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THE PHOTOISOMERIZATION OF 2-METHYLENEBICYCLO[3.2.1]OCTA-3,6-DIENES; INTRAMOLECULAR ALLENE CYCLOADDITIONS

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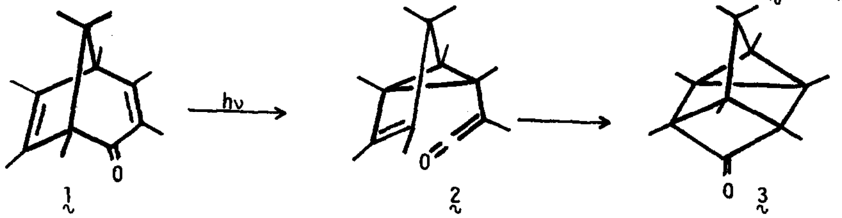
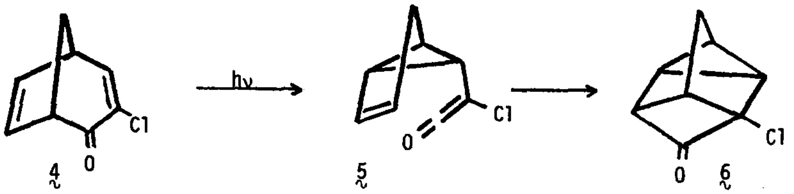
Bicyclo[3.2.1]octa-3,6-dien-2-ones photoisomerize to ketenes (1 → 2; 4 → 5)[1]. When the ketene is highly substituted, as in the octamethyl derivative 2[2] or is unusually reactive, as in the chloroketene 5[3], intramolecular cycloaddition (π2s + π2a) competes successfully with attack by external nucleophiles, giving tetracyclic cyclobutanones (3 and 6).



1 2 3

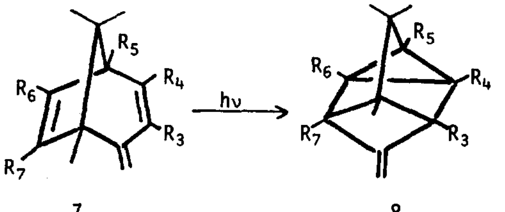
(ref 2)[4]



4 5 6

(ref 3)

To determine whether methylene analogs of these ketones would react similarly, we prepared and irradiated (ether, 450W Hanovia lamp) trienes 7a-e. In each case the tetracyclic alkene 8 was obtained in >95% yield. Since the trienes exhibit λ_{max} in the region 244-250 nm the photoisomerizations proceeded more rapidly using Vycor rather than Corex filtered light.

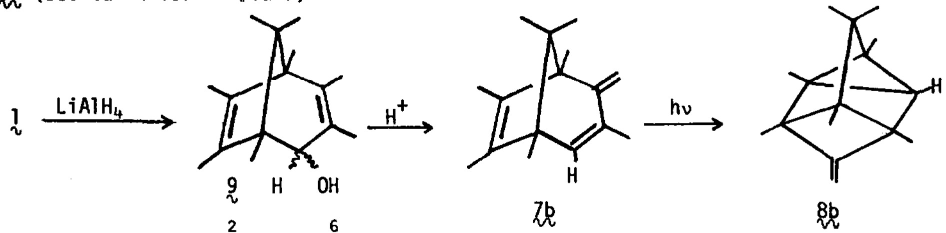


7 8

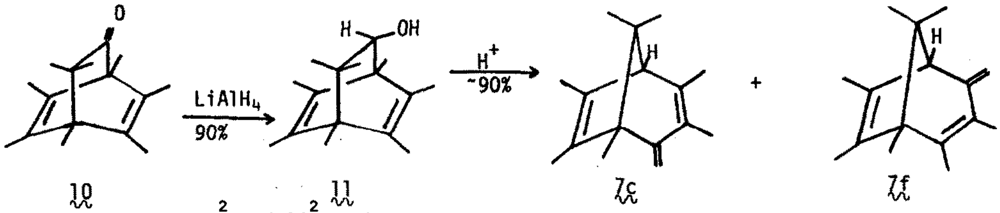
	R_3	R_4	R_5	R_6	R_7
a	CH_3	CH_3	CH_3	CH_3	CH_3
b	CH_3	H	CH_3	CH_3	CH_3
c	CH_3	CH_3	H	CH_3	CH_3
d	ϕ	ϕ	CH_3	CH_3	CH_3
e	CH_3	CH_3	CH_3	ϕ	ϕ

Triene 7a[5] gave 8a, whose structure was proved by independent synthesis from 3 and methylenetriphenylphosphorane (rt, 3 days, ca. 100%).

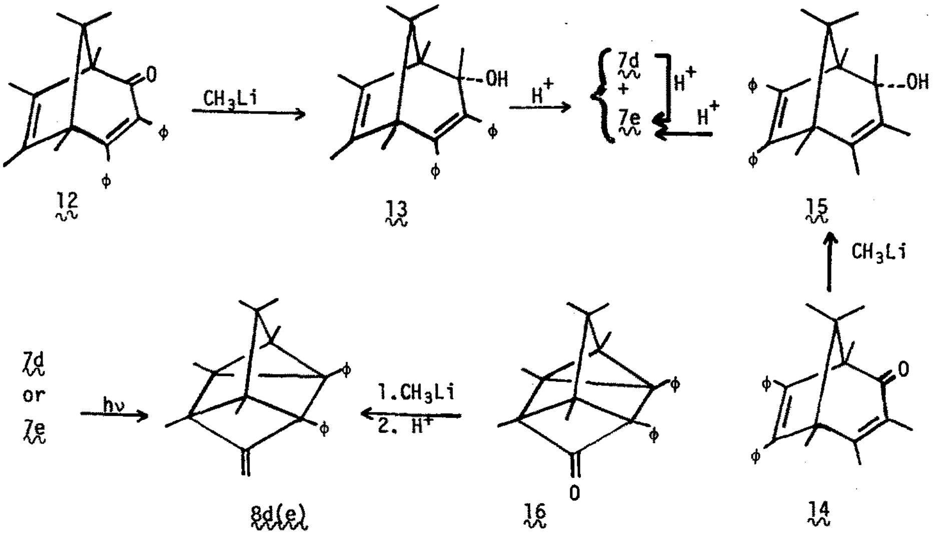
Reduction of 1 with LiAlH$_4$ gave a mixture of epimeric alcohols 9 (6 endo: 5 exo)[6] which was dehydrated (3% HCl in 65% aq acetone, rt, 30 min) quantitatively to 7b. Irradiation gave 8b (see table for nmr data).



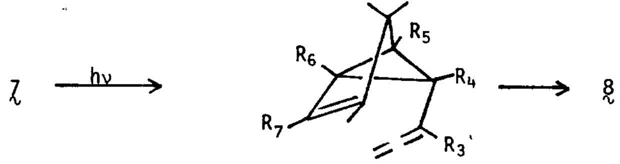
Reduction of 10[2] gave 11[6] which rearranged on dehydration (3% HCl in 65% aq acetone, rt, 24 hr) to a mixture of 7c and 7f (7:3, vpc separable).[7] Irradiation of 7c gave only 8c.[8]



Treatment of 12[2] and 14[2] with methyllithium gave 13 and 15 respectively, which were dehydrated (0.2-0.3% HCl in 65-80% aq acetone, rt, 3 hr) to 7d and 7e as shown in the scheme.[9] Irradiation of either 7d or 7e gave the same tetracyclic product 8d(e), which was also synthesized from 16[2] and methyllithium followed by dehydration.



Although we have no direct evidence, it seems likely that the photoisomerizations 7 → 8 proceed via allene 17. Furthermore, the conversion 7a → 8a was sensitized by acetone, suggesting a triplet excited state reaction.



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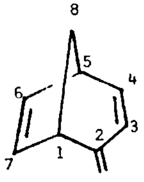
Acknowledgement. We are indebted to the National Science Foundation for support of this research.

PMR Chemical Shift Data for 7 and 8*

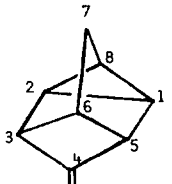
	C1	C2	C3	C4	C5	C6	C7	$C8^a$
7a	0.98	4.78,4.83	1.72	1.77	0.98	1.53^b	1.38^b	0.82,0.67
7b	1.02	$4.92,4.93^c$	1.70^c	5.62^c	0.90	1.55^b	1.38^b	0.83,0.70
7c	0.95	4.74,4.83	1.67^b	1.82^b	1.93	1.67^b	1.37^b	0.95,0.75
7d	1.13	4.42,4.98	← aryl →		0.70	1.68^b	1.57^b	0.95,1.13
7e	1.02	4.98,5.11	1.90^b	1.68^b	0.98	← aryl →		1.17,0.80
7f	2.35^d	$4.62(m)^d$	1.68^b	1.75^b	0.95	1.55	1.55	0.95,0.82
8a	0.90	0.90	0.90	4.15	0.90	0.73	0.68	0.93
8b	0.74	1.05	0.90	4.13	0.98	0.72	0.69,0.72	1.11
8c	1.05	1.05	0.92	4.15	0.92	0.68	0.80	1.17
8d(e)	0.95	← aryl →		4.57	1.07	0.82	0.80,0.87	1.18

* For the data in this table, 7 and 8 are numbered as follows:



7

and



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[a] With 7a-f, the first chemical shift is for the methyl group exo to the 2-carbon bridge.

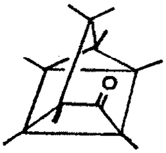
[b] Broadened or quartets as a consequence of homoallylic coupling.

[c] Irradiation at δ5.62 caused collapse to singlets of the doublets at δ4.92 (J=2.0Hz) and δ1.70 (J=1.5Hz).

[d] Irradiation at δ4.62 sharpened the broad peak at δ2.35.

REFERENCES

1. The generality of this reaction of the 2,5-cycloheptadienone moiety in a variety of ring systems was first recognized by O. L. Chapman, et. al. [*J. Amer. Chem. Soc.*, **91**, 6856 (1969)]; for a general discussion and other leading references see H. Hart, *Pure Appl. Chem.*, **33**, 247 (1973).
2. H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, **93**, 6266 (1971).
3. Z. Goldschmidt, U. Gutman, Y. Bakal and A. Worchel, *Tetrahedron Lett.*, 3759 (1973).
4. The alternate cyclization product i was obtained in minor amounts (H. H. and M. K., unpublished results).



i

5. H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, **95**, 4096 (1973).
6. Detailed spectral data will be presented in the full paper.
7. The bridgehead proton in **7f** was at lower field than that of **7c**, and was coupled with the adjacent vinyl protons. A little hexamethylbenzene was formed with **7c** and **7f**.
8. In contrast, irradiation of **7f** was complex and will not be considered here.
9. **13** gave a mixture of **7d** and **7e** whose ratio depended on the reaction conditions, whereas **15** gave only **7e**.