Photolysis of Diethyl Diazomalonate in the Presence of Thiobenzophenone

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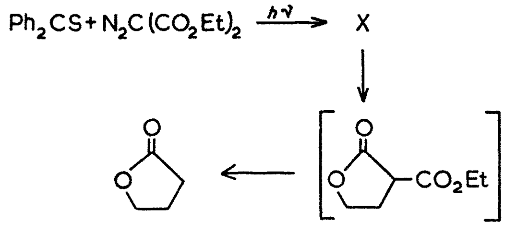
Summary The photolysis of diethyl diazomalonate with thiobenzophenone in cyclohexane produces significant amounts of γ-butyrolactone.

ALTHOUGH many studies have been made of intramolecular carbene insertion reactions, only one has been reported for an alkoxycarbonyl carbene.[1] We report a second such reaction where, unlike the first case, the lactone constitutes a major portion of the products.

Equimolar mixtures of diethyl diazomalonate and thiobenzophenone in cyclohexane were irradiated for 1—3 days in a Rayonet reactor at 2537 Å. One of the products proved to be γ-butyrolactone, isolated by column chromatography and g.l.c. and shown to be identical with an authentic sample. Other major products identified by g.l.c. included diethyl cyclohexylmalonate, diethyl 2,2-diphenylethylene-1,1-dicarboxylate, and benzophenone (probably formed during work-up). The molar ratios of lactone : malonate : alkene were 1·7 : 1·0 : 1·1; these three compounds represent almost the entire yield of photoproducts derived from the diazo-ester.

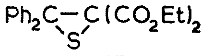
As already indicated,[2] and confirmed by us, diethyl cyclohexylmalonate is the primary photolysis product from diethyl diazomalonate alone in cyclohexane (80%). Lactonic materials, if present, represent only a very small fraction of the photoproducts. We observed the yield of dialkyl cyclohexylmalonate to be greatly reduced in the presence of thiobenzophenone, a phenomenon previously noted when dimethyl diazomalonate was photolysed in the presence of benzophenone.[3]



It seems reasonable that the lactone was formed by an intramolecular insertion reaction. While the presence of α-ethoxycarbonyl-γ-butyrolactone, the expected insertion product, has not been confirmed, the photolysis of this ester lactone in cyclohexane does lead to γ-butyrolactone. When the diazo-ester–thioketone photolysis is monitored by g.l.c., the diazo-ester disappears fairly rapidly, accompanied by the concomitant appearance of diethyl cyclohexylmalonate. Very little butyrolactone is present during this early stage; as time goes on, however, the butyrolactone peak increases in size, while the diethyl cyclohexylmalonate peak remains unchanged. This suggests the intermediacy of an adduct unobserved in the g.l.c. which on further irradiation gives rise to the lactone.

$Ph_2C:S:C(CO_2Et)_2$

(I)



$Ph_2C{-}C(CO_2Et)_2$ (bridged by S)

(II)

We are investigating the possible intermediacy of ylide (I) and/or thiiran (II) in these transformations [it is already known that the reactants do not combine thermally to form (II) at room temperature;[4] in refluxing diglyme, good yields of diethyl 2,2-diphenylethylene-1,1-dicarboxylate are obtained].

(*Received, April 10th, 1969; Com.* 494.)

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