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THE PHOTOCHEMICAL REARRANGEMENT OF CIS-2-CYCLODECENONE

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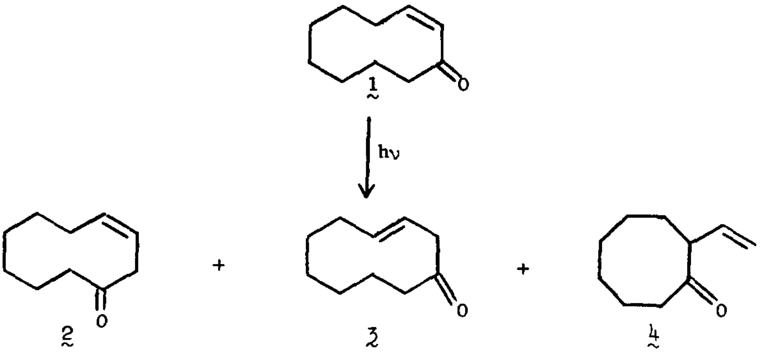
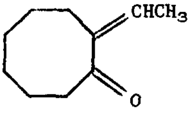
The fate of cyclic α,β-unsaturated ketones on irradiation with ultraviolet light depends markedly on the size of the carbocyclic ring. Cyclopentenone (1) affords two isomeric dimers in nearly equal amounts, while cyclohexenones undergo either dimerization (2) or rearrangement (3). In contrast, 2-cycloheptenone (4) and 2-cyclooctenone (5) undergo isomerization to the highly strained *trans*-2-cycloalkenones. 2-Cyclododecenone (6) is converted to the photochemically stable *cis*-3-cyclododecenone, a process analagous to the rearrangements of acyclic α,β-unsaturated ketones possessing a γ-hydrogen (7). We wish to report that *cis*-2-cyclodecenone (**1**) undergoes a novel isomerization on photolysis to give a ring contracted cyclooctanone derivative.

Irradiation (8) of a 1% solution of **1** in either benzene or *t*-butyl alcohol led to rapid isomerization to a mixture of *cis*- and *trans*-3-cyclodecenone (**2** and **3**) (9). After one hour another product was detectable by vapor phase chromatography (vpc) whose concentration gradually increased until an apparent photostationary state was achieved after *ca*. 18 hr. At this time vpc analysis indicated the presence of two major components in the ratio 3:2 along with several very minor components.

The major product (~50% yield) collected by preparative vpc after vacuum distillation of the crude product is an inseparable mixture of *cis*- and *trans*-3-cyclodecenone (10). The infrared spectrum of the mixture showed absorption at 3030, 1706, 1620, 980 and 707 cm^{-1} and an ultraviolet absorption maximum (EtOH) at 287mμ (ε 67). The nmr spectrum (11) of the mixture was consistent with the assigned structures and the appearance of two distinct doublets in the region δ 3.1-2.7 (J = 7 cps, C-2 methylene protons) of approximately equal area indicated that **2** and **3** were present in nearly equal amounts. On catalytic hydrogenation over palladium on charcoal the mixture absorbed one mole of hydrogen and gave cyclodecanone in quantitative yield.



The second major product (~35% yield) isolated by preparative vpc under carefully controlled conditions gave analytical results which indicated it was an isomer of the starting material. The infrared spectrum of this product showed absorption at 3100, 1705, 1630, 990 and 915 cm^{-1} and an ultraviolet absorption maximum (EtOH) at 293 mμ (ε 81) consistent with a non-conjugated ketone containing a terminal vinyl group. The nmr spectrum (11) confirmed these assignments and showed, inter alia, a typical vinyl pattern in the region δ 6.00-4.80 (3H) and a multiplet at δ 3.1 (1H) for a methinyl proton adjacent to a carbonyl group and double bond. These data suggested that the photoproduct was 2-vinylcyclooctanone (4). This assignment was confirmed by catalytic hydrogenation to 2-ethylcyclooctanone, identical with an independently prepared sample. Compound 4 underwent a facile isomerization on vpc if the conditions were not rigorously controlled to an isomeric ketone, 2-ethylidenecyclooctanone (5). Compound 5 showed infrared absorption at 3025, 1680 and 1620 cm^{-1} and had an ultraviolet absorption maximum (EtOH) at 241 mμ (ε 5000). The nmr spectrum showed a one proton absorption at δ 5.60 (quartet, J = 7 cps) for the olefinic proton and a three proton



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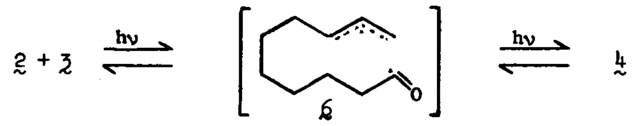
doublet at δ 1.77 (J = 7 cps) for the methyl group. Catalytic hydrogenation produced 2-ethylcyclooctanone.

The photochemical formation of the ring contracted ketone **4** is reversible since irradiation of 2-vinylcyclooctanone (**4**) (containing some **5**) led to partial conversion to the isomeric 3-cyclodecenones **2** and **3**. One possible mechanism for these photochemical transformations would involve cleavage of the bond between C-1 and C-2 in the β,γ-unsaturated ketones (12, 13) to give the diradical **6**. It is likely that **6** is not generated in a free state with an appreciable lifetime, but that the conformation is held with the radical centers in close proximity and bond formation occurs at either allylic position. If **6** had a sufficiently long lifetime to become essentially a ten-carbon acyclic diradical, it is unlikely that ring closure to eight- and ten-membered rings would occur (14). Cleavage reactions of this type have previously been observed with acyclic and bridged bicyclic β,γ-unsaturated ketones, but this represents the first example of such a rearrangement with a simple monocyclic ketone.



We are currently examining the generality of this type of ring contraction reaction with other medium ring ketones.

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2. H. Ziffer, N. E. Sharpless, and R. O. Kan, Tetrahedron, **22**, 3011 (1966) and references cited therein.
3. For a recent summary see R. O. Kan, "Organic Photochemistry," McGraw-Hill, Inc., New York, N. Y., 1966, Chapt. 4.

4. P. E. Eaton and K. Lin, *J. Am. Chem. Soc.*, **87**, 2052 (1965); E. J.Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965).
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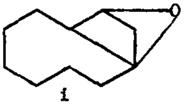
6. H. Nozaki, T. Mori and R. Noyori, *Tetrahedron*, **22**, 1207 (1966).
7. N. C. Yang and M. J. Jorgenson, *Tetrahedron Letters*, 1203 (1964).
8. Irradiations were conducted under nitrogen in a Vycor tube mounted in the center of a Rayonet Photochemical Reactor equipped with RPR-2537 Å lamps.
9. The ultraviolet spectrum of an aliquot of the photolysis mixture showed that **1** had completely disappeared after *ca*. 20 min.
10. All new compounds gave satisfactory elemental analyses.
11. Determined at 100 Mc. Appropriate decoupling experiments were performed where pertinent.
12. For leading references see (a) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967); (b) E. F. Kiefer and D. A. Carlson, *Tetrahedron Letters*, 1617 (1967); (c) N. C. Yang and D. Thap, *ibid.*, 3671 (1966); (d) D. E. Bays and R. C. Cookson, *J. Chem. Soc.*, (B), 226 (1967).
13. Other possible mechanisms cannot be excluded at this time. For example, intramolecular oxetan formation to give **i** which can open to give either **2** and **3** or **4**



i

is another possibility. Intramolecular oxetan formation has been noted with γ,δ-unsaturated acyclic ketones: N. C. Yang, M. Nussim, and D. R. Coulson, *ibid.*, 1525 (1965).

14. E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, Inc., New York, N. Y., 1962, pp. 198-202.