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PHOTOREDUCTION OF DIMETHYL TEREPHTHALATE BY AROMATIC HYDROCARBONS

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While there has been much recent interest in the photoreduction of carbonyl compounds by a variety of hydrogen donors, such as alcohols[1], hydrocarbons[1] and especially amines[2], no studies on the photoreduction of carboxylate esters have yet been reported. In an extension of our study on the photochemistry of carboxylate ester, having an electron-withdrawing substituent adjacent to the ester group[3], we wish to report here our preliminary finding concerning the photoreduction of dimethyl terephthalate by aromatic hydrocarbons as the hydrogen donors.

A solution of dimethyl terephthalate (0.005 mole) in an aromatic hydrocarbon (SH, 0.5-1.0 mole) was irradiated through Pyrex with a 500 W high-pressure mercury arc under nitrogen at room temperature for 150-300 hr. In various aromatic hydrocarbons possessing labile hydrogen, the photoreduction of dimethyl terephthalate (I) did take place readily to give rise to the formation of the corresponding coupling products*, consisted of the pinacols (III and V) and the _tert_-carbinols (IV and VI), along with the formation of the pure dimers of aromatic hydrocarbons (II). In each case, it was of very interest that the formation of appreciable amounts of methanol was observed. The results are listed in Table I.

On the other hand, although it may be assumed that the hemiacetal radical (VII) appears to be formed by hydrogen abstraction by triplet of (I), no coupling products derived directly from (VII) were isolated at all. This is probably due to the lack of stability of (VII).

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* For all new compounds described in the present letter, satisfactory analytical and spectral data were given.

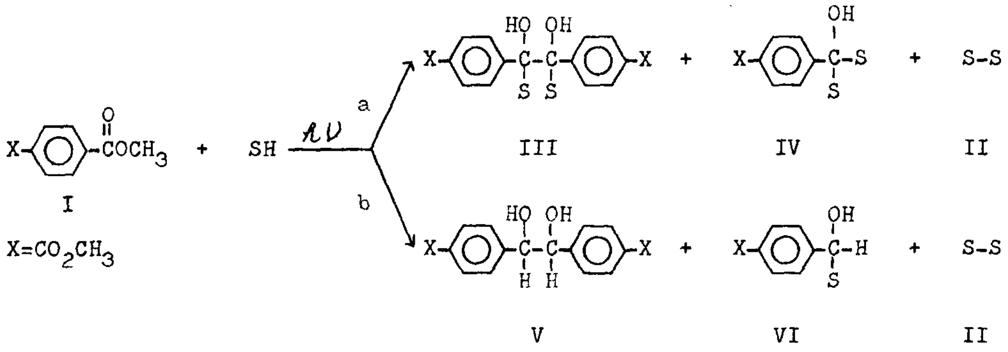
TABLE I

Photoreduction of Dimethyl Terephthalate by Aromatic Hydrocarbons

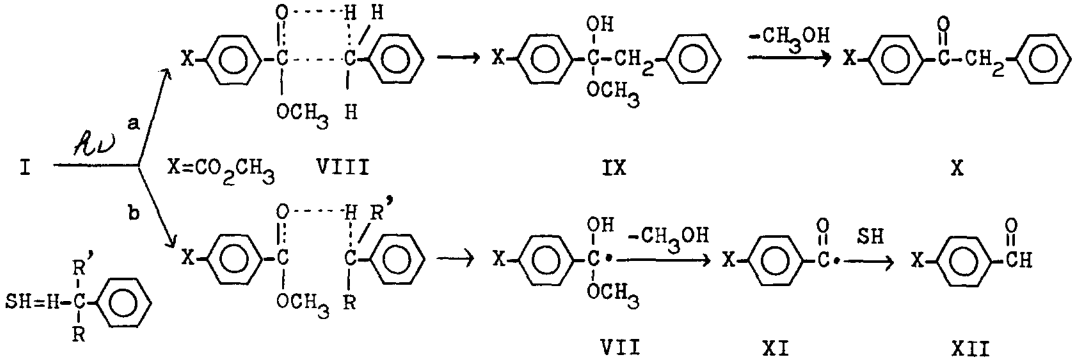
Aromatic hydrocarbons	Products[a] , (mMol.)				
	II	III[b]	IV	V[b]	VI
Toluene	0.41	0.13	0.40	—	—
p-Xylene	0.52	0.08	0.43	—	—
Ethylbenzene	0.72[b]	—	—	0.15	0.45[c]
Cumene	1.07	—	—	0.11	0.55
Diphenylmethane	1.21	—	—	0.12	0.61

[a] Yield based on 1 mMol. of reacted (I). [b] Consisted of a mixture of the rac.- and meso-isomers. [c] Consisted of a mixture of the threo- and erythro-isomers.

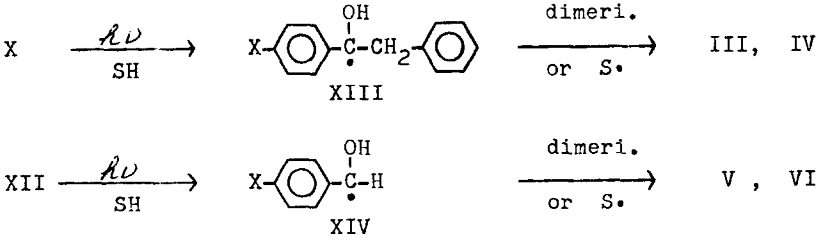
As shown in Table I, one of the most significant results in the above photoreduction is the finding that the variation in hydrogen donors has definitive influence on the photoreduction paths; namely, the photoreduction by toluene or p-xylene, (path a), differs from that by ethylbenzene, cumene or diphenylmethane, being highly substituted on the benzylic carbon, (path b), according to the scheme shown below.



To account for these results, we would like to propose a mechanism. Since we have recently pointed out that the excited state of (I) involved in the photoaddition reaction was the n-π* triplet and, as a general rule, the photoexcited state of (I) would not be different in a series of the present hydrogen donors, it is reasonable to assume that the hydrogen-transfer steps between the n-π^* triplet state of (I) and the hydrogen donors are of critical importance in determining the path of photochemical reaction. In path (a), hydrogen abstraction seems to proceed through a cyclic intermediate (VIII) in a concerted manner to form a hemiketal (IX), in analogy to what has been suggested for the photochemical cyclobutanol formation from saturated ketone[4]. Whereas, in path (b), the formation of (VIII) may be prevented by steric hindrance due to the bulky substituents on the benzylic carbon and, in consequence, only hydrogen abstraction, without formation of new C-C bond, may occur to give a hemiacetal radical (VII). Since (IX) and (VII) are thought to be extremely unstable, they may undergo elimination of methanol rapidly to yield (X) and (XI), from which (XII) may be produced *via* hydrogen abstraction[5].



Hydrogen abstraction photochemically by (X) and (XII) results in formation of two carbinol radicals, (XIII) and (XIV), which are precursors of the two sets of the coupling products.



These proposals and other refinements of the mechanism are being considered in further detail and will be reported shortly.

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5) Although (X) and (XII) have not been detected at present, we certainly have not denied their formation.