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THE PHOTOSENSITIZED REARRANGEMENT OF ARYL-SUBSTITUTED TRICYCLO[2.2.0.0^{2,6}]HEXANES TO BICYCLO[3.1.0]HEX-2-ENES

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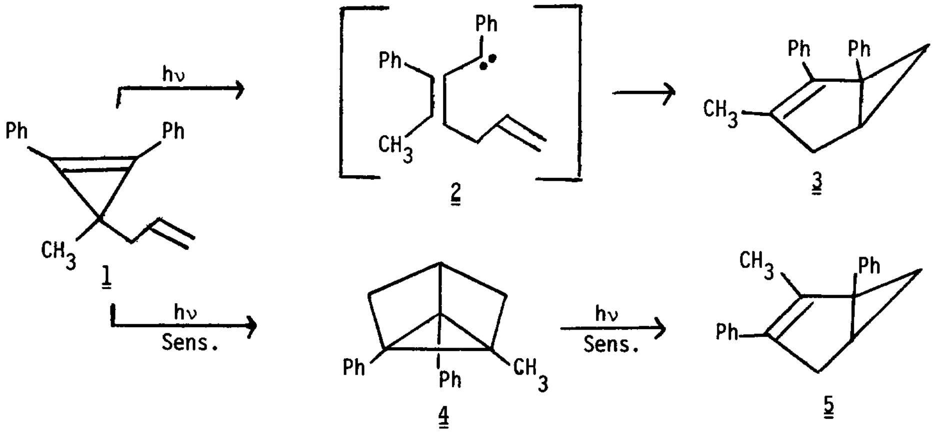
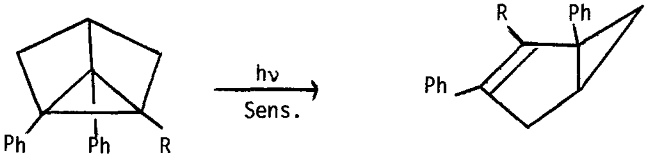
Abstract: The triplet sensitized irradiation of 3-allyl-diaryl-substituted cyclopropenes to bicyclo[3.1.0]hex-2-enes proceeds via an intramolecular [2+2]-cycloaddition followed by a subsequent rearrangement of the initially formed tricyclo[2.2.0.0^{2,6}]hexane skeleton.

Previous work from this laboratory has shown that the direct irradiation of 3-allyl-3-methyl-1,2-diphenylcyclopropene (1) afforded 1,2-diphenyl-3-methylbicyclo[3.1.0]hex-3-ene (3) as the exclusive photoproduct.[1] The most reasonable explanation to account for the formation of 3 involves ring opening of the electronically excited singlet state of 1 to a vinylcarbene intermediate (2).[2-4] Attack of the carbene carbon on the neighboring double bond generates the bicyclo[3.1.0]hexene skeleton. The photochemical reaction encountered on direct irradiation proceeds through the singlet manifold since irradiation of 1 in the presence of a triplet sensitizer gave rise to the isomeric bicyclohexene 5.[5]



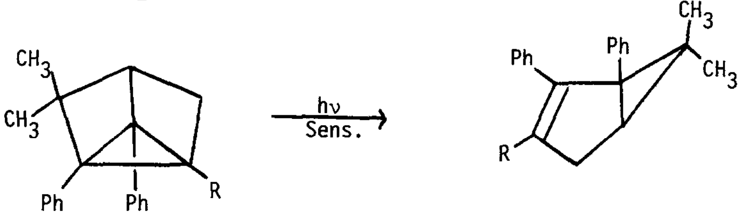
Subsequent studies showed that 5 is not a primary reaction product but is formed by a secondary photoreaction of tricyclohexane 4. With short exposures, tricyclohexane 4 accounts for nearly all of the product produced. At longer exposures, owing to a secondary photoreaction of 4, the amount of 5 increased. This was independently demonstrated by the conversion of 4 to 5 under triplet sensitized conditions. The formation of tricyclohexane 4 can be attributed to a novel intramolecular 2+2-cycloaddition of the triplet state of cyclopropene 1.

The sensitized conversion of aryl-substituted tricyclo[2.2.0.0^{2,6}]hexanes to bicyclo[3.1.0]-hex-2-enes was found to be a general reaction.[6] Thus, irradiation of tricyclohexanes 6 and 7 in the presence of thioxanthone afforded bicyclohexenes 8 and 9 in high yield. Similar results were encountered with tricyclohexanes 10 and 11. With these compounds, the reaction was found to be highly regiospecific producing bicyclohexenes 12 and 13 as the exclusive photoproducts.



6; R=H
7; R=Ph

8; R=H
9; R=Ph

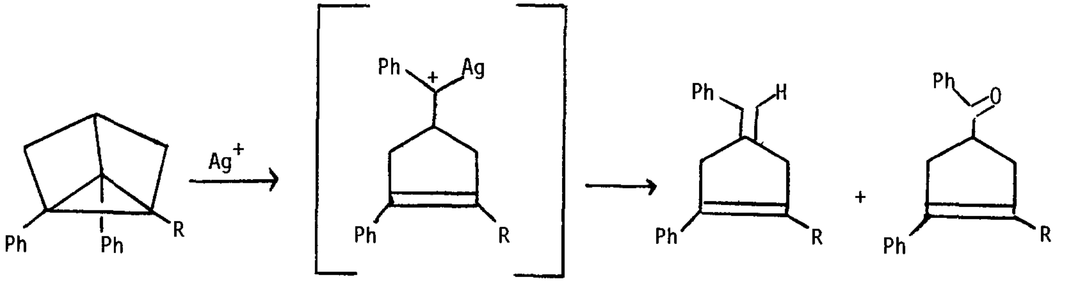


10; R=Ph
11; R=CH$_3$

12; R=Ph
13; R=CH$_3$

Prior to concerning ourselves with the molecular details of the reaction mechanism, two points are of interest. First, the reaction clearly proceeds via the triplet state, since the photorearrangement of the tricyclohexane ring system could not be induced by direct irradiation. Secondly, it should be noted that Roth and Katz had previously demonstrated the rearrangement of tricyclo[2.2.0.0^{2,6}]hexane to bicyclo[3.1.0]hex-2-ene in the presence of silver ion.[7] We have found, however, that treatment of 4 with silver ion in benzene results in the formation of cyclopentenes 14 and 15. Similar results were encountered with tricyclohexane 6. The products obtained are explicable in terms of an argento carbonium ion (18)^8 which can either undergo a 1,2-hydrogen shift to give 14 or react with water to give 15. When the reaction of 6 with silver ion was carried out in aqueous methanol, benzoylcyclopentene 17 was the only product produced.

A reasonable mechanism to account for the formation of the bicyclo[3.1.0]hexene system involves a sequence consisting of sensitized ring opening of the tricyclohexane to a bicyclo-[2.1.1]hexane diradical (19) which subsequently undergoes a 1,2-methylene shift. Fragmentation of the tricyclohexane ring to the alternate bicyclo[2.2.0]hexane diradical 20 should have produced bicyclohexenes 21 or 22. Neither of these compounds were observed with any of the tricyclohexanes studied.

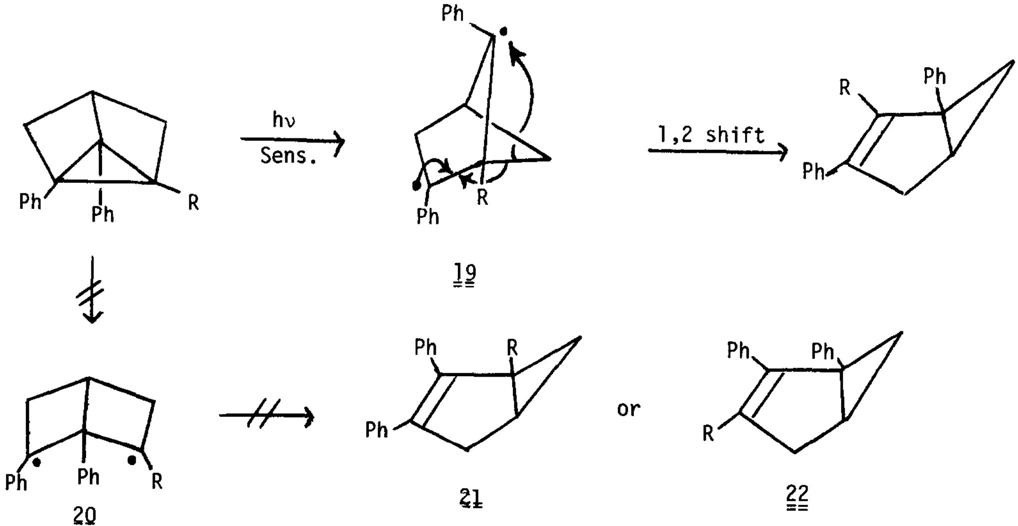


4; R=CH_3
6; R=Ph

18

14; R=CH_3
16; R=Ph

15; R=CH_3
17; R=Ph



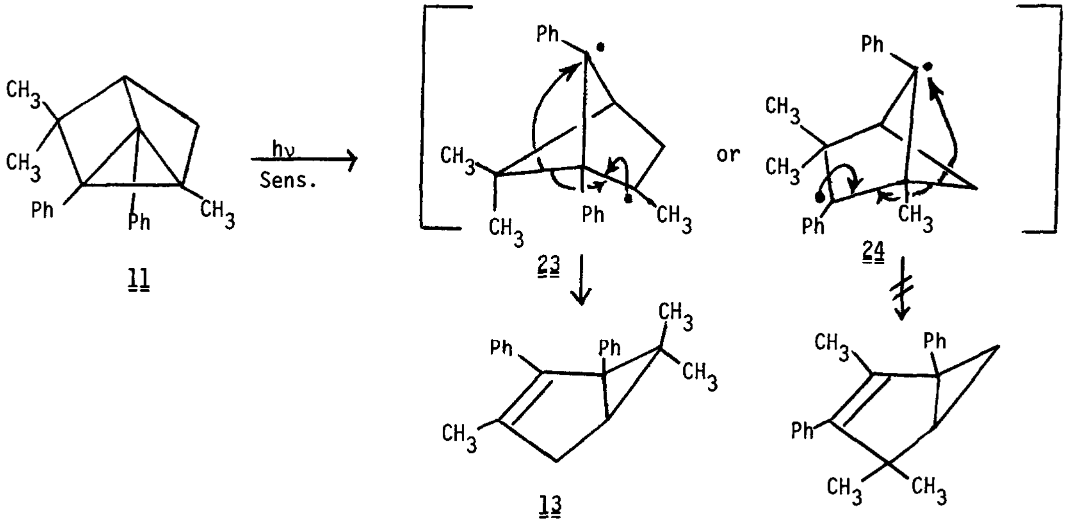
19

20

21

22

Finally, it is of interest to note that tricyclohexane 11 produced bicyclohexene 13 as the exclusive photoproduct. According to the mechanism outlined above, two possible diradicals could be formed. The preferential formation of bicyclohexene 13 is probably a result of the development of radical character on the tertiary carbon in the transition state for the C-C bond shift. Migration of the methylene bond in 24 would have resulted in a less stable primary radical on the migrating carbon. It seems that the stability of the radical center on the migrating carbon is more important than the stability of the initial ring-opened intermediate.



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2. D. R. Arnold, J. A. Pincock and R. Morchat, J. Am. Chem. Soc., 95, 7536 (1973).
3. G. E. Palmer, J. R. Botton and D. R. Arnold, J. Am. Chem. Soc., 96, 3708 (1974).
4. J. H. Davis, W. A. Goddard and R. G. Bergman, J. Am. Chem. Soc., 98, 4015 (1976); 99, 2427 (1977).
5. All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given in our full publication. Compound 5: NMR ($CDCl_3$, 100 MHz) δ 0.77 (t, 1H, J = 4.0 Hz), 1.48 (dd, 1H, J = 8.0 and 4.0 Hz), 1.60-1.84 (m, 1H), 1.70 (t, 3H, J = 2.0 Hz), 2.76 (brd, 1H, J = 17.5 Hz), 3.24 (ddd, 1H, J = 17.5, 8.0 and 2.0 Hz) and 7.2-7.4 (m, 10H).
6. Tricyclohexanes 6, 7, 10 and 11 were prepared in high yield by the triplet sensitized 2+2 cycloaddition reaction of the corresponding 3-allyl substituted cyclopropene system.
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