

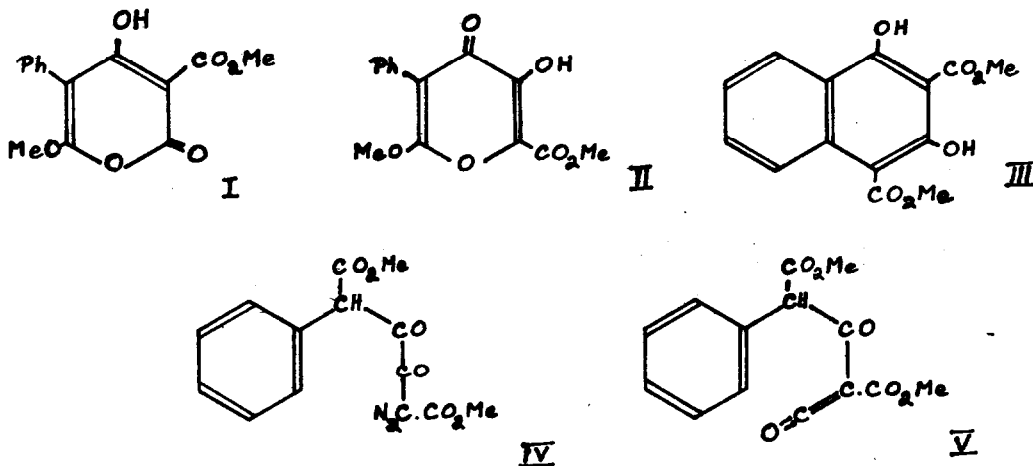
SOME REACTIONS OF DIMETHYL 2,5-BIS(DIAZO)-3,4-DIKETOADIPATE

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In furtherance of our studies on the generation of bisketens¹ we have examined the chemistry of dimethyl 2,5-bis(diazo)-3,4-diketoadipate. Photolysis of a methanol solution of this compound has been reported² to yield tetramethyl ethane-1,1,2,2-tetracarboxylate, presumably via Wolff rearrangement to the bisketen.



Photolysis or thermolysis of the bisdiaz compound in benzene provides two compounds. The major product (54%), m.p. 189-190^o, is assigned the pyrone structure (I) on the basis of its spectral properties. The infrared spectrum shows bands at 2500-3500(O-H), 1760 (C=O), and 1620 cm⁻¹ (hydrogen bonded C=O). The p.m.r. spectrum exhibits singlets at 4.92(CH₃O), 5.00(CH₃O₂C-), 7.32(C₆H₅) and 14.39 δ (O-H). The ultraviolet spectrum, λ_{max} 314 nm. (14,300) and 234 nm. (21,200) undergoes a pronounced bathochromic shift, λ_{max} 278 nm. (13,000) and 234 nm. (29,000), on addition of alkali thereby³ excluding the alternative structure(II).

Structure(III) is assigned to the minor product (16%) of the reaction, m.p. 147-8^o.

The infrared spectrum exhibits bands diagnostic of strongly hydrogen-bonded ester groups at 1590 and 1620 cm^{-1} . The p.m.r. spectrum shows singlets at 4.05($\text{CH}_3\text{O}_2\text{C}$), 13.40(O-H), 13.62(O-H) and a complex set of signals 7.20-8.80 δ (C_6H_4).

Analogous reactions occur between the bisdiazo compound and anisole, toluene, chlorobenzene, naphthalene and thiophene. The major product in each case is the α -pyrone.

We assume that the first step in the formation of (I) and (III) is the generation of (IV). The intermediacy of a free carbene in this step seems unlikely since the bisdiazo compound appears perfectly stable under comparable thermal conditions in the absence of an acceptable substrate. Subsequent Wolff rearrangement of (IV) to the keten (V) is then followed by cyclisation to (I) or (III).

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