Photoinduced Reactions. LXXVII. On the Applicability of Excited Acetone to Induce Photoaromatization of Dihydroheteroaromatics[1)]

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Photoaromatization of various dihydroheteroaromatics and some carbocyclic dihydroaromatics with excited acetone was examined. Among the tested compounds, indoline, 2,3-dihydro-2-methylbenzofuran, and 9,10-dihydroanthracene were found to be photoaromatized. 2-Thiazolines, 2-oxazolines, 2-isoxazolines, 9,10-dihydrophenanthrene, 2,3-dihydro-5,6-dimethylpyrazine, 3,4-dihydro-1-methylisoquinoline, and 6-methyl-3(2*H*)-pyridazinone did not undergo photoaromatization, but recovered unchanged or underwent their own photochemical reactions.

In a previous paper,[2)] we have reported that excited states of acetone could be used to dehydrogenate imidazolines to imidazoles. Our attention, then, was focused to see whether this photoaromatization could be extended to other dihydroaromatics. The present paper shows that it is not always the case but various types of reactions take place, although the photoaromatization occurs in some cases. Interpretation of the results with the Hückel molecular orbital (HMO) energy was attempted with some success.

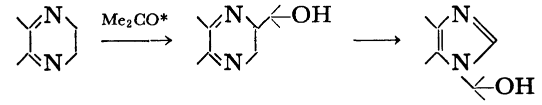
An acetone solution of various dihydroheteroaromatics (AH_2), including a few carbocyclic dihydroaromatics, was irradiated with light mainly at 2537 Å and the products were separated by chromatographic methods. The results are summarized in Table 1, which also includes the results obtained with 2-imidazolines (No. 3—5)[2)] for comparison. Various types of reactions occurred and they can be classified into the following six categories. A hydroaromatic radical (·AH), which is produced by hydrogen abstraction with excited acetone from AH_2, may undergo four types of processes; (i) dehydrogenation to an aromatic compound (A), (ii) coupling with the acetone ketyl radical (iii) dimerization, and (iv) regeneration of AH_2 by hydrogen transfer from the acetone ketyl radical. Process (iv) has been proved to occur in part in the case of imidazolines.[2)] Other processes will involve the excited states (AH_2^*) of the substrate itself; namely, (v) deactivation to AH_2 and (vi) its own photochemical reaction leading to products.

$$\mathrm{AH_2 + Me_2CO^* \longrightarrow \cdot AH + Me_2\dot{C}OH}$$

$$\begin{tikzcd}
\mathrm{A} & \mathrm{\cdot AH} \arrow[l, "\text{(i) }-\mathrm{H}\cdot"'] \arrow[r, "\text{(ii) }\mathrm{Me_2\dot{C}OH}"] \arrow[dl, "\text{(iii) }\cdot\mathrm{AH}"'] \arrow[dr, "\text{(iv) }\mathrm{Me_2\dot{C}OH}"] & \begin{array}{c}\mathrm{Me_2C\text{–}AH}\\ \mathrm{|}\\ \mathrm{OH}\end{array} \\
\mathrm{(AH)_2} & & \mathrm{AH_2 + Me_2CO}
\end{tikzcd}$$

$$\mathrm{AH_2} \underset{\text{(v)}}{\overset{h\nu\text{ or }\mathrm{Me_2CO^*}}{\rightleftarrows}} \mathrm{AH_2^*} \xrightarrow{\text{(vi)}} \text{Products}$$

Only indoline (No. 1), 2,3-dihydro-2-methylbenzofuran (No.2), and 9,10-dihydroanthracene (No.11) gave the corresponding aromatized product or its further photolysis product, *e.g.* dianthracene from dihydroanthracene.[11)] The intermediary formation of radical ·AH is demonstrated in the latter two cases giving a cross-coupling product and a dimer, respectively. While 2-methyl-2-thiazoline (No. 6) and 3,5-diphenyl-2-isoxazoline (No. 10) gave *N*-vinylthioacetamide[5)] and 4,5-diphenyl-3-oxazoline,[7)] respectively, other compounds (No. 7, 9, 12, 14, and 15) were unreactive under the conditions except 2-methyl-2-oxazoline (No. 8) which gave a complex mixture of products. The photochemical isomerization of 2,3-dihydro-5,6-dimethylpyrazine (No. 13) to 1,4,5-trimethylimidazole has already been reported.[12)] Since the transformation of this imidazole to the imidazole-acetone adduct, 1-(2-hydroxy-2-methylpropyl)-4,5-dimethylimidazole, did not occur under the similar photolytic conditions, it is assumed that the adduct is formed by a similar photoisomerization of the dihydropyrazine-acetone adduct [type (ii) product] as depicted below.

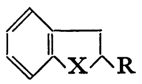
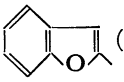
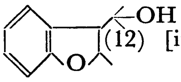
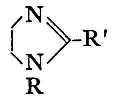
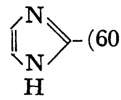
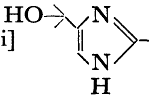
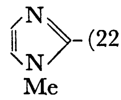
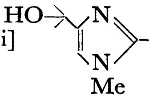
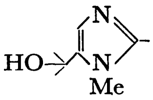
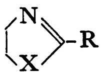
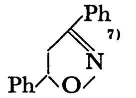
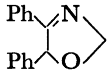
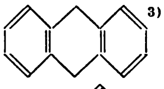
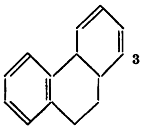
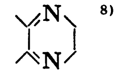
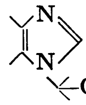
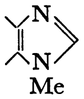
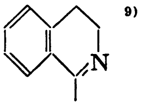
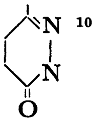


Although the present data are insufficient to make a proper prediction about the reaction courses which dihydroaromatic compounds will follow, we have attempted to interpret the results, particularly on photoaromatization, in terms of HMO π-electron energy (Table 1). We previously showed[2)] that $\Delta E_{\pi 2}$ value, which implies the stabilization energy of π-electron for the aromatization step ($\cdot AH \rightarrow A$), has a more important meaning to the photodehydrogenation of imidazolines to imidazoles than $\Delta E_{\pi 1}$ value which might contribute to lowering the activation energy of the hydrogen abstraction step ($AH_2 \rightarrow \cdot AH$). This argument may be valid in the case of the five-membered dihydroheteroaromatics. Thus, indoline (No. 1) having a higher $\Delta E_{\pi 2}$ value than those of imidazolines is easily photoaromatized and 2,3-dihydro-2-methylbenzofuran (No. 2) having a somewhat low $\Delta E_{\pi 2}$ value undergoes slow photoaromatization. 2-Methyl-2-thiazoline (No. 6), and 2-phenyl-2-oxazoline (No. 9) having a low $\Delta E_{\pi 2}$ value suffered no photoaromatization. These results are not interpreted in terms of the $\Delta E_{\pi 1}$ value. Attempts to interpret the data for the six-membered hydroaromatics in terms of either $\Delta E_{\pi 1}$ or $\Delta E_{\pi 2}$ value proved unsuccessful.

Experimental

All the melting points are uncorrected. NMR spectra were taken on an NEVA T-60 spectrometer with tetramethylsilane

TABLE 1. PHOTOCHEMICAL REACTIONS OF DIHYDROAROMATICS (AH$_2$) IN ACETONE AT 2537Å

No.	AH$_2$		Concn. g/220 ml	Irrad. time (hr)	Recovered (%) (iv or v)	Products (% yield)[a] [Type of product][b]	HMO calculation[c]	
							$\Delta E_{\pi1}(\beta)$	$\Delta E_{\pi2}(\beta)$
1		R=H, X=NH[3]	0.70	21	0	Indole (46) [i]	0.61668[d]	2.71792
2		R=Me,[4] X=O	2.19	186	31	 (4) [i]  (12) [ii]	0.72735[d]	2.41491
3		R=H, R'=Me[2]	2.09	26	0	 -(60) [i]  -(9) [ii]	0.67520	2.58100
4		R=Me, R'=Me[2]	1.85	24	0	 -(22) [i]  -(6) [ii]  -(5) [ii]	0.69020	2.55070
5		R=H, R'=Ph[2]	2.60	75	36	2-Phenylimidazole (36) [i]	0.73246	2.52744
6		R=Me, X=S[5]	2.26	113	e)	*N*-Vinylthioacetamide (15)[5] [vi]	0.75309[d]	2.39559
7		R=Ph, X=S[5]	2.39	48	f)	—	—	—
8		R=Me, X=O[6]	2.80	119	g)	—	—	—
9		R=Ph, X=O[6]	2.20	45	f)	—	0.68715[d]	2.28541
10	 [7]		2.26	52	29	 *etc.* (7)[7] [vi]	—	—
11	 [3]		3.10	88	19	Dianthracene (15) [i] 9,10,9',10'-Tetrahydrodianthranyl (15) (iii)	1.09174	2.22194
12	 [3]		2.04	24	f)	—	0.63098	2.50456
13	 [8]		2.17	22	e)	 (19) [ii]  (40) [vi]	0.73885	2.94457
14	 [9]		2·24	142	f)	—	0.68485[d]	2.67979
15	 [10]		1.86	48	f)	—	0.74023[d]	2.60967

a) Based on the initial amount of the starting material. b) A[i], HA-C(OH)Me$_2$[ii], (HA)$_2$[iii], and others[vi]. c) See ref. 2) for the method of calculation. E_π: total π-electron energy of the aromatic system ($E_{\pi A}$), ·AH ($E_{\pi\cdot AH}$), or AH$_2$ ($E_{\pi AH_2}$). $\Delta E_{\pi1}=E_{\pi\cdot AH}-E_{\pi AH_2}$. $\Delta E_{\pi2}=E_{\pi A}-E_{\pi\cdot AH}$. d) Intermediates having the radical center at 3 position for indoline, 2 for 2,3-dihydro-2-methylbenzofuran, 4 for 2-methyl-2-thiazoline, 4 for 2-phenyl-2-phenyl-2-oxazoline, 3 for 3,4-dihydro-1-methylisoquinoline, and 5 for 4,5-dihydro-6-methyl-3(2*H*)-pyridazinone were assumed as ·AH on the basis of their larger π-delocalization energy than those having the radical center at another position. e) The starting material decomposed during column chromatography on silica gel. f) Essentially no reaction occurred judging from NMR, IR, and tlc analyses of the photolysate. g) It gave a complex mixture which contained no 2-methyl-2-oxazole.

as the internal standard. IR spectra were measured on a JASCO IRS spectrophotometer. Mass spectra were determined on a HITACHI RMS-4 spectrometer. Vapor phase chromatography (vpc) was carried out with a Shimadzu GC-2C. Unless otherwise specified, column chromatography (cc) was carried out with Mallinckrodt silica gel (100 mesh) and thin layer chromatography (tlc) with Merck Kieselgel GF_{254}.

Materials. The starting materials were commercially available or prepared according to the methods of literatures cited in Table 1.

Irradiation. A given amount (Table 1) of the substrate was dissolved in 220 ml of acetone and the solution was irradiated internally with a 10-W low-pressure mercury lamp (Vycor housing) under bubbling nitrogen with external cooling with tap water. After evaporation of the solvent under reduced pressure, the residue was submitted to separation in the following way.

Isolation and Characterization of Photoproducts. Indole was isolated by vpc (Silicone DC 550, 40—60 mesh; helium, 1.1 kg/cm^2 gauge; 140 °C), mp 48.5—51 °C (lit,[13] mp 52 °C), which was identical with an authentic sample (IR). Yield of indole was determined by vpc using diphenyl as the internal standard.

The crude photolysate obtained from 2,3-dihydro-2-methylbenzofuran was chromatographed on 70 g of silica gel. Elution with 300 ml of petroleum ether gave 90 mg of 2-methylbenzofuran. The IR spectrum was identical with the Sadlter Standard Spectrum of this compound. Further elution with 1.3 l of petroleum ether afforded 680 mg of the starting material (tlc and IR). After elution of 440 mg of unidentified products, 380 mg of 2,3-dihydro-3-(α-hydroxyisopropyl)-2-methylbenzofuran was eluted with 1.1 l of benzene–chloroform (1 : 1) which was further purified by preparative tlc (benzene–chloroform, 5 : 1), and distilled to give a colorless oil; bp 75—80 °C (bath temp.)/2 mmHg; $\nu_{\max}^{\text{neat}}$ 3470, 1595, 1240, 1135, 750 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 289 nm (ε 3600), 283 nm (4300); τ^{CDCl_3} 2.60—3.34 (4H, m, aromatic H), 5.18 (1H, d-q, J=3 Hz, J'=7 Hz, $-\overset{|}{C}\underline{H}-O$), 7.02 (1H, slightly diffused d, J=3 Hz, $-\overset{|}{C}\underline{H}-\overset{|}{C}H-O$), 7.83 (1H, broad s, disappeared on deuteration, O$\underline{H}$), 8.63 (3H, d, J=7 Hz, $C\underline{H}_3-\overset{|}{C}H-$), 8.78 (6H, d, J=1.5 Hz, $(C\underline{H}_3)_2-\underset{|}{C}-$); *m/e* (rel. int.) 192 (M$^+$, 11), 134 (M$^+$$-$$(CH_3)_2CO$, 100), 133 (M$^+$$-$$(CH_3)_2COH$, 83), 119 (134$-$$CH_3$, 79), 105 (73), 91 (58), 59 (70).

Found: C, 74.77; H, 8.42%. Calcd for $C_{12}H_{16}O_2$: C, C, 74.97; H, 8.39%. Further elution with more polar solvents (chloroform and acetone) gave 1.20 g of a mixture of unidentified products.

During the photolysis of 9,10-dihydroanthracene, dianthracene (450 mg) precipitated as colorless crystals which were identical with an authentic sample[11] (IR). After removal of dianthracene and the solvent, the residue was chromatographed on 90 g of silica gel. Elution with 1.1 l of petroleum ether yielded 590 mg of the recovered starting material (tlc and IR). Further elution with 2.4 l of the same solvent gave 470 mg of 9,10,9′,10′-tetrahydrodianthranyl, mp273—274°C (lit,[14] mp 256—257 °C), which was identical with an authentic sample[14] (IR, NMR). Further elution with more polar solvents (benzene and chloroform) gave 1.57 g of a mixture of unidentified products.

The photolysate from 2,3-dihydro-5,6-dimethylpyrazine was found by NMR analysis to consist of mainly three components, the starting material, 1,4,5-trimethylimidazole, and 1-(2-methylpropyl)-4,5-dimethylimidazole, in the ratio of 0.8 : 2.6 : 1.6. The product mixture was chromatographed on 80 g of neutral alumina (Merck). Elution with 1 l of benzene–chloroform (2 : 1) gave 90 mg of a mixture of unidentified products. Further elution with 2.2 l of the same solvent afforded 870 mg of crude 1,4,5-trimethylimidazole, which was purified by preparative tlc (Aluminiumoxid GF_{254} Type E, Merck; chloroform–acetone, 2 : 1). Picrate, mp 216—217.5 °C (lit,[12] mp 219—220 °C). The NMR and IR spectra were consistent with those reported.[12] Further elution with 1.8 l of benzene–chloroform (1 : 2) and 1 l of chloroform yielded 610 mg of 1-(2-hydroxy-2-methylpropyl)-4,5-dimethylimidazole, which was purified by preparative tlc as mentioned above. A colorless viscous oil crystallized on standing; mp 90.5—92.5 °C; $\nu_{\max}^{\text{neat}}$ 3150, 1500, 1220, 1180, 915, 725 cm^{-1}; $\lambda_{\max}^{\text{EtOH}}$ 226 nm (ε 5600); *m/e* (rel. int.) 168 (M$^+$, 100), 110 (M$^+$$-$$(CH_3)_2CO$, 93), 109 (M$^+$$-$$(CH_3)_2CHO$, 89), 95 (110$-$$CH_3$, 76), 59 (67); τ^{CDCl_3} 2.64 (1H, s, $-CH=$), 4.86 (1H, s, disappeared on deuteration, OH), 6.28 (2H, s, $-CH_2-$), 7.90 (6H, s, $=\overset{|}{C}-CH_3$), 8.80 (6H, s, $(CH_3)_2-\underset{|}{C}-$).

Found: C, 64.00; H, 9.66; N, 16.77%. Calcd for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65%.
Further elution with more polar solvents (ethanol) gave 370 mg of a mixture of unidentified products. The starting dihydropyrazine decomposed during chromatography and could not be recovered.

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