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NOVEL PHOTOREDUCTIVE ALKYLATION OF METHYL 4-PHENYLBENZOATE WITH ALIPHATIC TERTIARY AMINES

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A photoinduced electron-transfer reaction of methyl 4-phenylbenzoate with triethylamine leads to an aminoketone (**4**), and a photoreductive ethylation product (**2**) which results from the Norrish Type II reaction of the aminoketone.

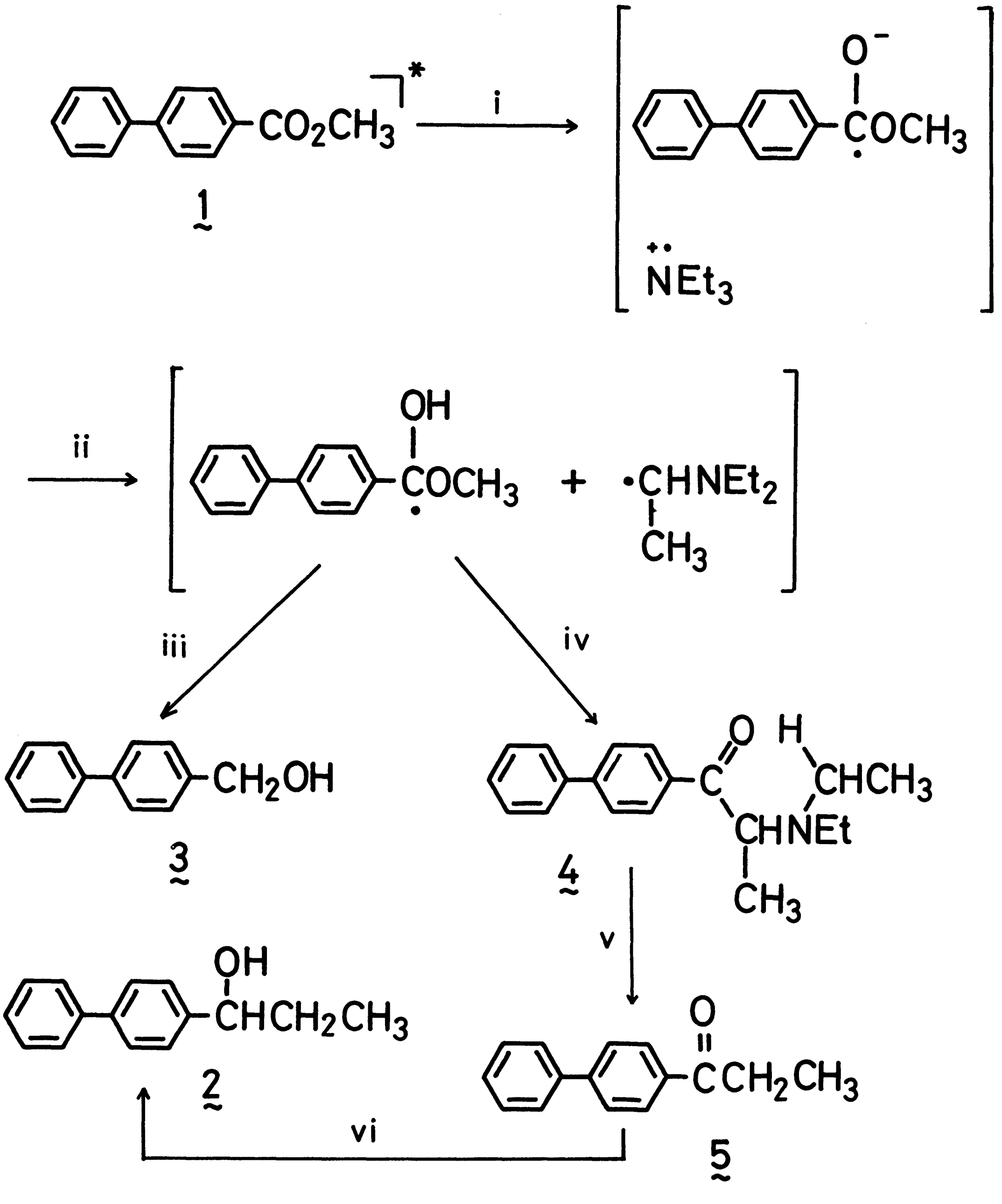
Although the photoreduction of ketones is well-investigated,1) the reduction of esters has scarcely been studied.2) Our interest has focussed on the photoreduction of aromatic esters through electron-transfer from an aliphatic amine as a donor.

In the photochemical reactions of aromatic esters with aliphatic amines as originally shown by Barltrop4) two functional groups can be reduced; (a) the photoinduced Birch-type reduction of aromatic rings and (b) the reduction of carbonyl groups.

Rabideau and his co-workers3) have reported that the thermal reduction of biphenylcarboxylic acid esters with Na/NH_3 exclusively gives 1,4-dihydroaromatics, while Barltrop showed that biphenyl itself is photochemically reduced in the presence of an aliphatic amine to yield dihydro- and tetrahydrobiphenyls.4)

We have examined the photochemical behavior of a biphenylcarboxylic acid ester to clarify which reaction is predominant, a or b. And we wish to report that on the irradiation of methyl 4-phenylbenzoate in the presence of triethylamine the photochemical reduction of the ester group instead of the aromatic rings takes place together with ethylation.

Irradiation of an acetonitrile solution (420 cm^3) of methyl 4-phenylbenzoate (1, 650 mg) in the presence of triethylamine (10.0 cm^3) under an atmosphere of nitrogen with a 16-W low pressure mercury arc for 6 h gave 1-(4-biphenylyl)-1-propanol (2, 92.6 mg) and 4-biphenylylmethanol (3, 50.2 mg) with the recovery of 1 (217 mg). The fluorescence of 1 was efficiently quenched by triethylamine at the Stern-Volmer rate constant of $k_q\tau=51\ dm^3mol^{-1}$. The reaction did not take place without the amine or irradiation. These facts[4)] suggest that an electron-transfer reaction as shown in the step (i) in the scheme participates in the series of reactions.



(i) one-electron-transfer from triethylamine to 1 (ii) proton-transfer from the α-position of triethylamine (iii) hydrogen abstraction, elimination of methanol and then photoreduction of the resulted aldehyde (iv) radiacal coupling and then elimination of methanol (v) The Norrish Type II reaction of the carbonyl group upon irradiation (vi) photoreduction of the carbonyl group.

Scheme.

A similar reaction of 1 (506 mg) with tripropylamine (4 cm^3) afforded 1-(4-biphenylyl)-1-butanol (21.0 mg) and 3 (34.0 mg) with the recovery of 1 (367 mg).

In the presence of α,α-dideuteriotriethylamine instead of triethylamine the compound 1 was photolyzed to give deuterated 2 (d_1 20%, d_2 6%) and 3 (d_1 2%). If an ethyl radical which would be generated from the reactive species of triethylamine added to the compound 1 directly, the product 2 should be deuterated by d_2 33%. The alkyl cation mechanism seems to be excluded on the basis of the fact that the compound 1 is photoreductively propylated without the isomerization of the propyl cation in the presence of tripropylamine.

These facts suggest the reaction mechanism shown in the scheme.

The isolation of the intermediate product 4 from the reaction mixture at the initial stage of reaction did not succeed.5) However, in accord with this mechanism, irradiation of an acetonitrile solution (10.0 cm^3) of 1-(4-biphenylyl)-2-(N,N-diethylamino)-1-propanone (4, 33.0 mg),7) in the presence of triethylamine (0.1 cm^3) for 2 h gave 2 (2.1 mg) with recovery of 4 (10.0 mg). A similar irradiation on an acetonitrile solution (10.0 cm^3) of 4 (39.3 mg) in the absence of triethylamine afforded 1-(4-biphenylyl)-1-propanone (5, 13.0 mg) with recovery of 4 (6.0 mg).6) The product 5 was also photolyzed in the excess of triethylamine to furnish 2 in 12.8% yield.

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5) Neither of **4** nor **5** was detected by GC even at the low concentrations of triethylamine.

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7) The compound **5** was synthesized by Friedel-Crafts' reaction of biphenyl with propionyl chloride in the presence of aluminium chloride in dry carbon disulfide. To a suspension of aluminium chloride (1.0 g) in ethereal solution (100 cm^3) of **5** (2.4 g) was added bromine (3.0 g) dropwise at 0°C. After half an hour water (50 cm^3) was added dropwise to the mixture. The ethereal extraction and recrystallization from ethyl alcohol gave 1-(4-biphenylyl)-2-bromo-1-propanone (2.9 g) in 89% yield. A dry benzene solution (60 cm^3) of the bromopropanone obtained (1.1 g) and diethylamine (0.8 cm^3) was refluxed for 20 h. After addition of 0.1 M KOH solution etheral extraction afforded dark brown liquid, which was column-chromatographed on Al_2O_3 with eluent 9% $CHCl_3$ in hexane to furnish 1-(4-biphenylyl)-2-(N,N-diethylamino)-1-propanone (0.22 g). IR 1680 cm^{-1}; MS m/z (rel intensity) 281(M+.,2), 210(9), 198(68), and 181(100); ^{1}HNMR (60 MHz, CCl_4) δ=1.02(6H, t, J=7 Hz), 1.20(3H, d, J=6.4 Hz), 2.58(4H, q, J=7 Hz), 4.28(1H, q, J=6.4 Hz), and 7.3-8.3(9H, m).

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