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6,7-DICARBOMETHOXYBICYCLO[3.2.2]NONA-3,6,8-TRIEN-2-ONE:
SYNTHESIS AND THERMAL ISOMERIZATIONS

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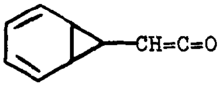
The currently active interest in dimerization and cycloaddition reactions of tropone is due in part to the novel molecular structures that can be so generated (1) and in part by the contributions that can be made to the theory of cycloaddition reactions, particularly with regard to tests of and possible correlations with Woodward-Hoffman orbital symmetry arguments (2).

Several examples of thermal 4 + 2 cycloaddition reactions with tropone to yield substituted or heteroatom derivatives of the bicyclo[3.2.2] nonane ring system are known (1b). The fully unsaturated carbocyclic parent compound of this series, 1, has only recently been prepared by thermolysis of ketene 2 (3).



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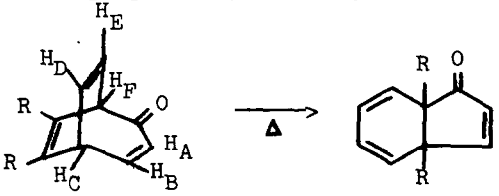


1; R=H
3; R=CO_2Me

4

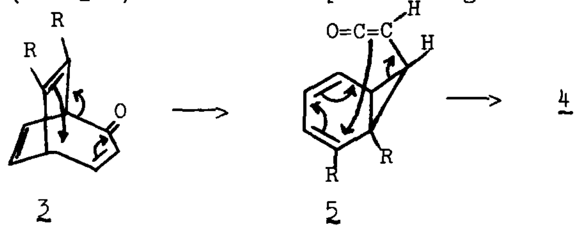
The benzoderivative of 1 represents the only lightly substituted derivative of 1 thus far reported (1c). In contrast to the well documented 1,4-mode of cycloaddition is the report (4) that dimethylacetylene dicarboxylate (DMADC) reacts with tropone in a 1,6-manner via a norcaradienone. We have restudied this reaction under a variety of conditions with the following results.

When tropone was heated with an 8:1 excess of DMADC in a xylene solvent at 145° for 24 hours, a dark reaction mixture was obtained from which a white crystalline material, melting range 127-132°, could be isolated in only modest yield after chromatography on alumina. In contrast to these results, warming tropone with an equimolar amount of DMADC in nitromethane as solvent at 100° during 7 days produced a different white crystalline material, mp 50-51° (from ether-hexane), in 43% yield (75% based on unrecovered DMADC). The nmr spectrum of the crude reaction product was very similar to that of the purified cycloadduct plus resonances due to starting materials, and no evidence for other products was obtained using these reaction conditions. The structure of this product must be **3**, based on the following spectral properties: ν_{max} 1730 cm^{-1} (shoulder, s), 1725 (s), 1678 (w), 1650 (w) and 1600 (w); $\lambda_{max}^{cyclohexane}$ 218 mμ (ϵ=1.17 x 10^4); mass spectral molecular ion at m/e 248 and a fragmentation pattern consistent with **3**; an nmr spectrum with olefinic resonances (1 proton each) at 4.15 ppm (H_C), 4.43 ppm (H_F), 5.17 ppm (H_A), 6.51 ppm (H_E), 6.79 ppm (H_D) and 7.07 ppm (H_B), as well as a 6 proton singlet at 3.75 ppm, and coupling constants (measured by decoupling experiments with a Varian HA-100) as follows: J_{AB} = 11.0 cps, J_{DE} = 8.60 cps, J_{EF} = J_{CD} = 6.25 cps, J_{AC} = 0.90 cps, J_{BC} = 8.40 cps, J_{CE} = J_{DF} = 1.50 cps, and J_{AF} = 1.00 cps (*cf.* 1c).

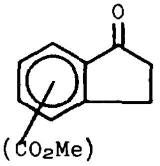
When a xylene solution of **3** was heated at 145° with an excess of DMADC for 12 hours, a fair yield of a white crystalline compound, mp 130-132° (recrystallized from ether-hexane, mp 132-3°) was isolated. This material was identical with the crystalline compound isolated in the high temperature cycloaddition reaction described above, as well as with authentic (5) 1,2,3,4-tetracarbomethoxybenzene, using spectral and mixed mp comparisons. Experiments designed to provide mechanistic details of this conversion are in progress.

During attempts to purify **3** by distillation, a mixture containing **3** and an isomeric material was obtained. Controlled pyrolysis of **3** through a glass bead filled column under high vacuum at 375° produced as the major product (>80% yield) a white crystalline solid, mp 77-78° whose mass spectrum was strikingly similar to that of **3**, including the molecular ion at m/e 248. Comparison of its nmr spectrum [peaks at 3.80 ppm (singlets, 6H), 5.50-6.20 ppm (multiplet, 4H), 6.52 ppm (doublet, J = 6 MHz, 1 H), and 7.92 ppm (doublet, J = 6 MHz, 1H); identical with the new absorptions in the distillate described above], with those of several compounds previously described (6) leads to 4 (R = CO_2Me) as the structural formulation for this compound. The cis-ring fusion is demanded by its ultraviolet spectrum (7) [λ_{max}, C_6H_{12}, 216 mμ (1.19×10^4), 256 mμ (3.17×10^3)] and its ability to form a maleic anhydride adduct, mp 280-281° (8). Pyrolysis of 3 in solution at 150° also produced 4 (R = CO_2Me) in 80% yield.

The mechanism of the conversion of 3 to 4 (R = CO_2Me) is of considerable interest. Goldstein and Odell (3) have demonstrated that ketene 2 forms cis-dihydroindenone 4 (R = H) and 1 in approximately equal yields. 1 was not converted to 4 (R = H) under their reaction conditions but the transformation could be effected photochemically. An attractive mechanism for the conversion of 3 ⟶ 4 (R=CO_2Me) is initial Cope rearrangement to ketene 5 followed by a concerted rearrangement to 4 (R = CO_2Me) as shown. Alternatively, ketene 5 might undergo a vinylcyclopropane diradical ring opening and reclosure to 4 (R =CO_2Me). The intermediacy of a ketene is supported by trapping experiments using methanol and cyclohexylamine in xylene at 150° (9).



3 5



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A remarkable facet of this thermolytic conversion is its structural specificity; i.e., why are not a number of isomers formed? Extensive chromatography of the small amount of oil formed in the pyrolysis does yield some evidence for the presence of an isomer 6 of unknown structure. Experiments designed to elucidate the mechanism and scope of this thermal reaction using structurally related bicyclononatrienones are underway.

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9. Professor O. L. Chapman (unpublished studies) has documented the presence of a ketene intermediate in the low temperature photochemical conversion of **3** to **4** ($R = CO_2Me$).