

THE ELECTRONIC STRUCTURE AND REACTIVITY OF SMALL RING COMPOUNDS. IV.
THE REACTION BETWEEN 1,5-DIMETHYLTRICYCLO[2.1.0.0^{2,5}]PENTAN-3-ONE AND
DIMETHYL ACETYLENEDICARBOXYLATE.

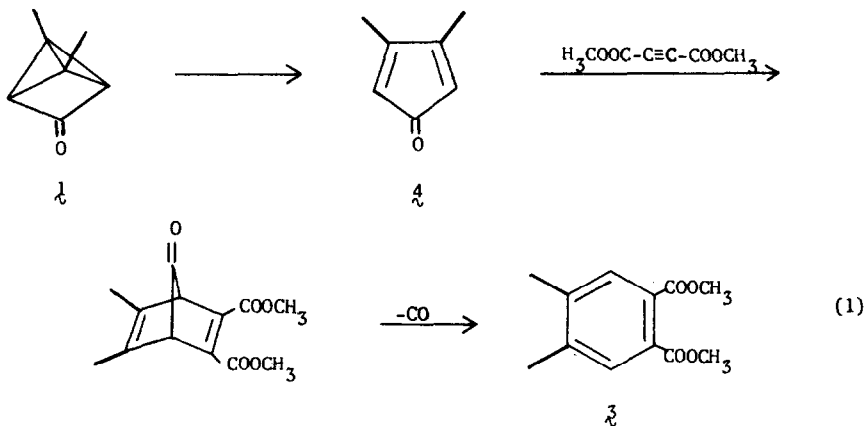
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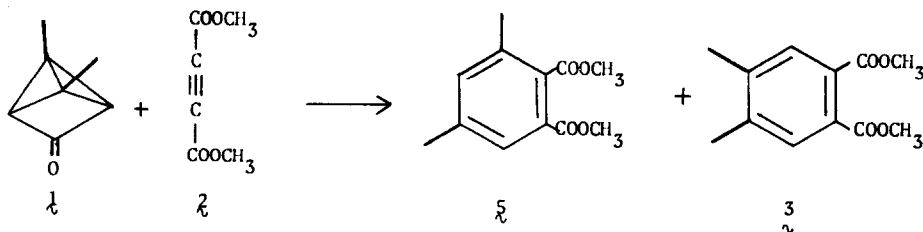
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(Received in USA 2 December 1968; received in UK for publication 23 December 1968)

Several years ago the reaction of 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one (**1**) with dimethyl acetylenedicarboxylate (**2**) at 198°, was reported to give two products (**2**). The minor product was identified as dimethyl 4,5-dimethylphthalate (**3**) and was postulated to arise by thermal isomerization of **1** to 2,3-dimethylcyclopentadienone (**4**) followed by Diels-Alder addition of **2** and decarboxylation to give **3** (eqn. 1). The major product was not identified.



Because of the current interest in the reaction of bicyclobutanes with dienophiles (1,3) we have reinvestigated the reaction between λ and ξ . We have found that the major product in the reaction at 198° is dimethyl 3,5-dimethylphthalate (ξ) and that the ratio of ξ to ζ produced is strongly dependent on the temperature at which the reaction is run.

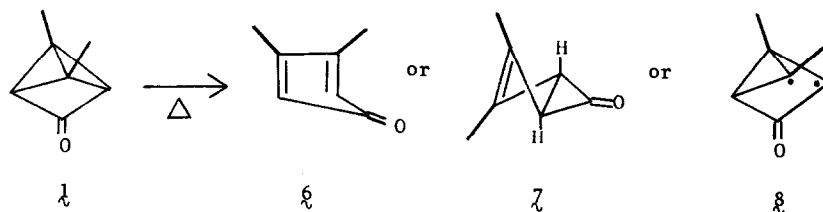


Identification of ξ was by comparison of its melting point and IR and nmr spectra with the known compound (4) which we synthesized by the reaction of 2-methyl-trans-1,3-pentadiene with dimethyl acetylenedicarboxylate followed by dehydrogenation with chloranil.

When λ and ξ were heated in a sealed tube at 375° the ratio of ξ to ζ was found to be ca. 1:1, at 250° the ratio was ca. 2:1; at 198° it was ca. 3:1 (5) while at 100° (and at room temperature) only ξ could be detected. The products were also shown to be thermally stable.

If one assumes that ξ is the product of a bimolecular reaction between λ and ξ and that ζ is the product of the slow, rate determining isomerization of λ to μ , followed by a rapid Diels-Alder reaction and decarbonylation, it follows that the former reaction should have a more negative entropy of activation. Therefore the unimolecular isomerization reaction has the higher activation energy.

It should be pointed out that if the isomerization of λ were concerted and followed one of the pathways outlined by Wiberg and Closs (6) for the bicyclobutane to butadiene rearrangement, one might expect either cis-trans-2,3-dimethylcyclopentadienone (η) or 2,3-dimethyl-trans-bicyclo[2.1.0]pent-2-en-5-one (ζ). The alternative, a diradical intermediate (θ), is perhaps more reasonable.



We are currently investigating the mechanisms of these novel and deepseated reactions and rearrangements in detail. Attention, will also be focused on why the reaction of **1** and **2** proceeds so readily and yet **1** does not react with the more reactive dienophile, benzyne (1).

Acknowledgement: Thanks are extended to the National Science Foundation for partial support of this work.

REFERENCES

1. Part III: M. Pomerantz, G. W. Gruber and R. N. Wilke, J. Amer. Chem. Soc., **90**, 5040 (1968).
2. W. von E. Doering and M. Pomerantz, Tetrahedron Letters, 961 (1964).
3. A. Cairncross and E. P. Blanchard, J. Amer. Chem. Soc., **88**, 496 (1966); M. Pomerantz, ibid., **88**, 5349 (1966); M. R. Rifi, ibid., **89**, 4442 (1967); P. G. Gassman and G. D. Richmond, ibid., **90** 5637 (1968).
4. K. Alder, R. Muders, W. Krane and P. Wirtz, Ann., **627**, 59 (1959).
5. M. Pomerantz, Ph.D. Thesis, Yale University, New Haven, Connecticut, 1963.
6. K. B. Wiberg, Tetrahedron, **24**, 1083 (1968); G. L. Closs and P. E. Pfeffer, J. Amer. Chem. Soc., **90**, 2452 (1968).