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THE PHOTOCHEMICAL TRANSFORMATIONS OF 1-METHOXYNAPHTHALENE IN THE PRESENCE OF PHENYLACETIC ACIDS

Jacqueline Libman
Department of Organic Chemistry, The Weizmann Institute of Science,
Rehovot, Israel

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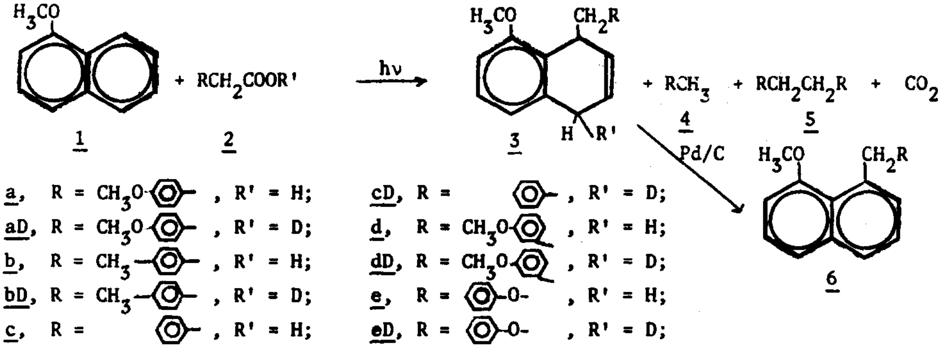
The pathway of the photochemical hydrogen isotope exchange in aromatic systems by acids has been a matter of controversy for several years. Whereas Mason and Smith[1] observed neither fluorescence quenching nor light induced hydrogen isotope exchange in polynuclear aromatic hydrocarbons by aqueous perchloric acid, Stevens and Strickler[2] reported recently on the photochemical hydrogen isotope exchange and fluorescence quenching of naphthalene by sulfuric acid. Investigations by Vesley[3] showed that the efficiency of the fluorescence quenching of anisole by acids depends on the nature of the acid, indicating participation of the conjugate base of the acid in the quenching process. Investigations by Havinga[4] demonstrated that the substitution pattern of the photochemical hydrogen isotope exchange in anisole by trifluoroacetic acid may not be correlated with the electron distribution in anisole calculated for the S_o, S_1, S_2, T_1 or T_2 states and mentioned the possibility that the substitution pattern of the exchange might be determined by the orientation of an intermediate complex.

In order to determine how structural variations of an acid might effect its different modes of interactions with photoexcited aromatic systems, the light induced transformations of 1-methoxynaphthalene (1) in the presence of various phenylacetic acids were investigated.

Irradiation of 1-methoxynaphthalene (1) (0.1 M) and p-methoxyphenylacetic acid (2a) (0.1 M) in either acetonitrile or benzene with a medium pressure mercury lamp through Corex or Pyrex filter resulted in the formation of one major alkylation product 3a in addition to decomposition products of the acid 2a according to the scheme. Compound 3a exhibits: mp 68-69°; uv max (ethanol) 281 (ε 3220) and 275 nm (ε 2800); nmr ($CDCl_3$) δ 2.66 (dd, 1, $J_{gem.}$=13Hz, $J_{vic.}$=9Hz, $ArC\underline{H}_2$), 2.87-3.27 (m, 3, $ArC\underline{H}_2$), 3.8 (m, 1, $ArC\underline{H}$), 3.76 and 3.87 (s each, 3 each, $OC\underline{H}_3$), 5.83 (m, 2, $C\underline{H}=C\underline{H}$) and 6.58-7.32 ppm (m, 7, $Ar\underline{H}$); mass spectrum molecular ion 280 m/e. These data are compatible with structures derived from alkylation of 1-methoxynaphthalene (1) at position 5 or position 8. Treatment of 3a with Pd/C in xylene under reflux resulted in quantitative dehydrogenation to give the naphthalene derivative 6a (mp 52-54°) which uv spectrum exhibits features characteristic for 1,8-disubstituted naphthalene derivatives[5] [uv max (ethanol) 326 (ε 3370), 313 (ε 4390), 297 (ε 5890) and 286 nm (ε 6300)]. When 1-methoxynaphthalene (1) was irradiated in the presence of p-methoxyphenylacetic acid-D (2aD) deuterium incorporation was observed at position 5 of the alkylation product 3aD and in the recovered starting material 1. On the other hand no alkylation was observed upon irradiation of methoxynaphthalene 1 in the presence of p-methoxyphenylacetic acid ethyl ester under analogous conditions.



Phenylacetic acids 2b-e and their deuterated derivatives 2bD-eD reacted with photoexcited 1-methoxynaphthalene (1) similarly to give analogous photoproducts. The reaction conditions and product distributions are summarized in the table. Photoproducts 3b-e were identified by their analytical and spectroscopic properties and by dehydrogenation to the corresponding crystalline 1,8-disubstituted naphthalene derivatives 6b-e.

The quantum yields for the consumption of 1-methoxynaphthalene (1) in the presence of acids 2a-d in acetonitrile were found to correlate well with the Hammett σ constants of the respective phenylacetic acids giving a ρ value of 0.1 (table and figure).[6]

Hammett correlation in the Photoreaction of Methoxynaphthalene (1) with Phenylacetic acids

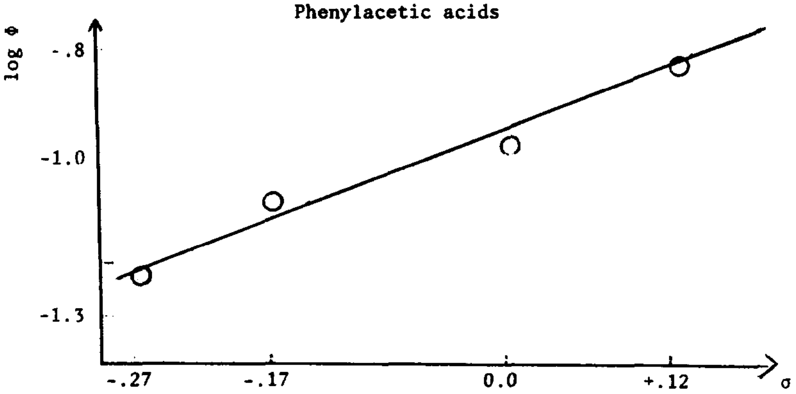


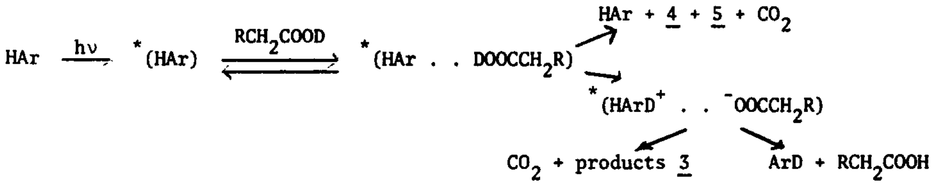
Table: Photoreaction of 1-Methoxynaphthalene with Phenylacetic Acids

Carboxylic acid	Solvent	Conversion of		Chemical yield[a] of		Deuterium incorporation in		Quantum Yield[d] Φ
		1 (%)	2 (%)	3 (%)	5 (%)	1[b] (%)	3[c] (%)	
2a	CH_3CN	20	40	24	19[e]			.06±.005
	C_6H_6	20	40	35	5			
2aD[f]	CH_3CN	20	45	26	17	16	85	
2b	CH_3CN	26	71	19	8[e]			.08±.005
	C_6H_6	18	42	25	5			.075±.005
2bD[g]	CH_3CN	20	36	10	h	4.5	80	.07 ±.005
2c	CH_3CN	20	50	27	4[e]			.11 ±.01
2cD[g]	CH_3CN	18	35	17	h	7	80	
2d	CH_3CN	40	46	11	10[e]			.15 ±.01
	C_6H_6	28	33	11	h			
2dD[g]	CH_3CN	15	15	11	h	4	65	
2e	CH_3CN	35	65	20	6[i]			
2eD[g]	CH_3CN	15	27	35	h	8	45	

[a] Chemical yields given are for isolated material relative to consumed starting material. [b] Deuterium incorporation determined by mass spectrometry. [c] Deuterium incorporation determined by nmr. [d] Quantum yield for the consumption of 1 (0.1M) in the presence of 2 (0.1M); excitation wavelength 313 nm. [e] G.H. Coleman, W.H. Holst and R.D. Maxwell, J. Amer. Chem. Soc., 58, 2310 (1936). [f] Isotopic purity 95% D. [g] Isotopic purity 85% D. [h] Yields not determined. [i] A.C. Cope, J. Amer. Chem. Soc., 57, 572 (1935).

The deuterium incorporation in the alkylation products 3aD-eD, the correlation of the quantum yields with the σ Hammett constants (figure) and the isotope effect on the quantum yield for the consumption of methoxynaphthalene (1) in the presence of tolylacetic acids 2b and 2bD suggest that the photoreaction of 1 with phenylacetic acids involves proton transfer from the acid to the naphthalene 1 in the rate determining step.

The photoreaction of 1-methoxynaphthalene 1 with phenylacetic acids may thus be visualized to involve formation of an encounter complex of the two components which may undergo proton transfer from the acid to the naphthalene moiety. This step may be followed by combination of the naphthalene nucleus



$$\begin{tikzcd}
 & & & HAr + 4 + 5 + CO_2 & \\
HAr \arrow[r, "h\nu"] & {}^{*}(HAr) \arrow[r, shift left, "RCH_2COOD"] & {}^{*}(HAr\ .\ .\ DOOCCH_2R) \arrow[l, shift left] \arrow[ur] \arrow[dr] & & \\
 & & & {}^{*}(HArD^{+}\ .\ .\ {}^{-}OOCCH_2R) \arrow[dl] \arrow[dr] & \\
 & & CO_2 + \text{products } 3 & & ArD + RCH_2COOH
\end{tikzcd}$$

with the benzyl residue to give the alkylation products 3 or by release of a proton resulting in deuterium incorporation. Alternatively the encounter pair may deactivate via decarboxylation of the acids.[7] If photochemical hydrogen isotope exchange of an aromatic system by acids does compete with photochemical addition of the aromatic system to those acids, the efficiency of the hydrogen isotope exchange may not be correlated directly with the acidity of the respective acid, but depends on the relative rates by which the intermediate protonated aromatic nucleus undergoes deprotonation and addition.

References and Footnotes

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