PHOTOCHEMICAL REACTION OF 9,10-ANTHRAQUINONE WITH CHLOROFORM AND TOLUENE

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The photochemical reactions of 9,10-anthraquinone (I) with radical reagents, which have interest as a possible way of inserting a substituent into the anthraquinone molecule, have been studied inadequately. Only one paper is known [1], in which the photoaddition of tert-butanol to (I) was studied, which proceeds at the carbonyl group to give 9-hydroxy-9-(2-hydroxy-2-methylpropyl)-10-anthrone.

When the photochemical trifluoromethylation of (I) by reaction with CF_3CO_2Ag [2] in $CHCl_3$ in an inert atmosphere was attempted, we obtained the fluorine-free adduct, and specifically 9-hydroxy-9-trichloromethylanthrone (II). Compound (II) is obtained in lower yield by running the reaction in the absence of CF_3CO_2Ag. Compound (II) is not formed in the presence of either 2,6-di-tert-butylphenol (DTBP) or atmospheric oxygen (Table 1). Evidently, (II) is formed by a scheme that is analogous to the addition of tert-butanol to (I) [1], and is the result of recombining the $\dot{C}Cl_3$ radical and anthrasemiquinone, which precedes the cleavage of H atom from $CHCl_3$ by the quinone in the excited state. The catalytic effect of CF_3CO_2Ag consists in increasing the concentration of the $\dot{C}Cl_3$ radicals via the analogous reaction of the $\dot{C}F_3$ radical, generated during the photolysis of CF_3CO_2Ag, with chloroform.

It might be assumed that the ability to add to the carbonyl group of weak H donors is a characteristic property of excited (I). In order to verify this we studied the photochemical reaction of (I) with toluene, since information is given in [3] on the formation of hydrocarbon radicals during the photolysis of (I) in solutions of aromatic, aliphatic, and cyclic hydrocarbons. The result of the photochemical reaction of (I) with toluene in the presence of tert-butyl peroxide (TBP) is also addition to the carbonyl group to give 9-hydroxy-9-benzyl-10-anthrone (III).

Anthrones (II) and (III) when heated are converted to (I), and their structure was confirmed by the analytical and spectral data.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrophotometer, the UV spectra were obtained on a Unicam SP-700c instrument in alcohol solution, the PMR spectra were obtained on a Varian A-56/56A instrument (60 MHz) in $CDCl_3$ solution, and the mass spectra were obtained on an MS-902 instrument. The chromatography was run on columns packed with Al_2O_3, and elution was with dry $CHCl_3$.

TABLE 1. Photoaddition of Chloroform and Toluene to Anthraquinone (in argon)

Addend	Time, h	Additive	Adduct and its yield, %	Anthraquinone conversion, %
$CHCl_3$	22	CF_3CO_2Ag	(II), 36	100
The same	24	–	(II), 6	35
»	91	–	(II), 23	72
»	50*	–	–	10
»	60	DTBP	–	40
$CH_3C_6H_5$	8	TBP	(III), 43	100

*In the presence of atmospheric oxygen.

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9-Hydroxy-9-trichloromethyl-10-anthrone (II). A mixture of 0.5 g of (I) and 0.2 g of CF_3CO_2Ag in 150 ml of $CHCl_3$ was irradiated at 25-30°C with the light from a DRSh-500 lamp in glass cylinders that transmitted light with $\lambda \geq 300$ nm. The distance from the light source to the sample was 25-30 cm. The mixtures were stirred by the continuous passage of argon. At the end of photolysis (22 h) the mixture was concentrated in vacuo to a volume of 5-10 ml. The precipitate was filtered, washed with methanol, and chromatographed to give 0.3 g (36%) of (II), mp 232-237° (from a C_6H_6– $CHCl_3$ mixture); λ_{max} 238, 262 i*, 281 nm, log ε 4.20, 4.00, 4.01. Infrared spectrum (KBr, ν, cm^{-1}): 1680 (C=O), 3390 (OH). PMR spectrum (δ, ppm): 3.60 s (1H, OH), 7.30-8.26 m (8H, aromatic protons). Mass spectrum, m/z† (intensity, %): 209 (100), 208 (10), 180 (6), 153 (8), 152 (14), 105 (5), 77 (6), 57 (6), 43 (5). Found: C 55.04; H 2.75; Cl 32.70; O 9.68%. $C_{15}H_9Cl_3O_2$. Calculated: C 54.96; H 2.75; Cl 32.51; O 9.77%.

The photolysis in the absence of CF_3CO_2Ag and in the presence of DTBP was run in a similar manner. The experimental results are given in Table 1.

9-Hydroxy-9-benzyl-10-anthrone (III). Similar to (II), from 0.5 g of (I) and 1.4 g of TBP in 250 ml of toluene we obtained 0.3 g (43%) of (III), mp 142-145° (from MeOH); λ_{max} 234, 266, 274 nm, log ε 3.98, 4.13, 4.14. Infrared spectrum (CCl_4, ν, cm^{-1}); 1680 (C=O), 2880, 2920, 2950 (CH_2), 3600 (OH). PMR spectrum (δ, ppm): 2.86 s (1H, OH), 3.06 s (2H, CH_2), 5.86-8.00 m (13H, aromatic protons). Found: C 83.94; H 5.15%; mol. wt. 300 (mass spectrometry). $C_{21}H_{16}O_2$. Calculated: C 84.00; H 5.33% mol. wt. 300.

CONCLUSIONS

The photochemical reaction of 9,10-anthraquinone with chloroform and toluene respectively gives 9-hydroxy-9-trichloromethyl-10-anthrone and 9-hydroxy-9-benzyl-10-anthrone.

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*Inflection.

†The peaks, whose intensity is at least 5%, are given.