The Photochemistry of Acetylenic Compounds: Methyl 4,4,4-Triphenylbut-2-ynoate

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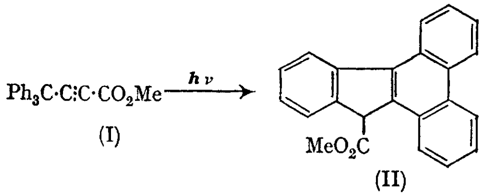
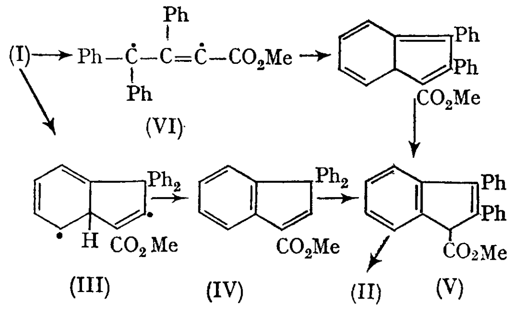
As a part of an investigation[1] of the photochemistry of conjugated acetylenic carbonyl compounds,[2] we have examined the title compound, (I), a conjugated acetylenic ester. The earlier study[1] of methyl 4,4-dimethylpent-2-ynoate revealed a photochemical reduction of the conjugated acetylenic ester to an olefinic ester. We report that the exchange of the tertiary butyl group for a triphenylmethyl group results in an unusual photochemical product of quite a different type, methyl 13*H*-indeno-[1,2-*l*]phenanthrene-13-carboxylate, (II). Compound (I) was prepared by the carboxylation of the Grignard reagent of 3,3,3-triphenylprop-1-yne, which was prepared from 3,3,3-triphenylprop-1-ene[3] by addition of Br_2 and elimination of HBr. A solution of (I) (1 g.) in cyclohexane (450 ml.) was irradiated with a 450 w Hanovia lamp until the intense triple-bond stretching frequency at 2240 cm.$^{-1}$ had disappeared (1·75 hr.). Chromatography of the reaction product on silica gel provided only two crystalline products: 39 mg. of biphenyl and 400 mg. of (II). Other fractions yielded oils that contained at least five other products. The structure of (II) was inferred from i.r., n.m.r., u.v., and mass spectral data. It was confirmed by synthesis from the known hydrocarbon, 13*H*-indeno[1,2-*l*]phenanthrene,[4] which was treated with n-butyl-lithium followed by carbon dioxide and finally methanol.



Two mechanistic rationales for the production of (II) are given. The path through (VI) is unusual in an acetylenic system, although analogies may be found in olefinic systems.[5] The cyclization of (I) to (III) is somewhat similar to several known photochemical intramolecular cyclizations between an aromatic ring and a triple bond.[6] The conversion of (IV) to (V) finds direct precedent in the reported conversion of 1,1,3- into 1,2,3-triphenylindene.[7] The conversion of (V) to (II) is an example of the well-known stilbene to phenanthrene ring closure.[8]



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