# Photoaddition of Carboxylate Esters to Diphenylacetylene

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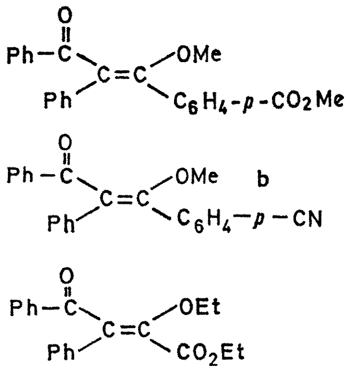
*Summary* Irradiation of some carboxylate esters and tolan (diphenylacetylene) gives the corresponding β-alkoxy-α-benzoylstyrene derivatives.

WHILE the photoaddition of aldehydes or ketones to acetylenes has been considerably explored,[1] no studies on the photoaddition of carboxylate esters to acetylenes have previously been reported. In continuation of our study of the photochemistry of carboxylate esters having electron-withdrawing groups,[2] we report here our preliminary findings concerning the photoadditions of some carboxylate esters with tolan.



A solution of carboxylate ester (0·03 mole) and tolan (0·01 mole) in benzene (250 ml.) was irradiated through Pyrex with a 250 w high-pressure mercury arc for 25 hr. In the present study, dimethyl terephthalate, methyl *p*-cyanobenzoate and diethyl oxalate were selected as the carboxylate esters. The photoproducts were characterized by elemental analysis, i.r. and n.m.r. spectra, and molecular-weight measurements. The results are presented in the Table.

TABLE

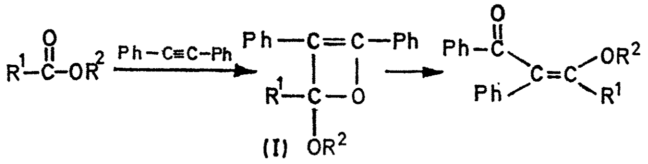
*Photoaddition of carboxylate esters to tolan*

| Carboxylate esters | Products (yield %)[a] | M.p.(°) |
|---|---|---|
| Dimethyl terephthalate | *trans*-(32) | 124—126 |
| | *cis*- (32) | 91—93 |
| Methyl *p*-cyanobenzoate | (86) | 150—152 |
| Diethyl oxalate | (25) | 48—50 |

[a] Figures in parentheses denote yield based on unrecovered carboxylate ester.

[b] The *cis*-isomer rapidly changed to *trans*- even during recrystallization. Therefore, the *cis*-isomer was not isolated in pure form.

For these photoadditions, we suggest the following mechanism which is similar to those postulated for the photoaddition of *p*-benzoquinone to tolan;[1] *i.e.*, the reaction probably proceeds through the attack of the carbonyl *n*,π* triplet state on the tolan triple bond to produce an unstable oxetene intermediate (I), followed by ring opening of (I) to give the observed photoproduct.



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[1] H. E. Zimmerman and L. Craft, *Tetrahedron Letters*, **1964**, 2131; D. Bryce-Smith, G. I. Fray, and A. Gilbert, *ibid.*, p. 2137.

[2] Y. Odaira, T. Shimodaira, and S. Tsutsumi, *Chem. Comm.*, **1968**, 757; T. Tominaga, Y. Odaira, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1967, **40**, 2451; Y. Shigemitsu, H. Nakai, and Y. Odaira, *Tetrahedron*, 1969, **25**, 3039.