

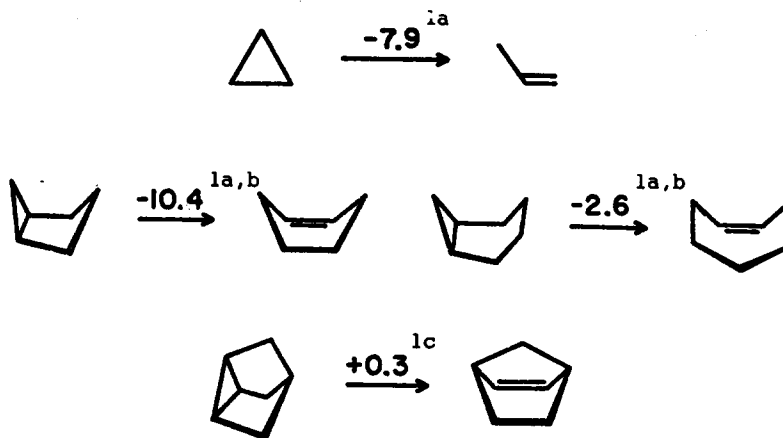
REARRANGEMENT OF $C_{11}H_{10}O$ KETONES.
TWO THERMODYNAMICALLY REVEALING EXAMPLES.

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Few isomerizations are as sensitive to structural environment as is the formation of an olefinic π -bond from a cyclopropane ring. Illustrated below, the exothermicity of the simplest example (-7.9 kcal/mol) rises to -10.4 kcal/mol upon fusion of the cyclopropane to a cyclopentane ring. It then falls if the second ring is, instead, a cyclohexane — still more if instead the cyclopentane fusion is three-fold. A more extreme thermodynamic preference, for two cyclopropane rings over two π -bonds, was illustrated in a closely related study.²



We now draw attention to two new more marginal examples. Both fall within the context of an expanding network of $C_{11}H_{10}O$ ketone isomerizations (Figure 1). We also indicate the mechanisms which permit such reactions to be unusually facile at the carbonyl level of oxidation but only partially so at the alcohol.

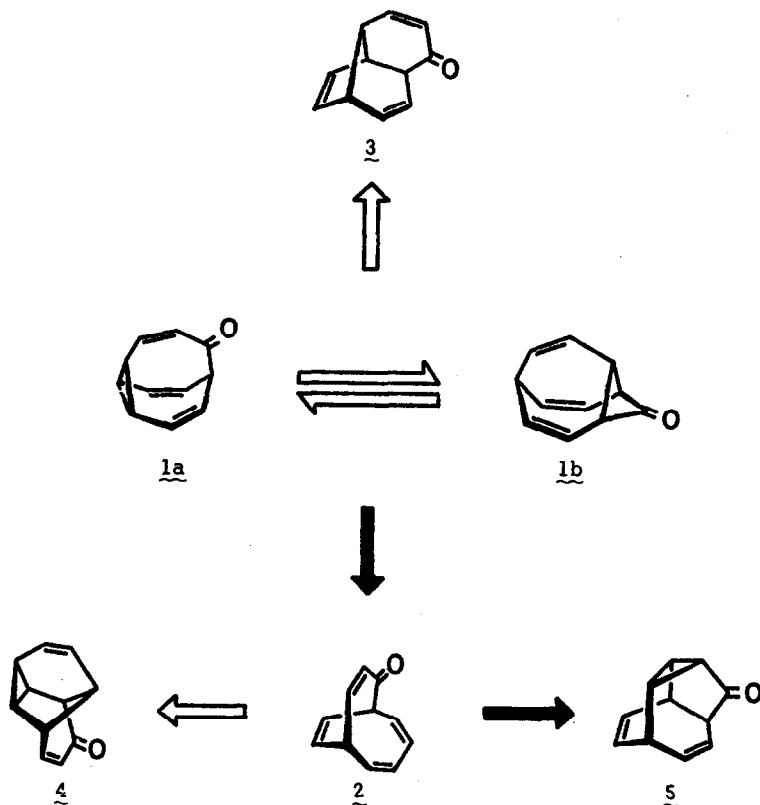
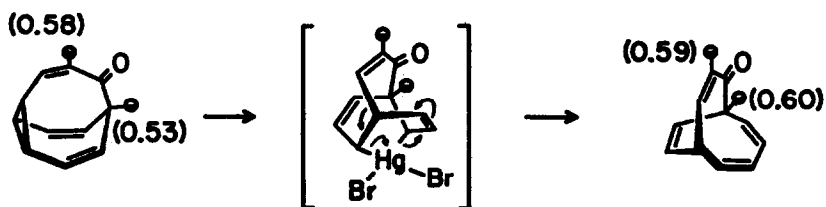


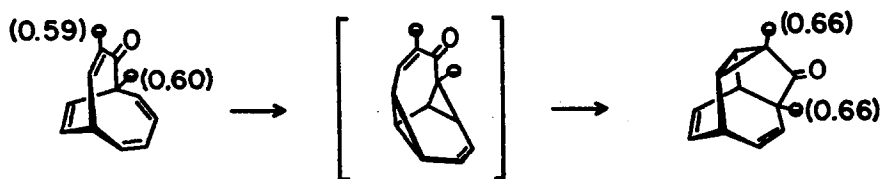
Figure 1. Old (open arrow) and new (filled arrow) rearrangements of $C_{11}H_{10}O$ ketones.

This network had previously been entered both at bicyclo[4.3.2]undecatetraenone (2)² and at homobullvalenone (1a).³ The latter had been shown to equilibrate with its Cope-related cyclobutanone isomer (1b);³ $[1b]/[1a] = 0.20 - 0.12$ between 15° and 104° .⁴ This branch was then elaborated by transforming 1 to the third tricyclic isomer, 3, and by elucidating the (less than obvious) mechanism of this thermal rearrangement.⁵

We now first join this branch to the rest by reporting that mercuric bromide in ether cleanly transforms 1 to 2 (mp 29° , spectroscopically indistinguishable from an authentic sample of mp 26°)² in 74% yield at room temperature. That the carbonyl function can here serve no important mechanistic function is suggested both by analogy with the model isomerization of bullvalene to bicyclo[4.2.2]decatetraene⁶ and by the results of deuterium labelling. As illustrated below, the versatile deuteriohomobullvalenone,^{3,5b} with label equally distributed between the two α -hydrogens, retains the connectivity of the three contiguous carbons as it isomerizes to 2-d. The normalized pmr areas, indicated in parentheses, were easily segregated from the rest by $Eu(fod)_3$ -shifting and are reliable to within ± 0.06 . All other individual pmr areas were indistinguishable from unity. The illustrated organomercury (IV) intermediate is attractively concise but hardly necessary.



Both this rearrangement and that of 2 to 5 have recently been reported by others, albeit under differing conditions and in unspecified yield.⁷ We obtain 5 (mp 66° in 84% yield) from a tetrachloroethylene solution of 2 at 100°. Despite the disparity in mp (and in assigned Chemical Abstracts name⁸), our ir spectrum and richly detailed spin-decoupled and Eu(fod)₃-shifted pmr spectra are sufficiently similar to those reported as to leave little doubt of the identity of the ketones or of their common structural assignment. As illustrated below, the retained isotopic integrity of both α-hydrogens is fully consistent with traditional expectation: intramolecular Diels-Alder cycloaddition followed by Cope rearrangement.^{2,7}



Less obviously expected, the tricyclic-bicyclic interconversion 1→2 illustrates the traditional advantage of the π-bond over the small ring. The opposite preference is then revealed by the subsequent descent in free energy⁹ from 2, either to 4^{10,11} or to 5.

Considering the still uncertain advantage of olefinic vs. cyclopropane stabilization of the carbonyl function,³ we have tried to confirm that the observed thermodynamic sequence applies at least also to the corresponding alcohols. Indeed, the previously reported (t-Bu)₂AlH-derived alcohol of 2² was correspondingly transformed to the alcohol of 5 (mp 81° in 69% yield) under essentially the same conditions as the ketone. In the upper branch of Figure 1, however, the similarly prepared alcohol of 1a¹² is irreversibly transformed to that of 1b (mp 120°). The mechanism of 1→3 interconversion^{5b} is then frustrated at those temperatures which had revealed the stability of 3 at the carbonyl level. Nevertheless, since this last transformation destroys a cyclopropane while retaining three double bonds, there need be little doubt but that the corresponding alcohol of 3 should also be the more stable.

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- (8) Tetracyclo[5.4.0.0^{2,11}.0^{4,10}]undeca-5,8-dien-3-one rather than tetracyclo[4.3.2.0^{3,5}]-undeca-7,10-dien-2-one.⁷ Cf. J. Meinwald and Y.C. Meinwald, *Advances in Alicyclic Chem.*, **1**, 2 (1966).
- (9) Neglect of entropic distinctions in such isomerizations is justified both by first principles (S.W. Benson, "Thermochemical Kinetics", John Wiley and Sons, Inc., New York, 1968, Chapt. 2.) and by experiment. (Cf. ref 1c and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958)).
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- (11) The thermodynamic control of this transformation is most cogently apparent in ref. 7.
- (12) Apart from this alcohol (whose pmr spectrum invariably revealed contamination by the alcohol of 1b), the homogeneity and structural assignment of all others was guaranteed both spectroscopically and by elemental analyses that agreed with expectation to within $\pm 0.3\%$.