

PHOTOCHEMISTRY OF anti-7,8-BENZOTRICYCLO[4.2.2.0<sup>2,5</sup>]DECA-3,7,9-TRIENE  
AND RELATED COMPOUNDS

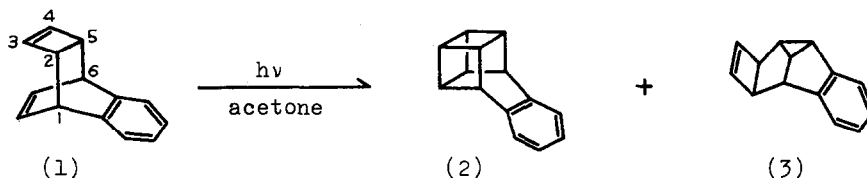
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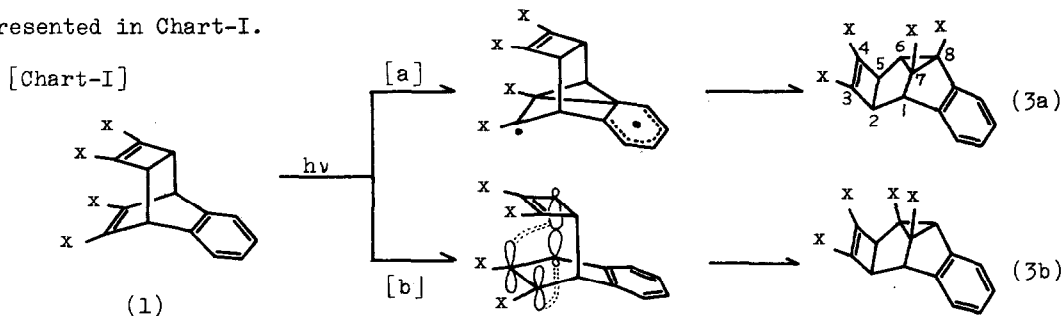
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It was recently reported that the acetone-sensitized photoisomerization of anti-7,8-benzotricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene (1) yields benzobasketene (2) and tetracyclic isomer (3).<sup>1</sup> We now wish to describe our related studies on the photosensitized isomerization of (1) and some related compounds.



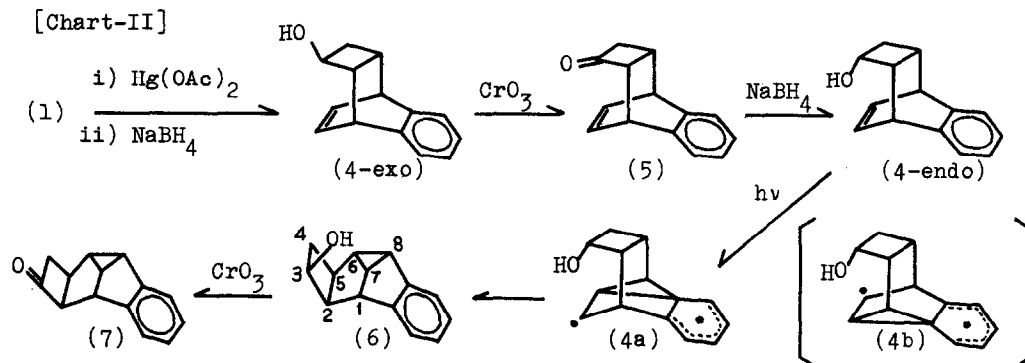
Two fundamentally different mechanisms for the interconversion, (1) to (3) including the di- $\pi$ -methane rearrangement [path-a] and the photochemically allowed concerted  $\pi^2_a + \sigma^2_a$  cycloaddition<sup>2</sup> [path-b] seemed a priori possibilities and are presented in Chart-I.



To determine which mechanism might be responsible for the formation of (3), the acetone-sensitized irradiation of vinyl-labeled anti-7,8-benzotricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene (1) was inspected. The vinyl deuterated compound (1: X=D) was conveniently prepared by the use of lithium N-deuteriocyclohexylamide in N,N-dideuteriocyclohexylamine.<sup>3</sup> After one such treatment deuterium was incorporated

at the vinyl sites with 66.6% which was shown by nmr integrations. Irradiation of (1: X=D) in acetone under condition identical with that used in undeuterated (1) resulted in a mixture of labeled products. It was found that the rearranged product was labeled exclusively at C-7 and C-8 as shown in (3a).<sup>4</sup> The results clearly support di- $\pi$ -methane mechanism of path-a.

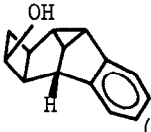
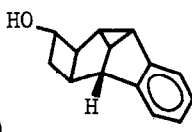
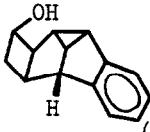
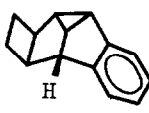
In order to clarify the effect of substituent at C-3 of (1), we have examined the photochemistry of the epimeric exo- and endo-alcohols, (4-exo) and (4-endo), respectively. Oxymercuration of (1) with mercuric acetate followed by demercuration with sodium borohydride gave (4-exo) in 61% yield, mp 86-87°; ir (KBr) 3240  $\text{cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ )  $\delta$  7.0(m, 4H, aryl), 6.45(m, 2H, vinyl), 4.0-3.5(m, 3H, benzyl and  $\underline{\text{H}}\text{-C-OH}$ ), 2.2(m, 2H, cyclobutyl), 1.7(m, 2H, cyclobutyl). Compound (4-exo) was oxidized with chromic anhydride in pyridine to the ketone (5), mp 140-141°; ir (KBr) 1762  $\text{cm}^{-1}$ , which on reduction with sodium borohydride in methanol gave 92% of the epimeric alcohol (4-endo), mp 118-119°; ir (KBr) 3280  $\text{cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ )  $\delta$  7.10(m, 4H, aryl), 6.67(m, 2H, vinyl), 4.4-3.8(m, 3H, benzyl and  $\underline{\text{H}}\text{-C-OH}$ ), 2.8-1.2(m, 4H, cyclobutyl). The configuration of these epimeric hydroxyl groups is readily understood by the reaction sequence [see Chart-II] and the comparison of the chemical shifts of vinyl hydrogens [ $\delta$  6.45 for (4-exo) and 6.67 for (4-endo)].



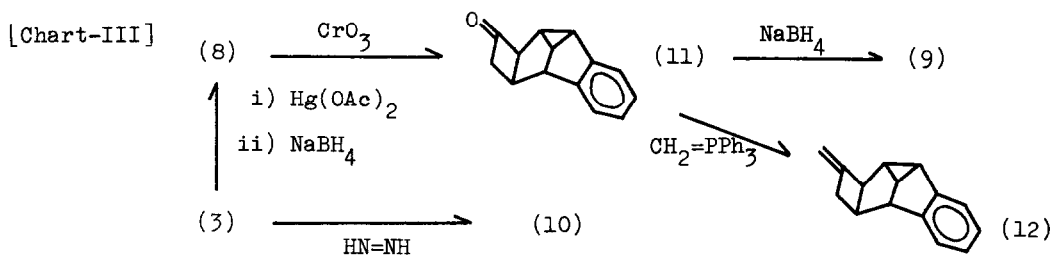
Irradiation of (4-exo) in pet. ether(bp 50-80°) containing 40% acetone with 450-W high-pressure Hg lamp for 6 hr gave a complex mixture of polymeric products and no definite photoproduct could be separated. In contrast to this result similar irradiation of (4-endo) yielded 35% rearranged alcohol (6). The structure assignment to (6) follows convincingly from: (a) its nmr spectrum in  $\text{CDCl}_3$

which displays a four proton multiplet at  $\delta$  7.0 (aryl), a multiplet of area 1 at  $\delta$  4.21 for the hydrogen attached to carbon bearing hydroxy group (H-3) and a one proton doublet at  $\delta$  3.73 ( $J=5.8$  Hz) for the benzylic hydrogen (H-1); (b) oxidation of (6) with chromic anhydride in pyridine gives the cyclobutanone (7), ir (film)  $1770\text{ cm}^{-1}$ , which is isomeric but not identical with the cyclobutanone (11) obtained from the alcohol (8) [see Chart-III]; (c) comparison of the chemical shift of benzylic hydrogen of (6) with those of the model compounds (8), (9) and (10) as shown in Table-I. These model compounds are easily derived from the hydrocarbon

[Table-I]

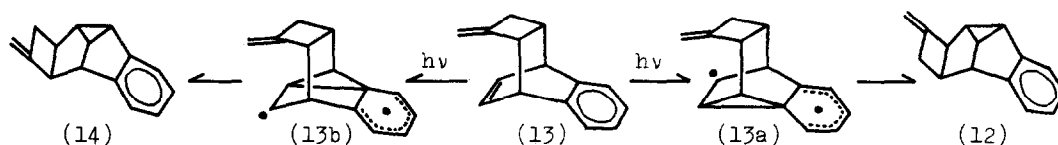
				
	(6)	(8)	(9)	(10)
$\delta_{\text{benzylic-H}}$	3.73	3.38	3.45	3.38
mp	100-102°	86-87.5°	97-98°	oil

(3) as illustrated in Chart-III. The hydroxyl group substitution in (6) is very probably on C-3 with  $\beta$ -configuration since the low-field chemical shift of the benzylic hydrogen clearly reflects the increasing proximity of this hydrogen to the hydroxyl group in (6).



The regioselectivity for benzo-vinyl bridging in di- $\pi$ -methane rearrangement of (4-endo) indicates a larger preference for intermediate (4a) than for (4b) [see Chart-II]. This is mainly due to the factors which involve hydrogen bonding or charge-transfer interaction between a developing radical and the oxygen.<sup>5</sup> In order to gain further evidence for the regioselectivity of the photorearrangement we have examined photoreaction of exo-methylene derivative (13), mp 67-68°; ir (KBr)  $872\text{ cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ )  $\delta$  7.12(m, 4H, aryl), 6.62(m, 2H, vinyl), 4.91(m, 2H, exo-methylene), 4.03(m, 2H, benzylic) and 2.98-2.03(m, 4H, cyclobutyl), obtained

from the ketone (5) by the Wittig reaction. Sensitized photolysis of an acetone solution of (13) with a 450-W high pressure Hg lamp fitted with a Pyrex filter resulted in rapid disappearance of (13) with concomitant formation of two isomeric products in 6:4 ratio. Independent synthesis indicates structure (12) for the minor photoproduct. Reaction of the ketone (11), mp 92.5-94°, ir (KBr) 1774  $\text{cm}^{-1}$ , nmr ( $\text{CDCl}_3$ )  $\delta$  7.0(m, 4H, aryl), 3.72(d, 1H,  $J=5.2$  Hz, benzyl), 3.44-2.26(m, 6H, cyclopropyl and cyclobutyl) and 2.00(dd, 1H,  $J=8.0, 6.1$  Hz, cyclopropyl), with methylenetriphenylphosphorane afforded (12), oil, nmr ( $\text{CDCl}_3$ )  $\delta$  7.02(m, 4H, aryl), 4.68(m, 2H, exo-methylene), 3.54(d, 1H,  $J=5.1$  Hz, benzyl) and 3.28-2.16(m, 6H, cyclopropyl and cyclobutyl) and 1.86(dd,  $J=8.1, 6.2$  Hz, cyclopropyl). The major product is, therefore, assigned to structure (14).<sup>6</sup>



The lack of regioselectivity of the rearrangement of (13) demands no preference for the benzo-vinyl bridging in the intermediates (13a) and (13b) which can lead to both the products (12) and (14), respectively. This result can be regarded as an example of the unusual substituent effect of the hydroxyl group which supports the recent proposal of Hart and Murray, Jr.<sup>5</sup>

We wish to thank Badische Anilin- und Soda-Fabrik for a generous gift of cyclooctatetraene required in the preparation of compounds reported in this paper.

#### REFERENCES AND FOOTNOTES

- (1) L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 2584(1970).
- (2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed.*, **8**, 781(1969); cf. L. A. Paquette and J. R. Malpass, *J. Amer. Chem. Soc.*, **90**, 7151(1968).
- (3) H. E. Zimmerman, R. S. Givens and R. M. Pagni, *ibid.*, **90**, 6096(1968).
- (4) Nmr data of (3) are accord well with those reported by Paquette et. al. see reference (1). The integrated areas of signals at  $\delta$  2.35(H-8) and at  $\delta$  2.68 (H-7) of the deuterated compound (3a) were found to be one-third its initial values.
- (5) H. Hart and R. K. Murray, Jr., *J. Amer. Chem. Soc.*, **91**, 2183(1969).
- (6) All new compounds reported here gave satisfactory elemental analyses.