

A Transition Metal Catalysed Photoreaction. Ferrocene-sensitized Photoalkoxycarbonylation of Azulene

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Summary Azulene undergoes a novel ferrocene-catalysed photoalkoxycarbonylation in carbon tetrachloride-alcohol solutions.

FERROCENE has been reported to photocatalyse *cis-trans* isomerisation and dimerisation and intramolecular cyclo-

addition of olefins.¹ We report a novel type of ferrocene-catalysed photo-induced alkoxycarbonylation of azulene in carbon tetrachloride-alcohol solution.

When a solution of azulene, ferrocene, and sodium acetate in carbon tetrachloride-ethanol (1:1 v/v) was irradiated (365 or 313 nm) ethyl 1-azulenecarboxylate (**1**)²

was obtained (52%). Ferrocene and azulene were recovered almost quantitatively, and no ethyl ferrocenecarboxylate, the photo-product³ in the absence of azulene, was detected. Formation of (1) was suppressed by the removal of sodium acetate from this system, and 1-chloroazulene (2) was produced. No trace of (1) could be detected in the absence of ferrocene. When 254 nm light was employed, the reaction above gave (1) (33%), (2) (10%), and diethyl 1,3-azulenedicarboxylate (2%).

Other alcohols including *t*-butyl alcohol, which afforded the corresponding ester (20%), were also effective in this reaction. When the reaction was carried out in a mixture of chloroform and ethanol, 1-formylazulene⁴ was

obtained (3%). But no reactions were observed when dichloromethane was used.

The photoreaction of azulene possesses the following three characteristics: (1) no effects of dissolved oxygen are observable in the initial stage of the reaction; (2) the addition of a radical scavenger such as cyclohexene or hydroquinone shows no effects on the reaction; (3) the u.v. and n.m.r. spectra suggest the formation of a complex between azulene, ferrocene, and CCl₄. Ethyl- and acetyl-ferrocene and other transition-metal compounds such as Fe(acac)₃, FeCl₂, FeCl₃ and NiCl₂ were less efficient as catalysts for this reaction.

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³ Y. Hoshi, T. Akiyama, and A. Sugimori, *Tetrahedron Letters*, 1970, 1485.

⁴ W. Treibs, *Tetrahedron Letters*, 1967, 4707.