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# THE THERMAL DECOMPOSITION OF α-DIAZOACETOPHENONE

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ALTHOUGH the uncatalyzed, thermal decomposition of several α-substituted α-diazoketones has yielded ketenes, these have not been isolated from the decomposition products of α-diazoketones of type $RCOCHN_2$ and investigation of such products has been scant.[3] In connection with a study of the Wolff rearrangement[4] we have examined the thermal decomposition of α-diazoacetophenone in dodecane.

The reaction was carried out in the dark at 140° under nitrogen for 12 hr. The major product (24%), m.p. 288-289° dec., $\lambda_{max}^{KBr}$ 5.68μ, was identical with the dilactone obtained by Pummerer and Buchta[5] by treatment of 3-benzoyl-2-phenylpropionic acid (I) with dehydrating agents in the presence of air; Wiberg and Hutton[6] have obtained the same product in 9% yield by the irradiation of solid α-diazoacetophenone. The dilactone is now assigned the revised structure (II) on the basis of its infrared spectrum.[6a]

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[3] W.E. Hanford and J.C. Sauer, Org.Reactions III, 108 (1946), and references quoted therein.

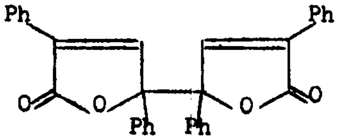
[4] T.J. Clark, Ph.D. Thesis, Harvard (1960).

[5] R. Pummerer and E. Buchta, Ber.Dtsch.Chem.Ges. 69, 1005 (1936).

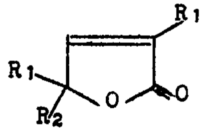
[6] K.B. Wiberg and T.H. Hutton, J.Amer.Chem.Soc. 76, 5367 (1954).

[6a] Professor H.H. Wasserman, Yale University, has kindly informed us that he has reached a similar conclusion regarding the structure of the dilactone: cf. R.M. Waters, Ph.D. Thesis, Yale University (1954); H.H. Wasserman, R.M. Waters, and J.E. McKeon, to be published.

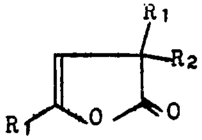
The related monolactone (III) m.p. 107-108°, $\lambda_{max}^{CH_2Cl_2}$ 5.68µ, $\lambda_{max}^{EtOH}$ 260 mµ (log ε 4.09), was also isolated in 4% yield; it was shown to be identical with the lactone m.p. 108° obtained by Pummerer and Buchta together with compound (II) in their dehydration of compound (I). An authentic sample was prepared by dehydration of compound (I) with acetic anhydride under nitrogen;



(II)



(III, $R_1$=Ph, $R_2$=H)
( V, $R_1$=Ph, $R_2$=$C_{12}H_{25}$)
(VIII,$R_1$=$(CH_3)_3C$, $R_2$=H)



(IV, $R_1$=Ph, $R_2$=H)
(VI, $R_1$=Ph, $R_2$=$C_{12}H_{25}$)
(VII, $R_1$=$(CH_3)_3C$,$R_2$=H)
(IX, $R_1$=$R_2$=Ph)

the crude syrupy product consisted largely of the enol lactone (IV) since its infrared spectrum showed an intense band at 5.55µ with a weaker band at 5.68µ, but the crystalline product, m.p. 107-108° isolated after chromatography on silica, showed a single intense carbonyl band in its infrared spectrum at 5.68µ and therefore must be the isomeric lactone (III).[7]

The following compounds were also isolated from the reaction mixture from the decomposition of α-diazoacetophenone and were identified by comparison with authentic samples: benzalacetophenone (8%), acetophenone (3.3%, as its 2,4-dinitrophenylhydrazone), trans-1,2,3-tribenzoylcyclopropane[9] (1.4%), 1,2-dibenzoylethane (0.4%), and benzoic acid (0.1%). In addition, a liquid product (0.7%) was isolated which is considered to be dodecyl phenylacetate since its infrared spectrum very closely resembled that of decyl phenylacetate[4] and it gave phenylacetic acid on hydrolysis. Two further products were isolated, but were obtained in insufficient amount for full purification and characterization: on the basis of their infrared and ultraviolet spectra they are believed to be lactones of type (V) and (VI).

The formation of compound (II) most probably proceeds *via* oxidation of compound (III), a process known to be facile.[6,10] Since the decomposition reaction was carried out in the absence of air, this oxidation must occur with the concurrent formation of reduction products; such must be the origin of the acetophenone and 1,2-dibenzoylethane. Compound (III) itself is most probably produced *via* formation of compound (IV); thus, Wiberg and Hutton[6] found that photolysis of 1-diazo-3,3-dimethyl-2-butanone gave, in addition to 2,2,6,6-tetramethyl-4-hepten-3-one,[11] the lactone (VII), which was isomerized to the lactone (VIII) at 180°. These authors suggested that the enol lactone was produced by reaction of the ketene formed by the photolytic decomposition of the diazoketone with unchanged diazoketone. Huisgen,[12] on

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[7] The recent suggestion[8] that the compound, m.p. 288-289°, has structure (IV) is unconvincing; we have found that on hydrolysis it yields both compound (I) and acetophenone, the formation of the latter is readily explicable in terms of structure (II), but not (IV).

[8] W. Davey and D.J. Tivey, *J.Chem.Soc.* 1230 (1958).

[9] C. Grundmann, *Liebigs Ann.* **470**, 284 (1929); J.F. Neumer, Ph.D. Thesis, Chicago (1957).

[10] Solutions of compound (III) on standing in air slowly deposited compound (II).

[11] *Cf*. the formation of benzalacetophenone in the thermal decomposition of α-diazoacetophenone.

the other hand, has suggested that the lactone is formed by reaction of the ketene with the species $RCO\ddot{C}H$, postulated as an intermediate in the *photo*chemical conversion of diazoketone to ketene. Because of our interest[4] in establishing whether, in the *thermal* decompsotion of diazoketones, the formation of ketenes occurs *via* an intermediate of type $RCO\ddot{C}H$ or directly by concerted migration and loss of nitrogen, we have sought to distinguish between these two types of pathway for lactone formation in the case of the thermal decomposition of α-diazoacetophenone.

The rate of decomposition at 139.2° of α-diazoacetophenone in dodecane in the presence of Tenox BHA[13] in evacuated, sealed ampoules was measured by the use of infrared spectrophotometry;[4] the rate was first order in diazoketone with $k = 5.1 \times 10^{-4} l.mole^{-1}sec^{-1}$. When an excess of diphenylketene was added to the reaction mixtures, the rate was too fast to measure, for over 90% of the diazoacetophenone had reacted in one minute. The product was shown to be the lactone (IX) by its properties, m.p. 120.8-121.4° (lit.[14] m.p. 117-118°), $\lambda_{max}^{CH_2Cl_2}$ 5.55μ, $\lambda_{max}^{EtOH}$ 270 mμ (log ε 4.18) and its hydrolysis to 3-benzoyl-2,2-diphenylpropionic acid, m.p. 184-185° (lit.[14] m.p. 182-183°), $\lambda_{max}^{KBr}$ 3-4, 5.86, 5.93μ. The accelerating effect of the addition of diphenylketene on the rate of decomposition of the diazoketone was also witnessed by the fact that, although no decomposition of α-diazoacetophenone in dodecane alone occurs at room temperature, decomposition does occur at room temperature in the presence of diphenylketene. The marked acceleration of the rate of decomposition can be accomodated only in terms of lactone formation by reaction between diazoketone and ketene as

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[12] R. Huisgen, *Angew.Chem.* *67*, 439 (1955).

[13] Tenox BHA (Tennessee Eastman Corporation) is a mixture of 2-t-butyl- and 3-t-butyl-4-methoxyphenol; variation in its concentration has been shown not to affect the rate of decomposition of α-diazoacetophenone.[4]

[14] F.R. Japp and F. Klingemann, *J.Chem.Soc.* *57*, 662 (1890).

proposed for the photolytic reaction by Wiberg and Hutton, and not in terms of a reaction scheme involving reaction of $\mathrm{RCO\ddot{C}H}$ with ketene. Thus these experiments provide no evidence for the intermediacy of the species $\mathrm{RCO\ddot{C}H}$ in the thermal conversion of diazoketones to ketenes. They do not, however, exclude this possibility, since rearrangement of such a species to the ketene might well predominate over alternative, intermolecular reactions.

*Note*: After the submission of this paper, a recent report on the thermal decomposition of α-diazoacetophenone in benzonitrile became available to us: R. Huisgen, H. König, G. Binsch, and H.J. Sturm, *Angew. Chem.* *73*, 368 (1961). A dilactone (19%) and a monolactone (32%) were obtained, which, although formulated as enol lactones, are most probably the compounds II and III, respectively, obtained in the present investigation. In addition, 2,5-diphenyloxazole (0.4%) was isolated; the yield of this product was appreciably increased when copper or copper compounds were used as catalysts. (The formation of 2,5-diphenyloxazole under the latter conditions has been observed in this Laboratory: P. Yates and M.J. Jorgenson, unpublished results.)