[Contribution from the Chemical Laboratory of Queens College]

PYROLYSES OF *cis*-PHENYLDIBENZOYLETHYLENE, ITS OXIMES, AND SOME RELATED HETEROCYCLIC COMPOUNDS

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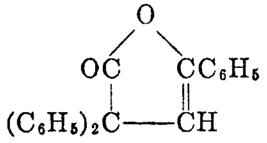
In this article are presented a number of observations made incidentally to a study of the oximes of *cis*-phenyldibenzoylethylene (1). In part these observations serve to correct some erroneous reports of long standing, in part they are new; collectively their application to analogously constituted compounds may be useful.

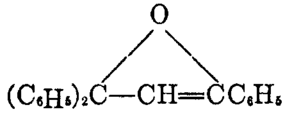
cis-Phenyldibenzoylethylene, its oximes, and the pyrroles and the 1,2,6-oxazines derived from the oximes undergo a variety of striking reactions on pyrolysis. These reactions include ring closure and ring opening as well as ring enlargement and contraction. *cis*-Phenyldibenzoylethylene (I) on pyrolysis undergoes ring closure to form triphenylcrotolactone (II) as Japp and Klingemann (2) reported many years ago. They also reported that the lactone on further heating lost carbon monoxide to furnish a product for which they suggested formula III.

$$C_6H_5COC(C_6H_5){=}CHCOC_6H_5$$

I



II

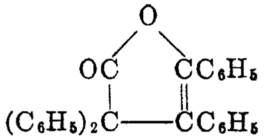


III

The physical properties of the pyrolysis product correspond, however, with those of β-phenylbenzalacetophenone, $(C_6H_5)_2C{=}CHCOC_6H_5$, and the suggestion was made in Beilstein's "*Handbuch*" that this final product might be β-phenylbenzalacetophenone (3). We have confirmed the correctness of this suggestion by a direct comparison of the pyrolysis product and the unsaturated ketone. This result brings the pyrolysis of *cis*-phenyldibenzoylethylene into line with that of dibenzoylstilbene (IV) which furnishes tetraphenylcrotolactone (V) and then diphenylbenzalactetophenone (VI) (2).

$$C_6H_5COC(C_6H_5){=}C(C_6H_5)COC_6H_5$$

IV

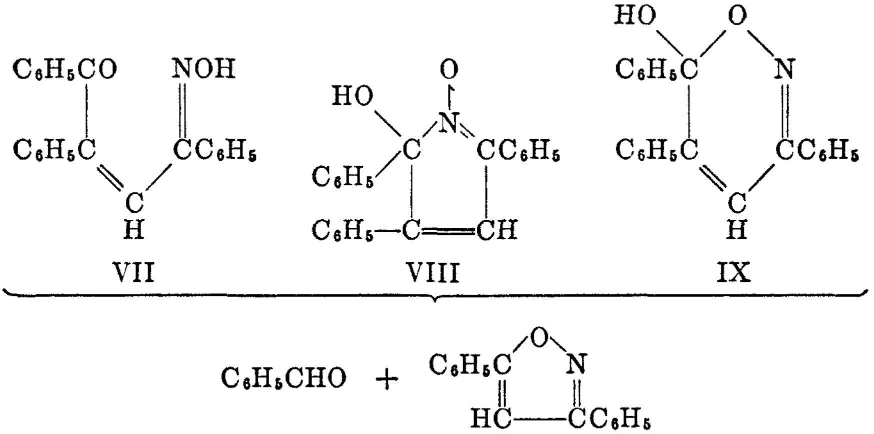


V

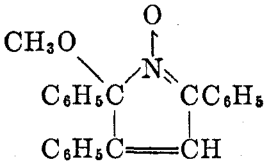
$$(C_6H_5)_2C{=}C(C_6H_5)COC_6H_5$$

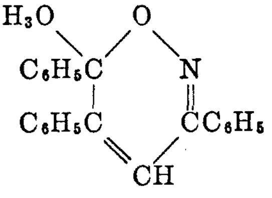
VI

The pyrolysis of *cis*-phenyldibenzoylethylene monoxime (VII) and its cyclic isomer (the nitrone VIII) was also described many years ago; the single pyrolysis product reported was benzonitrile (4). This was evidently the result of a faulty identification for both the oxime and the nitrone furnish benzaldehyde and 3,5-diphenylisoxazole on pyrolysis.

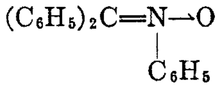

VII VIII IX

The same pyrolysis products, benzaldehyde and 3,5-diphenylisoxazole, are also obtained by heating the hydroxy-1,2,6-oxazine, IX. It seems reasonable to assume that the oxime on heating is converted *via* the nitrone to the hydroxy-1,2,6-oxazine which then undergoes thermal cleavage. The assumption that the nitrone, VIII, undergoes thermal ring enlargement to the hydroxy-1,2,6-oxazine, IX, is supported by the observation that the methoxy nitrone, X, does undergo an exactly comparable ring enlargement to furnish the thermally-stable methoxy-1,2,6-oxazine, XI, on pyrolysis.


X

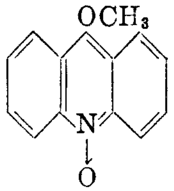

XI

The ring enlargement of the pyrrole nitrone, X, to the 1,2,6-oxazine, XI, is a new type of thermal behavior for nitrones. The open-chain nitrone, XII, yields benzaldehyde, nitrosobenzene, and azobenzene on pyrolysis (5), while the cyclic nitrone, XIII, furnishes acridone and formaldehyde (6). The open-chain nitrone, XIV, obtained from phenyldibenzoylethylene, undergoes ring closure on pyrolysis to yield triphenylfuran and, presumably, polymeric formaldoxime.

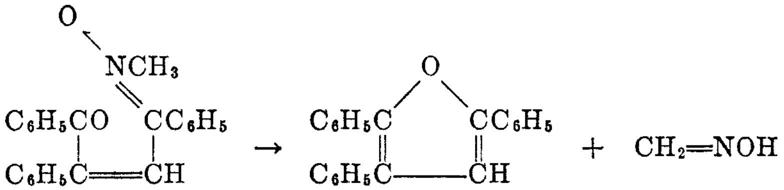


$(C_6H_5)_2C{=}N{\rightarrow}O$ (N—C_6H_5)

XII



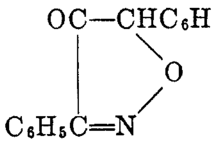
XIII



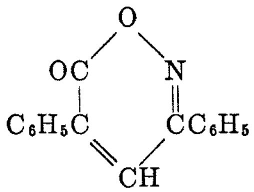
XIV

These three nitrones whose behavior on pyrolysis is known are not strictly comparable with the nitrone, X, for in this latter compound the group which shifts from nitrogen to oxygen during pyrolysis is both a benzyl and an allyl group. By analogy with the behavior of the nitrone, X, one would expect that open-chain nitrones with a benzyl or allyl group attached to nitrogen would undergo thermal pyrolysis to oxime O-ethers. Information on this point is not available in the literature, but Dr. A. C. Cope has informed us that he and Dr. A. C. Haven have found this type of rearrangement does take place.

In contrast to the novelty of the ring enlargement just described, the loss of a ring carbon atom as part of a carbonyl group, exemplified by the pyrolysis of the lactones, II and V, and the hydroxy-1,2,6-oxazine, IX, seems to be of some generality. Carbonyl bridges in diene adducts are frequently lost as carbon monoxide on heating (7), the isoxazolone, XV, loses carbon monoxide and yields benzaldehyde and benzonitrile (8), and the 1,2,6-oxazine, XVI, on heating in acetyl chloride loses carbon monoxide and furnishes 3,5-diphenylisoxazole (9).



XV



XVI

EXPERIMENTAL

Pyrolysis of cis-phenyldibenzoylethylene (10). Since the original description of this pyrolysis was lacking in details, some preliminary experiments were necessary. The diketone distills without change at 2 mm. At 25–30 mm. the diketone furnishes principally triphenylcrotolactone (II) (2) contaminated with a small amount of the *trans*-isomer of the diketone.

When triphenylcrotolactone was distilled at 150-160 mm., there was a noticeable evolution of gas and the distillate consisted of a mixture of β-phenylbenzalacetophenone and unchanged lactone. The lactone was removed by boiling with alcoholic potassium hydroxide and the β-phenylbenzalacetophenone, after crystallization from ethanol, was identified by a mixed melting point with an authentic specimen and by conversion to the oxime (11) and a mixed melting point with an authentic specimen of that material.

The remaining pyrolyses can for the most part be summarily described. They were carried out with 0.5–1.0-g. samples of material heated in Späth bulbs or test tubes in an air-bath and in the vacuum furnished by an effective oil-pump. Benzaldehyde, obtained from *cis*-phenyldibenzoylethylene monoxime (VII) (1a) and its cyclic isomers the nitrone, VIII, (1a) and the hydroxy-1,2,6-oxazine, IX, (1c) was condensed in a cold trap and identified by conversion to the phenylhydrazone and a mixed melting point with a known sample. 3,5-Diphenylisoxazole obtained from the same three pyrolyses was identified by comparison with a sample prepared from dibenzoylmethane and hydroxylamine (12). Triphenylfuran (13) obtained by pyrolysis of the open-chain nitrone, XIV, (1c) was also identified by comparison with an authentic sample.

The conversion of the methoxynitrone, X, (1a) to the methoxy-1,2,6-oxazine, (1c) XI, was studied with larger amounts of material as the pyrolysis is the most efficient method of preparing the methoxy-1,2,6-oxazine. When the methoxynitrone, X, is heated at a pressure less than 1 mm. the material distills at 215-220° and the product is the methoxy-1,2,6-oxazine, XI. From 4 g. of the nitrone, 3.8 g. of the 1,2,6-oxazine was obtained. The same conversion can also be effected without distillation. The nitrone in a distilling flask is heated in a vacuum until the solid melts and the liquid begins to boil. When the vigorous boiling ceases the product in the flask is the methoxy-1,2,6-oxazine.

SUMMARY

This article describes the behavior on pyrolysis of *cis*-phenyldibenzoylethylene, its oximes, and the heterocyclic compounds derived from these oximes.

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REFERENCES

(1) (a) Blatt, *J. Am. Chem. Soc.*, **56**, 2774 (1934); (b) **58**, 590 (1936); (c) *J. Org. Chem.*, **3**, 91, 506 (1938).
(2) Japp and Klingemann, *J. Chem. Soc.*, **57**, 669, 685, 689 (1890).
(3) Beilstein, **7**, 531, 836 (1925).
(4) Oliveri-Mendalà and Calderaro, *Gazz. chim. ital.*, **44** (II), 85 (1914).
(5) Staudinger and Miescher, *Helv. Chim. Acta*, **2**, 580 (1919).
(6) Kliegl and Brosamle, *Ber.*, **69**, 197 (1936).
(7) Allen, *Chem. Revs.*, **37**, 209 (1945).
(8) Blatt and Hawkins, *J. Am. Chem. Soc.*, **56**, 2190 (1934).
(9) Kohler and Goodwin, *J. Am. Chem. Soc.*, **49**, 222 (1927).
(10) The experiments with phenyldibenzoylethylene were done by Mr. C. M. Schwartz at the University of Buffalo.
(11) Dilthey and Last, *J. prakt. Chem.*, [2] **94**, 51 (1916); Vorlander, Osterburg, and Meyer, *Ber.*, **56**, 1136 (1923).
(12) Wislicenus, *Ann.*, **308**, 248 (1899).
(13) Smith, *J. Chem. Soc.*, **57**, 645 (1890).