Tetrahedron Letters No.57, pp. 5949-5952, 1968. Pergamon Press. Printed in Great Britain.

PHOTOREACTIONS OF AROMATIC COMPOUNDS XVI[1)]

PHOTOCHEMICAL VALENCE ISOMERISATION IN ANISOLE.

G. Lodder, P.E.J. du Mée and E. Havinga

Laboratory of Organic Chemistry, The University, Leiden, The Netherlands.

(Received in UK 18 October 1968; accepted for publication 25 October 1968)

Since 1960 several publications have appeared about valence isomerisations in benzenes under the influence of light (2). The question arose whether such transformations might play a part in the photodeuterations investigated in this laboratory by De Bie (3,4) and thus might have blurred the picture of the substitution patterns in the photochemical hydrogen-deuterium exchange. To this end we first studied anisole, tritiated in various positions.

Anisole-2-t, anisole-3-t and anisole-4-t were irradiated in hexane solution. The rearrangement of the tritioanisoles was studied by comparing the specific activities of the 2,4-dibromo derivatives of irradiated samples with those of non-irradiated ones. If 1-2 rearrangement occurs, the 2,4-dibromo anisole from irradiated anisole -2-t and anisole-4-t should contain more tritium than that from the non-irradiated compounds (i.e. the specific activities of the former should be higher). The specific activity of the derivative from irradiated anisole-3-t should be lower than that of the derivative from the non-irradiated sample.

The results are summarized in Table I. Each figure represents the average of several independent experiments.

Table I. specific activities (dpm/mmole)(accuracy ± 1.5%).

	anisole	2,4-dibromoanisole from non irradiated anisole	2,4-dibromoanisole from irradiated anisole
2-t	63.500	37.100 a)	41.700 b) 40.600 c) 43.400 d)
3-t	80.400	79.800	81.300 b)
4-t	74.800	1900	1900 b)

a) The specific activity is more than half of that of the anisole-2-t because the bromination of anisole in acetic acid has a small isotope effect. In a series of separate experiments with different conversions of anisole to dibromoanisole (5), the isotope effect was determined as $\frac{k_H}{k_T}$ - 1.4 in accordance with the value $\frac{k_H}{k_D} = 1.1$ found by Berliner (6).

N.B. Because of this isotope effect it is necessary to compare only dibromoanisoles from irradiated and non-irradiated anisole-2-t, which underwent the same degree of conversion in the bromination (in the table 100%).

b) 1500 ml solution illuminated at 35°C in a Rayonet photochemical reactor for 24 hrs.

c) 1300 ml solution illuminated under the same conditions.

d) 1500 ml solution illuminated at 30°C in the circulating device for 5 hrs.

Within the experimental error no rearrangement has been observed with anisole-3-t and anisole-4-t; anisole-2-t shows about 15 to 20 percent isomerisation, corresponding to a quantum yield of 0.004*.

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* The quantum yield is based on comparison with the reaction rate of m-nitroanisole in 0.01 N NaOH (ϕ 254 mμ = 0.22) (7).

Conclusions:

a) Irradiation of anisole in hexane leads to 1-2 hydrogen scrambling, most probably by formation and rearomatization of a benzvalence (2 b, c), the 2-methoxy-tricyclo $\left[3.1.0.0^{2,6}\right]$hex-3-ene**.

b) The quantum yield of the scrambling is so small that it does not interfere to a significant extent in the photodeuteration of anisole in which the quantum yields for ortho, meta and para substitution are 0.10, 0.06 and 0.00 resp. (4).

Experimental.

Anisole-2-t, -3-t and 4-t were prepared by quenching the Grignard reagent from the corresponding bromoanisoles with tritiated water (8). The products were diluted with inactive anisole. Each isomer of the bromoanisoles contained about one percent of the other isomers (GLC, SE-30 5%, Benton-34 5% on embacel 60 - 100 M).

The 2,4-dibromoanisoles were prepared by bromination of the anisoles with Br_2 in 100% acetic acid. The extent of conversion of anisole to dibromoanisole was measured by GLC (SE-30 10% on chromosorb was-AW 60-100 M). It was checked that under the conditions used there was no hydrogen exchange. The dibromoanisoles were recrystallized several times from methanol. Purity was established by GLC.

The tritium analyses were carried out using a Packard 3310 Tricarb scintillation counter. The samples were dissolved in 15 ml of a scintillation solution of toluene containing 5 g PPO and 200 mg POPOP per 1000 ml.

Irradiations were performed in a quartz vessel placed in a Rayonet photochemical reactor provided with RUL 254 mμ lamps or in the apparatus designed by Havinga and Bots (9) in which the solution was circulated around a high pressure mercury arc lamp (Hanau S 1200). Batches of 2.0 g of the relevant anisole in 1500 ml purified hexane were used. The irradiated anisoles were recovered by distillation.

** In the PMR spectrum of anisole irradiated in pentane peaks (τ 4,5 6,8 and 8,1) attributable to the benzvalene could be recognized.

1. Part XV, R.O. de Jongh and E. Havinga, Rec.Trav.Chim. in the press.
2. a) A review until 1967 is given in D. Phillips, J. Lemaire, C. Burton and W. Noyes Jr. ''Isomerisations as a route for radiationless transitions'' in Advances in Photochemistry, Vol. V. p. 329. J. Wiley and Sons, New York, London, Sidney. (1968)
   b) K.E. Wilzbach, J.S. Ritscher, L. Kaplan, J.Amer.Chem.Soc. 89, 1031 (1967).
   c) K.E. Wilzbach, A.L. Harkness, L. Kaplan, ibid. 90, 1116 (1968).
   d) L. Kaplan, K.E. Wilzbach, ibid. 90, 3291 (1968).
3. D.A. de Bie, E. Havinga, Tetrahedron 21, 2359 (1965).
4. D.A. de Bie, Thesis, Leiden (1966).
5. L. Melander, Isotope effects on reaction rates, p. 56. The Ronald Press Comp., New York (1960).
6. E. Berliner, Chem. Ind. 177 (1960).
7. R.O. de Jongh, Thesis, Leiden (1965).
8. K. Halvarson, L. Melander, Arkiv Kemi 11, 77 (1957).
9. E. Havinga and J.P.L. Bots, Rec.Trav.Chim. 73, 393 (1954).