

New Oxetans from Carboxylate Esters: the Photocycloaddition of Ethyl Cyanoformate to Olefins

By YOSHINOBU ODAIRA, TAKASHI SHIMODAIRA, and SHIGERU TSUTSUMI

(Department of Chemical Technology, Faculty of Engineering, Osaka University, Osaka, Japan)

THE synthesis of various oxetanes by the photocycloaddition of ketones or aldehydes to olefins has been studied extensively in recent years.¹ There are, however, no reports about the formation of oxetans from carboxylate ester with olefins. We report here the photochemical synthesis of oxetans from ethyl cyanoformate with olefins.

Irradiation of a solution of ethyl cyanoformate

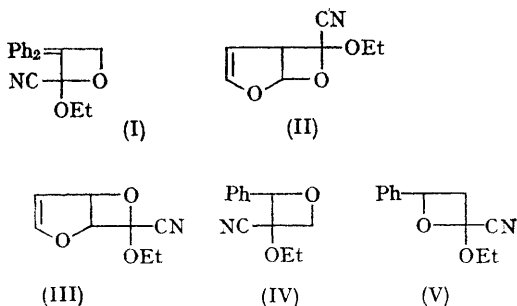
(0.5 M) and 1,1-diphenylethylene (0.1 M) with a 450w high-pressure mercury arc led to the formation of the oxetan (I) in 24.1% yield (based on consumed ethyl cyanoformate). Similarly, (II) and (III) were found upon irradiation of ethyl cyanoformate (0.22 M) in the presence of furan (0.66 M) in 16.2 and 8.1% yield, respectively.

When ethyl cyanoformate (0.66 M) and styrene (0.33 M) were subjected to these conditions, the products, (IV) and (V), were obtained in 17.1 and 8.5% yield.

The structures of the oxetanes obtained were characterized primarily by their distinctive n.m.r. spectra. In addition, the assigned structures of (I), (IV), and (V) were established by identifying the corresponding ring-opening products formed by acid hydrolysis of the above adducts.

Attempts to prepare new oxetans from diethyl oxelate with olefins are in progress.

(Received, June 22nd, 1967; Com. 634.)



¹ N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, 1965, pp. 208; J. S. Bradshaw, *J. Org. Chem.*, 1966, **31**, 237; Y. Shigemitsu, Y. Odaira, and S. Tsutsumi, *Tetrahedron Letters*, 1967, 55.