

PHOTOINDUCED REACTION OF ORGANIC COMPOUNDS WITH TRANSITION METAL COMPLEXES.

XVIII. OXIDATION OF SATURATED AND ALKYLAROMATIC COMPOUNDS BY  $\text{CrO}_3$  IN ACETONITRILE ON IRRADIATION

G. B. Shul'pin and M. M. Kats

UDC 541.145.542.943:547.53

It has been shown that alkylaromatic and saturated hydrocarbons are readily oxidized to a mixture of ketone (aldehyde) and alcohol on light-irradiation of a solution of the hydrocarbon and  $\text{CrO}_3$  in  $\text{CH}_3\text{CN}$ .

We have shown previously that oxochromium(VI) compounds are able, on irradiation by light, to oxidize unsaturated and alkylaromatic hydrocarbons [1, 2]. Acetic acid or a mixture of  $\text{CH}_2\text{Cl}_2$  and water were used as solvents, in the latter case in the presence of a phase-transfer catalyst; the reaction takes place stoichiometrically. When only a small quantity of oxochromium compound is introduced into the reaction system it is found that the yield of photooxidation product is several times greater than 100% calculated on Cr(VI). In these reactions, using a  $\text{CH}_2\text{Cl}_2$ -water mixture (a two-phase system, with phase-transfer catalyst) [3] or acetonitrile [4] as solvents, molecular oxygen (as air) plays the part of oxidant of the organic substrate, and the oxochromium(VI) compound is a catalyst. We were interested in studying the possibility of carrying out a stoichiometric photooxidation of saturated and alkylaromatic hydrocarbons in a neutral aprotic medium. We selected acetonitrile as the solvent and cyclohexane and ethylbenzene, together with toluene and styrene, as substrates.

Ethylbenzene (0.47 M) was reacted with a solution of  $\text{CrO}_3$  ( $2.5 \cdot 10^{-3}$  M) in acetonitrile while irradiating with the full light of a high-pressure mercury lamp to yield acetophenone and 1-phenylethanol.

Time $\tau$ (h)	1	3	6
Quantity of acetophenone ( $\times 10^3$ M)	0.36	0.70	1.00
Quantity of 1-phenylethanol ( $\times 10^3$ M)	0.19	0.25	0.42

After 6 h irradiation the solution became opaque and the yield of acetophenone and 1-phenylethanol amounted to 53 and 11%, respectively, calculated on  $\text{CrO}_3$ . The reaction also proceeded in the dark but was very slow (the quantity of 1-phenylethanol in this case was small and was not determined; conditions were the same).

---

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from *Zhurnal Obshchei Khimii*, Vol. 61, No. 3, pp. 754-755, March, 1991. Original article submitted May 10, 1989.

Time $\tau$ (h)	2	3	6
Quantity of acetophenone ( $\times 10^3$ M)	0.16	0.20	0.30

It should be noted that changing the concentration of the  $\text{CrO}_3$  in the solution had no significant effect on the reaction rate. Thus, the concentration of acetophenone formed depended as shown below on the  $\text{CrO}_3$  concentration (ethylbenzene 0.47 M, 1 h irradiation):

$\text{CrO}_3$ ( $\times 10^3$ M)	1.0	2.5	5.0	10.0
Acetophenone ( $\times 10^3$ M)	0.33	0.37	0.47	0.56

The rate of the reaction is practically independent of the concentration of ethylbenzene when its concentration is sufficiently high (1 h irradiation,  $\text{CrO}_3$  concentration  $2.5 \cdot 10^{-3}$  M).

Ethylbenzene (M)	0.23	0.46	0.93
Acetophenone ( $\times 10^3$ M)	0.22	0.36	0.33

Under the same conditions, cyclohexane gives a mixture of cyclohexanone and cyclohexanol.

Time $\tau$ (h)	1	3	5
Quantity of cyclohexanol ( $\times 10^3$ M)	0.12	0.13	0.33
Quantity of cyclohexanone ( $\times 10^3$ M)	0.27	0.58	0.80

No oxidation of cyclohexane in  $\text{CH}_3\text{CN}$  takes place in the dark. We note that in  $\text{CH}_3\text{COOH}$  cyclohexane is oxidized by  $\text{CrO}_3$  under the influence of light to adipic acid.

Toluene (0.47 M) and  $\text{CrO}_3$  ( $2.5 \cdot 10^{-3}$  M) in  $\text{CH}_3\text{CN}$  give, after 1 h irradiation, only  $2.7 \cdot 10^{-5}$  M benzaldehyde. Styrene under the same conditions gives  $8.9 \cdot 10^{-5}$  M benzaldehyde as the sole product.

Thus, the photooxidation of hydrocarbons by chromium trioxide in acetonitrile is a convenient method for the mild oxygenation of saturated and alkylaromatic hydrocarbons.

#### EXPERIMENTAL

The quantity of products formed was determined on an LKhM-80-6 chromatograph with a  $2000 \times 4$  mm column packed with 0.25-0.315 mm Inerton AW-HMDS impregnated with 5% Carbowax 1500. The reactions were carried out in a cylindrical glass vessel provided with a water jacket for cooling ( $10^\circ\text{C}$ ) and with constant stirring provided by a magnetic stirrer. Irradiation was by the full light of a DRSh-1000 (1000 W) high-pressure mercury lamp.

#### LITERATURE CITED

1. G. B. Shul'pin, P. Lederer, and E. Matsova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 11, 2638-2639 (1986).
2. G. B. Shul'pin, E. Matsova, and P. Lederer, *Zh. Obshch. Khim.*, 59, No. 11, 2604-2611 (1989).
3. G. B. Shul'pin and M. M. Kats, *Zh. Obshch. Khim.*, 59, No. 11, 2615-2617 (1989).
4. G. B. Shul'pin and A. N. Druzhinina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 5, 1185-1188 (1989).