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DECOMPOSITION OF 1-DIAZO-3-(2,2,3-TRIMETHYLCYCLOPENT-3-ENYL)PROPAN-2-ONE.

A NOVEL SYNTHESIS AND REARRANGEMENT OF A TRICYCLO[3.2.1.$0^{3,6}$]OCTAN-4-ONE

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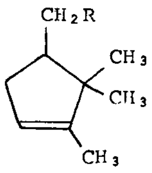
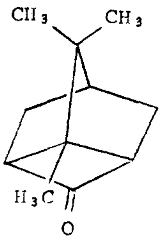
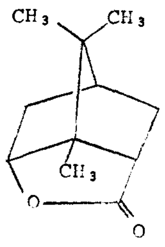
PHOTOLYSIS of (±)-1-diazo-3-(2,2,3-trimethylcyclopent-3-enyl)propan-2-one (I) (1) in 0.5% solution in pentane in Pyrex with a 450-w. medium pressure Hanovia lamp gave 6,7,7-trimethyltricyclo[3.2.1.$0^{3,6}$]octan-4-one (II), m.p. 166-168°, in 79% yield. The structure of II is assigned on the basis of its spectra [$\lambda_{max}^{CCl_4}$ 5.65; δ^{CCl_4} 1.00 (*s*, 6H), 1.13 (*s*, 3H), 1.5-2.7 (7H); m/e 164 (3%)] and the following reactions. Oxidation with



I, R = COCHN$_2$
V, R = CH$_2$CO$_2$H
VII, R = CH=C=O
VIII, R = CH$_2$COCl

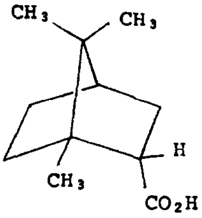


II

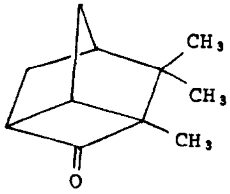


III

m-chloroperbenzoic acid gave a lactone, $C_{11}H_{16}O_2$, m.p. 206-207.5° [$\lambda_{max}^{CCl_4}$ 5.60μ; δ^{CCl_4} 0.95 (*s*, 6H), 1.12 (*s*, 3H), 1.15-2.3 (6H), 4.34 (broadened *d*, J = 7.4 Hz, 1H); m/e 180 (4%)], assigned structure III. Treatment of II with potassium *t*-butoxide-water (2) gave *endo*-2-bornanecarboxylic acid (IV), identified by comparison with an authentic sample (3). Treatment of II with ethanolic potassium hydroxide gave the carboxylic acid V (*vide infra*). Photolysis of (+)-I (4) gave II, m.p. 165.5-168°, showing no optical activity at 250-700 mμ (*c*, 0.50, hexane).



IV



VI

Decomposition of the diazo ketone (±)-I [or (+)-I] with silver oxide in boiling aqueous dioxane gave the normal Wolff rearrangement product V (14%) and a mixture of II and its isomer VI, m.p. 168-170° [$\lambda_{max}^{CCl_4}$ 5.65; δ^{CCl_4} 0.92 (*s*, 3H), 0.94 (*s*, 6H), 1.0-2.4 (6H), 2.88 (*d* of *d*, *J* = 4.0, 8.4 Hz, 1H); $\delta^{C_6H_6}$ 0.70 (*s*, 3H), 0.81 (*s*, 3H), 0.88 (*s*, 3H); m/e 164 (20%)], showing no optical activity at 250-750 mμ (*c*, 0.41, hexane). Similar decomposition of I at room temperature gave V and II, but no VI, suggesting that II may undergo thermal rearrangement to VI. This was confirmed and the rearrangement of VI to II demonstrated by the observation that either II or VI is converted to a mixture of the two on being heated in boiling xylene.

Evidence was obtained that II is formed from I via the ketene VII from the observation that treatment of the acid chloride VIII with triethylamine in refluxing benzene gave the ketone II (18%) and VI (4%). This ketene must also be the precursor of the acid V, formed together with II from I in aqueous medium. It is noteworthy that intramolecular addition of the ethylenic double bond of the ketene function of VII to the isolated ethylenic double bond competes effectively with intermolecular reaction with solvent water. A related cycloaddition reaction of a ketene derived from an unsaturated α-diazo ketone has been reported during the course of the present work, although the proximate product was not obtained pure because of its instability (5,6,7).

The interconversion of the tricyclic ketones II and VI is of considerable interest (9). No acid V was formed when II was converted to a mixture of II and VI in boiling aqueous dioxane. Thus, if interconversion proceeded via the ketene VII under these conditions, reclosure would have to be remarkably rapid. This suggests that the interconversion may proceed by a more concerted pathway.

Another facet of interest of the present results is their promise of convenient synthetic routes to hitherto difficultly accessible bridged tricyclic ketones. Compounds with the tricyclic system of II and VI are rare (10), and their 4-ones have not been obtained previously.

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References

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6. Cf. S. Masamune and N. T. Castellucci, *Proc. Chem. Soc.* 298 (1964); A. Small, *J. Am. Chem. Soc.* **86**, 2091 (1964).
7. Decomposition of diazo ketone I with copper metal in benzene gave the carbene addition product, 1,8,8-trimethyltricyclo[3.2.1.$0^{2,7}$]octan-3-one, m.p. 152-154° (76%), but no II nor VI (6,8).

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