}/0.5$  mm., m. p.  $54.5-55.5^{\circ}$  (from aqueous MeOH) (Found: C, 68.0; H, 9.0; N, 6.95.  $\text{C}_{12}\text{H}_{19}\text{NO}_2$  requires C, 68.85; H, 9.15; N, 6.7%).

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<sup>5</sup> Cf. Bailey, *Chem. Rev.*, 1958, **58**, 925.

<sup>6</sup> Smith and Horwitz, *J. Amer. Chem. Soc.*, 1949, **71**, 3418.

<sup>7</sup> Brown and Van Gulick, *J. Amer. Chem. Soc.*, 1955, **77**, 1083.