

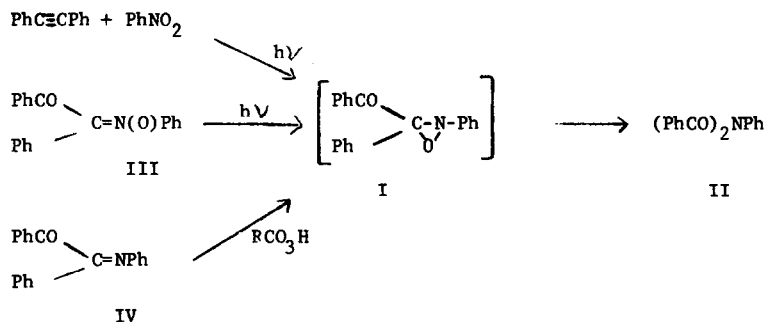
N-PHENYLDIBENZOYLOXAZIRANE

Monte L. Scheinbaum

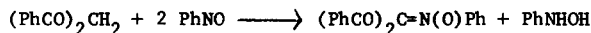
Esso Research and Engineering Company  
Linden, New Jersey

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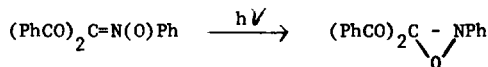
N-Phenylphenylbenzoyloxazirane (I) has been postulated as an intermediate in the photochemical reaction of diphenylacetylene with nitrobenzene.<sup>1,2</sup> The oxazirane has not been isolable; it presumably undergoes rapid thermal rearrangement to dibenzanilide (II). Similarly, this oxazirane has been proposed as an intermediate in the photolytic rearrangement of N-phenylphenylbenzoylnitron (III)<sup>1,2,3</sup> and in the reaction of peracids with benzil-anil (IV).<sup>2,3</sup> In each case the product is dibenzanilide.



We now wish to report the preparation of a related, but stable oxazirane by irradiation of N-phenyldibenzoylnitron (V). The latter is obtained from reaction of nitrosobenzene with dibenzoylmethane.<sup>4</sup> The photolysis of the nitron is carried out in benzene solution, with Pyrex apparatus, employing 3500 Å lamps. The photochemical conversion to N-phenyldibenzoyloxazirane (VI)<sup>5</sup> is essentially quantitative.



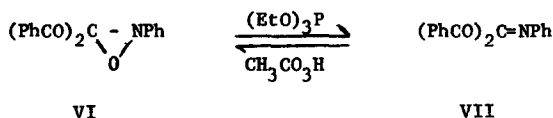
V



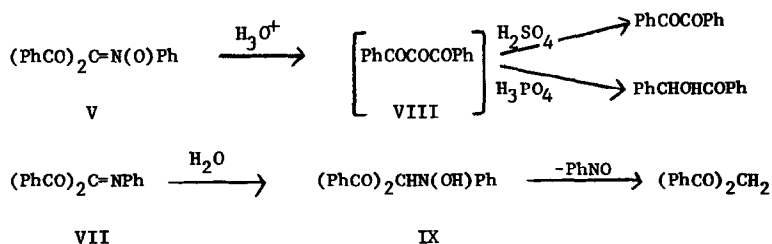
V

VI

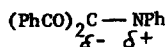
The oxazirane is quite stable, showing no tendency to undergo rearrangement to an N-benzoylated derivative or to regenerate nitron. The oxazirane can be recovered unchanged after heating to 250° in an inert atmosphere. Treatment with triethylphosphite affords the orange-red anil of diphenyltriketone (VII)<sup>6</sup>. The anil can be reconverted to the oxazirane on oxidation with peracetic acid.



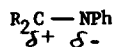
The anil undergoes gradual hydration in wet solvents. The hydration is catalyzed by mineral acid; introduction of one drop of dilute hydrochloric acid to an orange solution of the anil in 95% ethanol results in immediate disappearance of color. The n.m.r. spectrum of the product indicates that, aside from aromatic peaks, a one-proton peak is exchangeable with D<sub>2</sub>O and is concentration dependent. Another signal corresponding to one proton at  $\delta = 6.5$  ppm (in CDCl<sub>3</sub>) is unchanged in the presence of water, p-toluenesulfonic acid or mineral acid; and its position is independent of concentration. The hydroxylamine structure (IX)<sup>7</sup> is assigned to the product. The hydration appears to have taken place in a direction opposite to that usually encountered with Schiff bases. This is in contrast to the behavior of the nitron V, whose hydrolysis is believed to involve the intermediate formation of diphenyltriketone, VIII. The final products in this case are benzil or benzoin, depending upon whether the reaction is run in sulfuric or phosphoric acid.<sup>4</sup> The conversion of the anil, VII, to the hydrate IX occurs quantitatively. Pyrolysis of IX gives dibenzoylmethane in less than 10% yield.



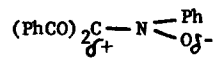
The unusual course of hydration of the anil (VII) is attributable to the influence of the electron-withdrawing benzoyl groups on the polarization of the C=N bond. The result (VIIa) is a reversed polarity with respect to an ordinary Schiff base (X) and to the nitron (VIIIa).



VIIa



X



VIIIa

Acknowledgment - The author is indebted to Mr. J. J. Porcelli for experimental assistance.

## REFERENCES

1. M. L. Scheinbaum, J. Org. Chem. 29, 2200 (1964).
2. M. L. Scheinbaum, Ph. D. Thesis, Harvard University, 1963.
3. A. Padwa, J. Amer. Chem. Soc. 87, 4365 (1965).
4. A. Schönberg and R. C. Azzam, J. Chem. Soc. 1428 (1939).
5. White crystals, mp 121° (from 95% alcohol), ir (CHCl<sub>3</sub>) 1680 with shoulder at 1700 cm<sup>-1</sup>, uv max. (95% EtOH), 2500 Å (log ε=4.32). Calculated for C<sub>21</sub>H<sub>15</sub>NO<sub>3</sub>: C, 76.58; H, 4.59; N, 4.25. Found: C, 76.73; H, 4.76; N, 4.31.
6. Red-orange precipitate, mp ~138°. Calculated for C<sub>21</sub>H<sub>15</sub>NO<sub>2</sub>: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.19; H, 4.73; N, 4.22.
7. White crystals, mp 176° (from 95% ethanol); ir (CHCl<sub>3</sub>) 1630 and 1690 cm<sup>-1</sup> (C=O) along with hydroxyl group absorption. Calculated for C<sub>21</sub>H<sub>12</sub>NO<sub>3</sub>: C, 76.12; H, 5.17; N, 4.23. Found: C, 75.75; H, 4.96; N, 4.05.