

SYNTHESIS AND REARRANGEMENT OF
TRICYCLO[4.3.2.0^{1,6}]UNDEC-10-EN-2-ONE

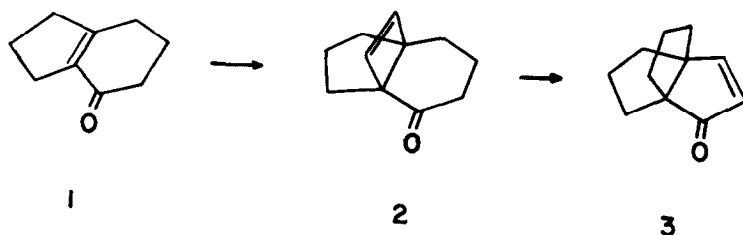
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(Received 3 October 1966; in revised form 7 November 1966)

In previous publications^{2,3} we have described the synthesis of tricyclo[m.n.2.0^{1,m+2}]-ketones. We now report the synthesis of tricyclo[4.3.2.0^{1,6}]undec-10-en-2-one (2) and its rearrangement to tricyclo[3.3.3.0^{1,5}]undec-2-en-4-one (3).

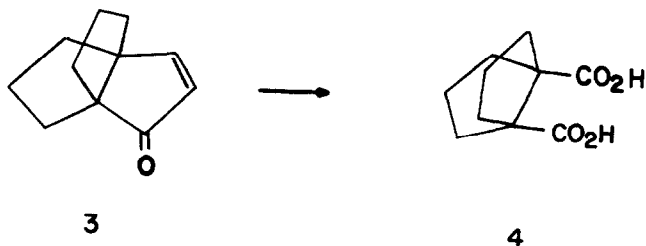
When the synthesis of 2 was carried out in the manner previously described for the synthesis of tricyclo[3.3.2.0^{1,5}]dec-9-en-2-one,³ a tricyclic enone was isolated which has the correct empirical formula,⁴ but whose ultraviolet, infrared, and nuclear magnetic resonance spectra were inconsistent with the formulation of 2 as the reaction product. Formula 3 did, however, appear to fit the spectral data. Ketone 2 was therefore prepared by a slightly modified procedure. Subsequent treatment of 2 with acid caused rearrangement to ketone 3, identical with the product obtained via the direct procedure.



Photochemical cycloaddition of 1,2-dichloroethylene (cis, or trans) to bicyclo[4.3.0]non-1(6)-en-2-one (**1**)⁵ proceeded smoothly to give a mixture of tricyclic, dichloro ketones. Immediate dechlorination of the crude product with sodium in liquid ammonia yielded a mixture of the desired ketone **2** and the corresponding alcohol(s). The ketone could be isolated by alumina chromatography, or alternatively, the entire mixture could be treated with chromic acid to give **2** in 31 - 35% yield from **1**.

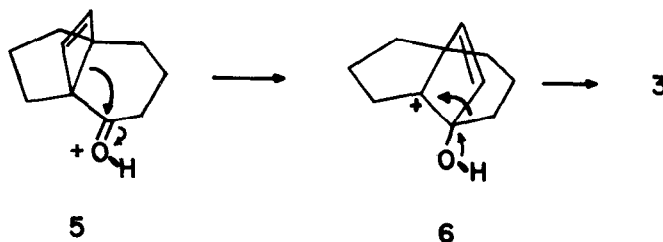
The spectral data: λ_{\max} 296 m μ (ϵ 85), interacting β,γ -unsaturated ketone; $\tilde{\nu}_{\max}$ 1700 cm⁻¹, cyclohexanone; and an AB quartet centered at 5.97 ppm, $\delta_A - \delta_B = 10.5$ cps and $J_{AB} = 2.8$ cps, nonequivalent vinyl protons on a cyclobutene ring, along with the mass spectrum⁴ and the mode of formation establish structure **2**.

Since in the previous attempt to prepare **2**, acid catalyzed hydrolysis of the corresponding ethylene ketal resulted in a rearranged product, ketone **2** was subjected to the action of *p*-toluenesulfonic acid in boiling benzene. Rearrangement was complete in less than one hour, and a single product (**3**) was formed. Pure **3**, obtained by preparative gas chromatography, has λ_{\max} 228 m μ (ϵ 7200) and $\tilde{\nu}_{\max}$ 1710 cm⁻¹, conjugated cyclopentenone; and doublets at 5.91 and 7.33 ppm, $J_{AX} = 6$ cps, α - and β -protons of cyclopentenone, respectively. The remaining protons gave rise to a complex multiplet between 1.3 and 2.1 ppm. Final proof of structure was provided by oxidation of ketone **3** to diacid **4**, previously obtained by oxidation of tricyclo[3.3.2.0]-dec-9-en.⁶



The rearrangement of ketone $\tilde{2}$ to $\tilde{3}$ must involve vinyl migration in the protonated ketone $\tilde{5}$ to produce the ion $\tilde{6}$, a type already known to be highly stabilized.⁷ Further bond migration provides the observed ketone

$\tilde{3}$.



Ketone $\tilde{3}$ provides the first example of the tricyclo[3.3.3.0^{1,5}]-undecane ring system. A detailed account of the chemistry of ketones $\tilde{2}$ and $\tilde{3}$, as well as of other tricyclic ketones, will be described in a later paper.

Acknowledgment. We thank the National Science Foundation for support of this research, for a traineeship to J.W.C., and for an institutional grant toward the purchase of a Varian A-60 nmr spectrometer.

References

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- 3) R. L. Cargill, J. R. Damewood, and M. M. Cooper, J. Amer. Chem. Soc., **88**, 1330 (1966).
- 4) The mass spectra of ketones $\tilde{2}$ and $\tilde{3}$ are consistent with the assigned structures. We are pleased to thank Prof. A. L. Burlingame and Dr. H. K. Schnoes for the mass spectra.
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