

MERCURY SENSITIZED GAS PHASE PHOTODECARBONYLATION OF NORCAMPHOR^{1,2}

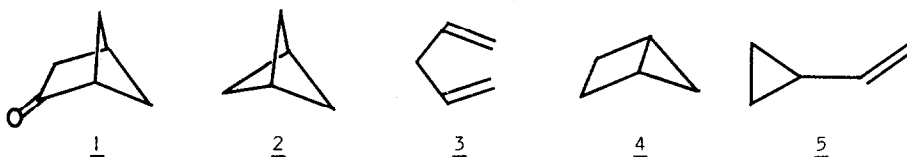
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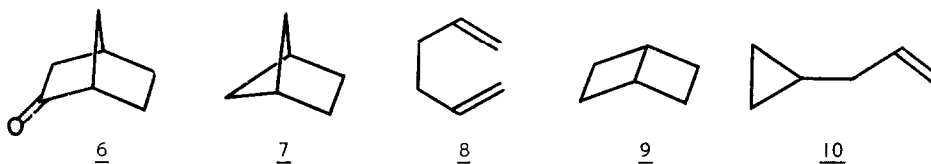
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(Received 20 March 1967)

The mercury sensitized gas phase photodecarbonylation of bicyclo[2.1.1]hexan-2-one (1) has just been reported (5) to give bicyclo[1.1.1]pentane (2), 1,4-pentadiene (3), bicyclo[2.1.0]pentane (4), and vinylcyclopropane (5). The latter two products were rationalized as secondary products, originating through mercury sensitized photoisomerization of 1,4-pentadiene.



This work prompts the present preliminary account of our quantitative investigation of the mercury sensitized gas phase photolysis of norcamphor (bicyclo[2.2.1]hexan-2-one, 6) which requires an analogous formulation for the origin of the decarbonylation products bicyclo[2.1.1]hexane (7), 1,5-hexadiene (8), bicyclo[2.2.0]hexane (9), and allylcyclopropane (10).



Concentration versus time data for the mercury sensitized decarbonylation were obtained by photolyzing small samples of norcamphor in sealed Vycor tubes with 2537 Å light and analyzing the products by glpc. The rates of 1,5-hexadiene and bicyclo[2.1.1]hexane formation were greatest at the beginning of the reaction and decreased thereafter, as would be expected for primary products. In contrast, the rate of allylcyclopropane formation was zero at the beginning of the reaction and increased with the increasing concentration of 1,5-hexadiene (6).

Under the reaction conditions, bicyclo[2.1.1]hexane formed both directly from norcamphor and through photoisomerization of 1,5-hexadiene. Bicyclo[2.2.0]hexane and (3-cyclopentenyl)ethanal were observed to be only very minor products. An excellent material balance for the decarbonylation products was observed throughout the first 68% of the reaction. Computer-generated concentration dependences based on the differential equations appropriate to the suggested origins of the decarbonylation products gave fine agreement with the experimentally observed dependences for 1,5-hexadiene, bicyclo[2.1.1]hexane, allylcyclopropane, norcamphor, and carbon monoxide.

An earlier (7) and often cited (8,9,10) report claiming that allylcyclopropane and bicyclo[2.2.0]hexane were primary photoproducts in the mercury sensitized gas phase photodecarbonylation of norcamphor, and some related studies on the photodecarbonylation of 3,3-dideuterionorcamphor (7) are at variance with our experimental findings and justifiable expectations (11,12,13).

REFERENCES

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2. Supported in part by the National Science Foundation and a DuPont Grant-in-Aid.
3. Alfred P. Sloan Foundation Fellow.
4. Eli Lilly Fellow, 1964-1965; Allied Chemical Fellow, 1965-1966; Standard Oil of California Fellow, 1966-1967.
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13. 1,5-Hexadiene should be able to easily compete with norcamphor for triplet mercury atoms (Ref. 8, p. 76).