

PHOTOOXIDATION OF CYCLOHEXANE BY $(\text{Bu}_4\text{N})_2\text{Cr}_4\text{O}_{13}$
IN ACETONITRILE OR CH_2Cl_2

G. B. Shul'pin, A. N. Druzhinina,
and G. V. Nizova

UDC 541.145+542.943.7:547.592.12

Upon irradiation using light with $\lambda > 520$ nm, $(\text{Bu}_4\text{N})_2\text{Cr}_4\text{O}_{13}$ oxidizes cyclohexane to cyclohexanol as the major product and cyclohexanone in acetonitrile and to cyclohexanol as the major product, cyclohexanone, and cyclohexyl chloride in CH_2Cl_2 . Carrying out this reaction in the presence of air leads to a sharp increase in the yield of cyclohexanone.

Cr(VI) oxo compounds oxidize alkanes to oxygen-containing products [1, 2]. Thus, cyclohexane is oxidized by Cr(VI) compounds in acetic acid in the air upon irradiation to give adipic acid as the major product [3].

In the present work, we studied the photooxidation of cyclohexane in aprotic solvents, namely, acetonitrile and CH_2Cl_2 . The oxidation of cyclohexane by $(\text{Bu}_4\text{N})_2\text{Cr}_4\text{O}_{13}$ in acetonitrile in an argon atmosphere leads to the formation of mainly cyclohexanol with a relatively small amount of cyclohexanone (Fig. 1). The analogous reaction in CH_2Cl_2 also gives cyclohexanol as the major product with small amounts of cyclohexanone and cyclohexyl chloride (Fig. 2).

The amount of cyclohexanol is virtually unchanged when the photooxidation is carried out in the air but the yield of cyclohexanone is sharply increased (Fig. 1).

These results may be interpreted as follows. The reaction of hydrocarbon RH with the photoexcited Cr(VI) oxo compound leads to the abstraction of a hydrogen atom from the alkane and formation of a Cr(V) hydroxy derivative. The resultant radical R' may abstract an OH group from the Cr(V) derivatives to form cyclohexanol or a chlorine atom from CH_2Cl_2 to form

N. N. Semenov Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow.
Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 1, pp. 212-213,
January, 1990. Original article submitted June 21, 1989.

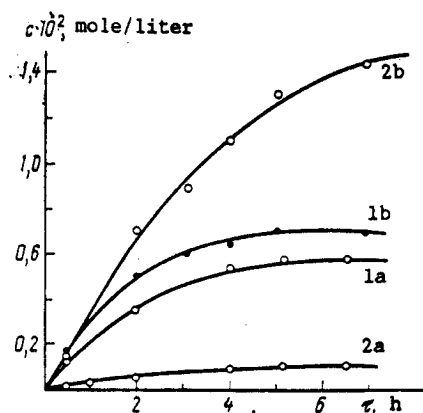


Fig. 1

Fig. 1. Oxidation of cyclohexane (0.46 mole/liter) by $(\text{Bu}_4\text{N})_2\text{Cr}_4\text{O}_{13}$ ($0.5 \cdot 10^{-2}$ mole/liter) in CH_3CN upon irradiation using light with $\lambda > 520$ nm in an argon atmosphere (a) and in air (b): 1-cyclohexanol; 2-cyclohexanone.

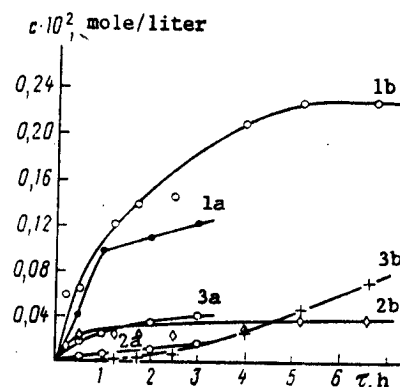
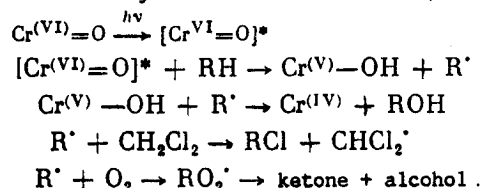


Fig. 2

Fig. 2. Oxidation of cyclohexane (0.46 mole/liter) by $(\text{Bu}_4\text{N})_2\text{Cr}_4\text{O}_{13}$ ($0.5 \cdot 10^{-2}$ mole/liter) (a) and $(\text{Bu}_4\text{N})_2\text{Cr}_2\text{O}_7$ ($0.5 \cdot 10^{-2}$ mole/liter) (b) in CH_2Cl_2 upon irradiation using light with $\lambda > 520$ nm in an argon atmosphere: 1-cyclohexanol; 2-cyclohexanone; and 3-cyclohexylchloride.

cyclohexyl chloride. In the presence of oxygen, R' is converted to a peroxy radical, which is then transformed to an alcohol and ketone. The Cr(V) and Cr(IV) compounds obtained in the reaction disproportionate and are finally converted to a Cr(III) derivative:



We note that the participation of atmospheric oxygen has been noted in the iodosobenzene oxidation of ethylbenzene catalyzed by Cr(VI) oxo compounds [4].

EXPERIMENTAL

The reaction was carried out in a cylindrical glass vessel with a water jacket maintained at 15°C upon irradiation with a 250-W DRL-250 fluorescent lamp filtered through aqueous $\text{K}_2\text{Cr}_2\text{O}_7$ ($\lambda > 520$ nm). Prior to the experiment, the solvent and substrate were distilled in an argon atmosphere. The reaction was carried out using a magnetic stirrer in an argon atmosphere or in the air. The amount of products formed was determined by gas-liquid chromatography using an LKhM-80-6 chromatograph and 2-m column packed with 5% Carbowax 1500 on 0.25-0.315 mm Inerton AW-HMDS with argon as the gas carrier.

LITERATURE CITED

1. G. Cainelli and G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer Verlag, Berlin (1984).
2. A. E. Shilov and G. B. Shul'pin, *Usp. Khim.*, **56**, 754 (1987).
3. G. B. Shul'pin, P. Lederer, and E. Matsova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 11, 2638 (1986).
4. G. B. Shul'pin and A. N. Druzhinina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 5, 1185 (1989).