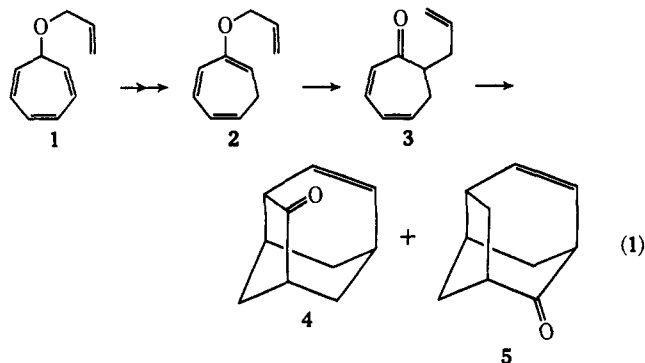## Multiple Thermal Rearrangements. II. The Pyrolysis of Alkenyl Dihydrotropones

Sir:

We recently reported that 7-allyloxycycloheptatriene (1) undergoes facile thermal rearrangement at 200° to produce 2-protoadamantenone (4) and 10-proto-adamantenone (5) in high yield.[1] This transformation requires three sequential pericyclic reactions for its

success: (i) [1,5]-hydrogen shift(s); (ii) [3,3]-sigma-tropic reactions; (iii) $[_{\pi}2_s + _{\pi}4_s]$ cycloaddition. We now report a method (revealed by the above transformation) with even greater potential for the synthesis of new bridged polycyclic systems. The efficacy of this new approach and its course in one case is illustrated by the synthesis of three new polycyclics, 9, 10, and 11.

The rearrangement of 1 and its derivatives, although quite useful synthetically, is limited to the preparation of compounds having the protoadamantane skeleton since delivery of the side chain to the ring occurs *via* a [3,3]-sigmatropic rearrangement, and thus necessitates a three-carbon unsaturated array as in 2 → 3. A method of obviating this limitation seemed to be offered by the direct synthesis of related (homologous) alkenyl dihydrotropones which would be anticipated to undergo isomerization and cycloaddition reactions similar to 3. Previous studies[2] have shown that alkyl dihydrotropones are readily available from 1,8 addition of organometallic reagents to tropone.

Toward this end, reaction of 3-butenylmagnesium bromide with tropone[3] at −78° gave a mixture of 2-(3-butenyl)dihydrotropones 6–8 (75%, bp 66–68° (0.4 mm)).[4,5] Pyrolysis of the dihydrotropones at 200–210° (neat, or in heptane) gave three tricyclic unsaturated ketones, the isomeric homoprotoadamantenones 9 and 10, and another C$_{11}$ tricyclic 11, in a ratio of 58:18:24 (60%).[7,8] Both 9 and 10 are homologs of 4

Figure 1. 100-MHz spectra of 9, 10, and 11.

and 5, respectively[9] and arise from dihydrotropone 8 while 11 originates from 6 in a mode of reaction not previously observed with 1.[10] The tricyclic ketone 12

is not observed in the pyrolysis, nor is any cycloaddition product expected from 7.[10]

Structure proofs for 9, 10, and 11 are based on nmr, ir, and mass spectra (parent ion) as well as on chemical conversions. Both 9 (mp 179–181°, $\nu_{max}^{CCl_4}$ 1715 cm^{-1}) and 10 (mp 165–166°, $\nu_{max}^{CCl_4}$ 1687, 1704 cm^{-1}) showed nmr spectra (Figure 1) analogous to those of 4

(1) C. A. Cupas, W. Schumann, and W. E. Heyd, *J. Amer. Chem. Soc.*, **92**, 3237 (1970).

(2) (a) G. L. Closs and L. E. Closs, *ibid.*, **83**, 599 (1961); (b) O. L. Chapman and D. J. Pasto, *Chem. Ind. (London)*, 54 (1961); (c) T. Nozoe, T. Mukai, and T. Tezuka, *Bull. Chem. Soc. Jap.*, **34**, 619 (1961); (d) A. P. ter Borg, R. van Helden, and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **81**, 591 (1962).

(3) P. Radlick, *J. Org. Chem.*, **29**, 960 (1964).

(4) Satisfactory analyses were obtained for all new compounds.

(5) The reaction mixture at this stage consists mainly of 6. Heating the mixture at 110° for 1 hr gives predominantly 7.[6] These and other mechanistic details, concerned with the thermal behavior of alkenyl dihydrotropones, will be discussed in a full paper.

(6) For interconversion of the unsubstituted 2,3- and 2,7-dihydro-tropones *via* [1,5]-hydrogen shifts see A. P. Ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 1189 (1963).

(7) IUPAC nomenclature: 9, tricyclo[4.4.1.0^{3,8}]undec-4-en-2-one; 10, tricyclo[4.4.1.0^{3,8}]undec-4-en-11-one; 11, tricyclo[5.3.1.0^{3,8}]undec-9-en-3-one.

(8) Separation of the ketones could be achieved by preparative gas chromatography on an 18% γ-methyl-γ-nitropimelonitrile column.[1]
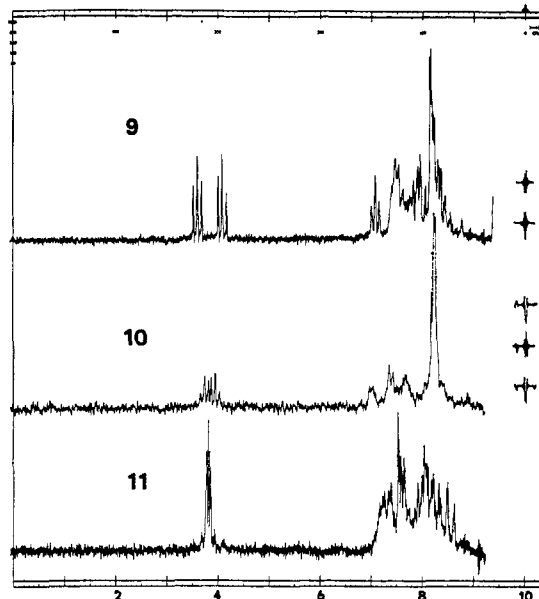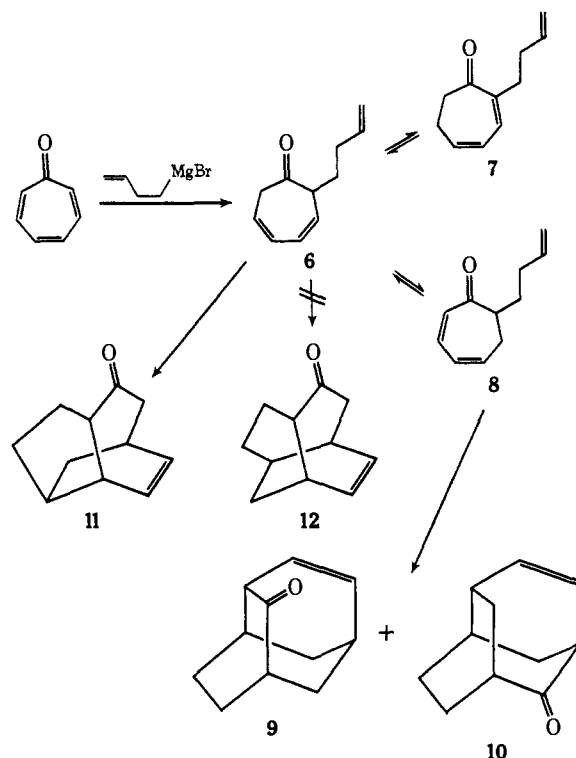
(9) It is for this reason that we suggest the trivial "homoprotoada-mantane" nomenclature for 9 and 10 and their derivatives.

(10) The fact that no tricyclic products arise from 2-allyl-2,7-dihydro-tropone in the pyrolysis of 1[1] is undoubtedly due to prohibitive strain in the cyclized product. Similar considerations apply to 7.

and 5;[1] in particular, due to the rigidity of the ring structure about the double bond, the resonances of the vinyl protons which appear as "triplets" are very revealing. The separation of 48 Hz for 9 is identical with that for 4, while the 20 Hz for 10 compares well with the 22 Hz for 5. In addition the unobscured triplet (τ 7.06)[11] assignable to the allylic bridgehead proton adjacent to the carbonyl in 9 has identical multiplicity and essentially the same chemical shift as the corresponding proton of 4 (τ 7.09).[1]

Hydrogenation of 9 gave saturated ketone 13 (mp 207–208.6°, $\nu_{max}^{CCl_4}$ 1702, 1717 cm^{-1}) while 10 gave the isomeric ketone 14 (mp 188–190°, $\nu_{max}^{CCl_4}$ 1694, 1715 cm^{-1}). Wolff–Kishner reduction of 9 and 10 each gave olefin 15 (mp 164.7–165.3°), which was converted

13   16

14

9 ⟶   ⟵ 10

15
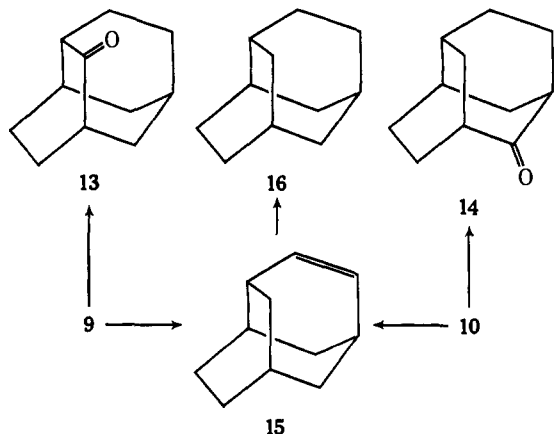
by hydrogenation to tricyclo[4.4.1.0^{3,8}] undecane (16) (mp 181–183°).[12]

The tricyclic ketone 11 (mp 123–125°, $\nu_{max}^{CCl_4}$ 1700 cm^{-1}) exhibited nearly equivalent vinyl proton resonances (Figure 1) presumably due to the more symmetrical disposition of the carbonyl group relative to the double bond.[13] Hydrogenation of 11 gave 17

17

20

11 ⟶

18   19
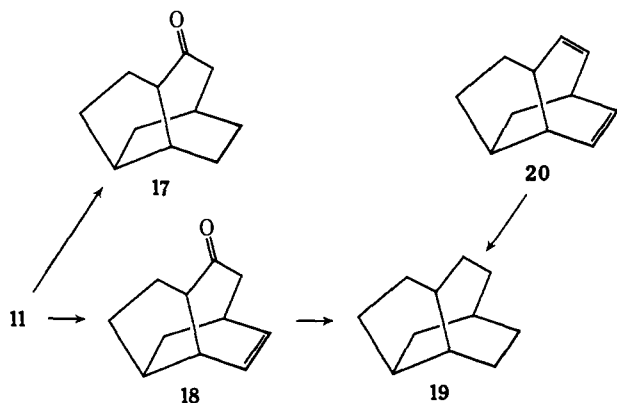
(mp 170.3–171.8°, $\nu_{max}^{CCl_4}$ 1696 cm^{-1}) while modified Wolff–Kishner reduction[15] gave olefin 18 (mp 133.3–134°),

(11) Nmr spectra were obtained on a Varian HA-100 spectrometer. Spectra were obtained in CCl$_4$ with chemical shifts reported as τ in parts per million relative to internal TMS.

(12) That 9 and 10 are nonenolizable was shown by the fact that no deuterium was incorporated under exchanging conditions. See ref 13.

(13) Deuterium exchange[14] of 11 (D$_2$O, K$_2$CO$_3$, dioxane, 48 hr, 100°) gave 78% d_2, 15% d_1, and 7% d_0 (by mass spectroscopic analysis), showing that it was enolizable, in contrast to 9 and 10.

(14) H. W. Whitlock, Jr., and M. W. Siefken, J. Amer. Chem. Soc., 90, 4929 (1968).

(15) Reduction of the semicarbazone with sodium methoxide in ethanol at 200° (sealed tube).[16]

(16) M. Jones, Jr., S. D. Reich, and L. T. Scott, J. Amer. Chem. Soc., 92, 3118 (1970).

which was converted by hydrogenation to tricyclo-[5.3.1.0^{4,8}]undecane (19) (mp 165–167°). The latter material was identical with that obtained upon hydrogenation of 20, which is a minor cycloaddition product observed in the pyrolysis of 7-(3-butenyl)cycloheptatriene.[17]

Studies concerned with extensions of this approach to the synthesis of other new bridged polycyclics are in progress.[19]

(17) C. A. Cupas, M. S. Kong, M. Mullins, and W. E. Heyd, Tetrahedron Lett., in press.[18]

(18) The formation of 20 from 7-(3-butenyl)cycloheptatriene is analogous to the formation of 7% tricyclic ether observed in the pyrolysis of 1.[1]

(19) The approach outlined in this report also constitutes an alternative synthetic entry to 4 and 5. We have found, however, that the overall yield is higher when 1 is pyrolyzed directly.

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Tricarbonyl(cyclooctadiene) Complexes of Iron(0), Ruthenium(0), and Osmium(0)

Sir:

Cycloocta-1,5-diene- and cycloocta-1,3-dieneiron tricarbonyl complexes have been reported previously.[1–3] However, the corresponding ruthenium and osmium complexes have not been established. We find that the reactivity of these adducts varies markedly with the metal and, for the cycloocta-1,5-diene derivatives, contrasts with the reactivity of the isoelectronic cobalt-(I), rhodium(I), and iridium(I) cyclopentadienyl adducts.

The reaction of cycloocta-1,3-diene with dodecacarbonyltriruthenium has been studied under a variety of conditions. The organometallic product isolated from these reactions was always C$_8$H$_{12}$Ru$_3$(CO)$_n$ (n = 9 or 10[4]). In contrast, reaction of cycloocta-1,5-diene with the same carbonyl in benzene under reflux led, after limited periods (up to 8 hr), to a reaction mixture containing the three isomeric forms of cyclooctadiene and a complex of composition C$_8$H$_{12}$Ru(CO)$_3$ (3). Isolation of 3 and analysis of its ^{1}H nmr spectrum showed it to be tricarbonyl(cycloocta-1,5-diene)ruthenium. Over more extended periods (~10 hr), complex 3 underwent slow conversion to a second isomer 7, the ^{1}H nmr spectrum of which establishes that both a carbon–ruthenium σ bond and h^3-allyl–ruthenium bond had been formed. A related product from the photochemical reaction of dodecacarbonyltriosmium and cyclooctatetraene had been observed previously.[5]

In contrast, reactions of dodecacarbonyltriosmium with either cycloocta-1,3-diene or cycloocta-1,5-diene

(1) J. E. Arnet and R. Pettit, J. Amer. Chem. Soc., 83, 1954 (1961).

(2) R. Pettit and G. F. Emerson, Advan. Organometal. Chem., 1, 1 (1964); M. A. Bennett, ibid., 4, 353 (1966).

(3) E. K. von Gustorf and J. C. Hogan, Tetrahedron Lett., 3191 (1968).

(4) J. P. Candlin, K. K. Joshi, and D. T. Thompson, Chem. Ind. (London), 1960 (1966).

(5) M. I. Bruce, M. Cooke, M. Green, and D. J. Westlake, J. Chem. Soc. A, 987 (1969).