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Photolysis of 7-Oxanorbornadienes Condensed with Tropone. A Facile Formation of 6-Hydroxyazulenes

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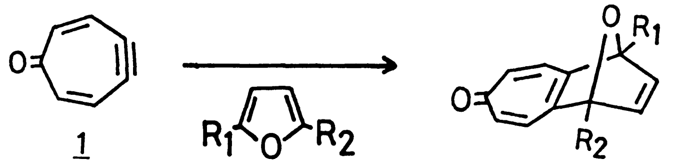
Irradiation of 12-oxatricyclo[7.2.1.0^{2,8}]dodeca-2(8),3,6,10-tetraen-5-ones having one or two bridge-head alkyl substituents in methanol with high pressure Hg lamp gave 6-hydroxy- or 1-alkyl-6-hydroxyazulenes together with 3-acyl- or 1-alkyl-3-acylazulenes as by-products in good combined yields.

Recently we have communicated that the reactions of 4,5-dehydrotropone (1)$^{1a)}$ with furans gave, in relatively good yields, 7-oxanorbornadienes condensed with tropone ring, 12-oxatricyclo[7.2.1.0^{2,8}]dodeca-2(8),3,6,10-tetraen-5-ones (2a, 2b, and 2g),$^{2)}$ the electronic spectra of which exhibit the intramolecular π-π interactions.$^{1b)}$

The known photoisomerizations of 7-oxanorbornadienes to 6-hydroxyfulvenes, 7-oxaquadricyclanes, and oxepines,$^{3a,b)}$ have prompted us to study the photochemical behaviors of 2. In this paper we describe a facile formation of 6-hydroxyazulenes from oxanorbornadienes 2 having one or two bridge-head alkyl substituents.



1
2

a: $R_1=R_2=H$
b: $R_1=R_2=CH_3$
c: $R_1=R_2=C_2H_5$
d: $R_1=R_2=n\text{-}C_3H_7$
e: $R_1=CH_3, R_2=C_2H_5$
f: $R_1=CH_3, R_2=n\text{-}C_3H_7$
g: $R_1=H, R_2=CH_3$
h: $R_1=H, R_2=n\text{-}C_3H_7$
i: $R_1=H, R_2=CH_2C_6H_5$

Oxanorbornadienes 2c—2f, 2h, and 2i have been prepared by the reactions of 1 with the corresponding furans in a similar manner as reported.$^{1b,4)}$

A methanol solution of 2b (2.38×10^{-4} mol/L) in a 1 cm UV cell was irradiated with 500 W Hg lamp through filters ($310 \leq \lambda \leq 390$ nm).$^{5)}$ The reaction could be monitored by the electronic spectroscopy, as shown in Fig. 1. The observed spectral changes revealed the efficient conversion of 2b into photoproducts which embrace azulene chromophore.

To characterize the photoproducts, a methanol solution of 2b (2.34×10^{-3} mol/L) was irradiated with 100 W or 450 W Hg lamp through Pyrex filter. During the photolysis a pale yellow solution of 2b turned reddish violet. The solvent was carefully evaporated under nitrogen and the residue was methylated with diazomethane and chromatographed on alumina with hexane and benzene-dichloromethane, giving 6-methoxy-1-methylazulene (4) (92%) and 1-acetyl-6-methoxy-3-methylazulene (5) (3%).[6—8] The products obtained from 2c—2i under the similar conditions are shown in Table 1.[8,9] Oxanorbornadienes 2b—2d having two identical alkyl groups gave two types of the products in good combined yields. For all the other oxanorbornadienes 2 shown in Table 1, the products can be more generally classified into four types, A, B, C, and D. In all runs, 6-hydroxyazulene or 1-alkyl-6-hydroxyazulenes, A and B, are the main products. Compounds, 2e and 2f afforded the product A and B in comparative yields, while 2g—2i having one alkyl substituent gave only the product A. As by-products, 1-acyl-6-hydroxyazulene or 1-acyl-3-alkyl-6-hydroxyazulenes, C and D, were obtained.

The reactions giving the main products, A and B, are new photochemical reactions of 7-oxanorbornadiene systems and provide a facile synthetic route to 6-hydroxyazulenes.

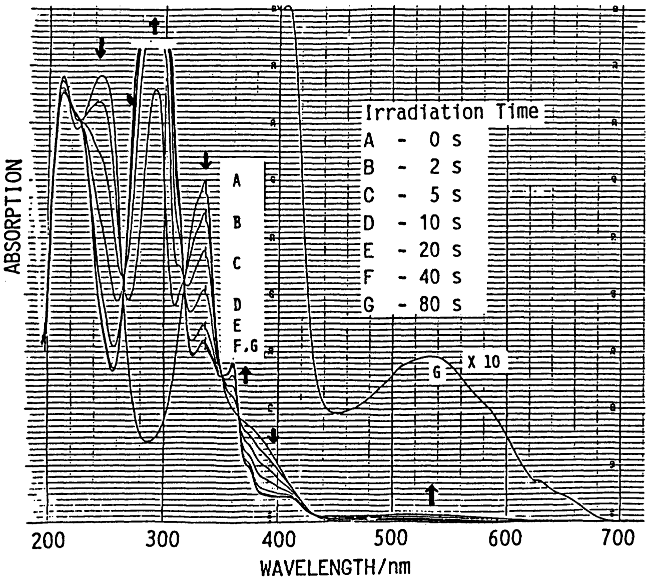
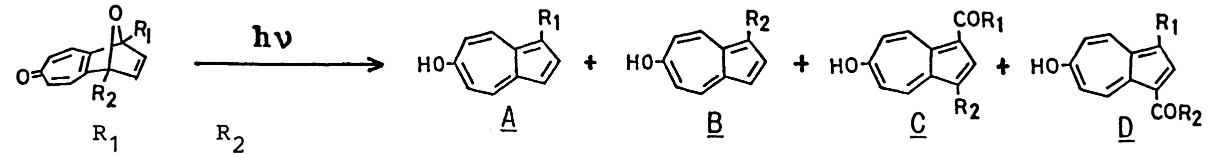


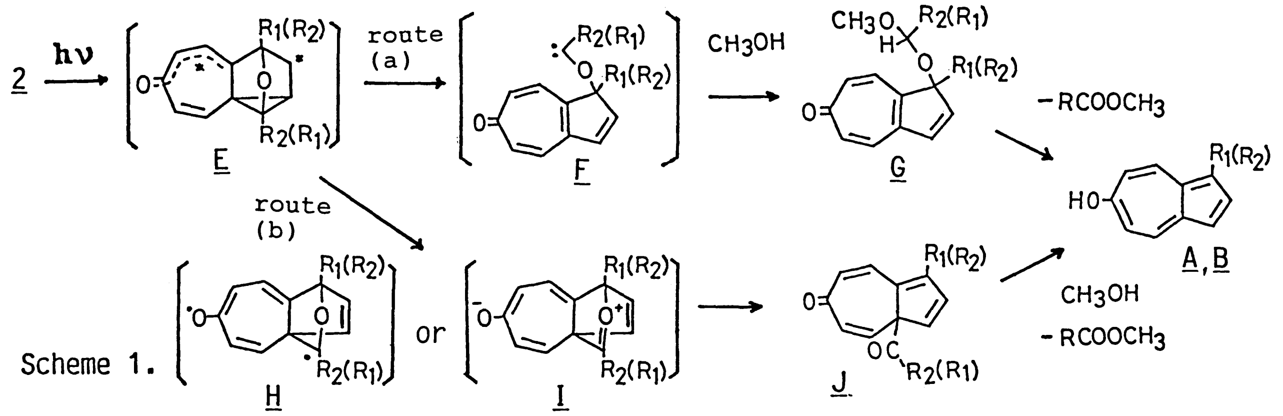
Fig. 1. UV/VIS spectral change of 2b in methanol upon irradiation of 500 W Hg lamp.

As to the reaction mechanism, the release of methyl ester, $RCOOCH_3$, with the formation of A and B from 2 was proved by the isolation of $C_6H_5CH_2COOCH_3$ (60%) in the photolysis of 2i. A route to 6-hydroxyazulenes, A or B by way of C or D can be ruled out through the failure in the photochemical transformation of 1-acetyl-6-hydroxy-3-methylazulene (7) to 6-hydroxy-1-methylazulene (6). Taking the photochemical rearrangements of dienones[11] and several di-π-methane systems[3a, 12] into consideration, two routes, (a) and (b), to A and B, each deriving from the hypothetical intermediate E, can be considered, as shown

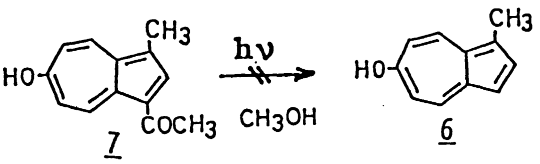
Table 1. The yields of 6-hydroxyazulenes A — D obtained from oxanorbornadienes 2

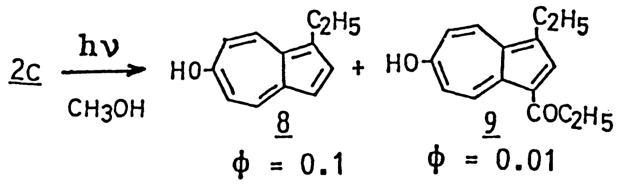


	R_1	R_2	A	B	C	D
2b	CH_3	CH_3[7]	92% (A=B)		3% (C=D)	
2c	C_2H_5	C_2H_5	74% (A=B)		11% (C=D)	
2d	$n-C_3H_7$	$n-C_3H_7$	81% (A=B)		9% (C=D)	
2e	CH_3	C_2H_5[7]	31%	45%	2%	4%
2f	CH_3	$n-C_3H_7$[7]	30%	37%	1-2%	6%
2g	H	CH_3[10]	66%	--	--	3%
2h	H	$n-C_3H_7$[10]	74%	--	--	4%
2i	H	$CH_2C_6H_5$[10]	65%	--	--	--



Scheme 1.





in Scheme 1.[13] The route (a) involves intermediate formation of oxacarbene F, trapping it with methanol, and the aromatization of G with the release of $RCOOCH_3$. The route (b) involves the rearrangement to J via biradical or zwitter ion intermediate H or I and the aromatization of J with the release of acyl group as $RCOOCH_3$. The decreased yield of 4 (49%) on the photolysis of 2b in less polar solvent, ethanol,[14] compared with that in methanol, would be in favor of the route (b), on which polar or ionic intermediate I participates.[15, 16]

The formation of 1-acyl-6-hydroxyazulenes, C and D, must proceed in analogy with that of 6-hydroxyfulvenes from 7-oxanorbornadienes.[3a] The regioselective formation of the products, A and D, from 2g and 2h could be explained in terms of the stabilities of the corresponding intermediates which have an alkyl substituent at radical or carbonium ion centers. The quantum yields (2c → 8) and (2c → 9) with light of 334 nm were 0.1 and 0.01 respectively, revealing low efficiencies of this reaction in spite of high synthetic yield.

Our results communicated here suggest that the photochemical reactions of the bridged systems condensed with tropone ring are expected to offer new synthetic methods for non-benzenoid aromatics containing seven-membered ring. In this regard the studies on the photochemistry of analogous bridged systems are now in progress.

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2) In Ref. 1b, 2 was named as 1,4-dihydro-1,4-epoxy-7H-benzocyclohepten-7-one, but the nomenclature for 2 written in this paper would be more acceptable.

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4) Compounds 2 dimerized easily at room temperature. The structures of 2c—2f 2h, and 2i were identified by means of ^{1}H NMR and UV spectra.

5) Toshiba UV-D33S and UV-31 filters were used.

6) 4: violet plates, mp 72.5-73 °C; exact mass, Found: m/z 172.0885. Calcd for $C_{12}H_{12}O$: M, 172.0889; ^{1}H NMR ($CDCl_3$) δ 2.58(3H, s), 3.84(3H, s), 6.56(1H, dd, J=11 Hz and 2.5 Hz), 6.61(1H, dd, J=11 Hz and 2.5 Hz), 7.11(1H, d, J=4.5 Hz), 7.39(1H, d, J=4.5 Hz), 7.98(2H, d, J=11 Hz). 5: red microprisms, mp 87.5-88.5 °C; exact mass, Found: m/z 214.0991. Calcd for $C_{14}H_{14}O_2$: M, 214.0994; UV (CH_3OH) λmax (log ε) 270(3.90), 329(4.48), 406(3.72), 502 nm(2.81).

7) The photoproducts were first methylated and then chromatographed owing to the labilities of 6-hydroxyazulenes and/or for the efficient separation of the reaction mixture by chromatography.

8) Because of the instability of 2,$^{4)}$ exact weight of 2 could not be measured. The concentrations of 2 were estimated from their UV spectra, in which absorption coefficients of the first absorption bands of tropones (λmax, ≈335 nm) were regarded as equal to those of their 10,11-dihydro-derivatives, 12-oxatricyclo-[7.2.1.0^{2,8}]dodeca-2(8),3,6-trien-5-one or its 1,9-dimethyl derivative.

9) All the new compounds were characterized by mass, IR, UV, ^{1}H NMR, and/or ^{13}C NMR spectra, and gave satisfactory exact mass spectral data.

10) For the spectral data of 6-hydroxyazulene, see K. Takase, T. Asao, Y. Takagi, and T. Nozoe, J. Chem. Soc., Chem. Commun., 1968, 368.

11) For example, D. I. Schuster, Acc. Chem. Res., 11, 65 (1978).

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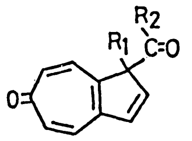
13) We are indebted to a referee for the valuable suggesions on the reaction mechanism of the route (b).

14) On the photolysis of 2b in ethanol, another type of photochemical reaction giving alkyl-substituted derivative of 8H-cyclohept[d]oxepin-8-one (10) took place, with the formation of 4 and 5. The results will be published soon.

15) As an intermediate in these reactions, alkyl-substitued derivative of 10 could be also ruled out, since the irradiation of a methanol solution of 10 resulted in the recovery of 10.

16) Considering the photochemical transformations of 2g—2i to 6-hydroxyazulene, a route to A or B by way of K, derived from oxacarbene F is unlikely, since K derived from 2g—2i should exist in methanol as 1-acylazulenes.$^{10, 17)}$



K

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