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PHOTOCHEMICAL GENERATION OF KETO-KETENE II FROM CYCLIC PHTHALOYL PEROXIDE.
INDIRECT EVIDENCE FOR BENZO-β-PROPIOLACTONE.

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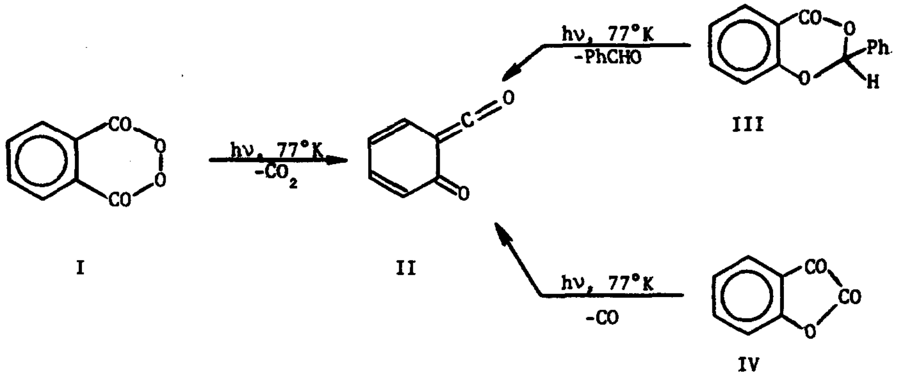
Cyclic phthaloyl peroxide (I) has been reported to give benzyne on irradiation in fluid solution.[1] We have investigated the photolysis of I in glassy matrices at low temperatures. In polar matrices, such as 2-methyltetrahydrofuran, ether-pentane-alcohol, and tetrahydrofuran-3-methylpentane mixtures, irradiation of I gives several products, among which II is most prominent. The identity of II was established by UV-visible spectral comparisons (Fig. 1) with authentic rigid solutions of II prepared by irradiation of III and IV, which had been shown to give II.[2,3] The spectra are strikingly similar to those of open forms of chromenes with



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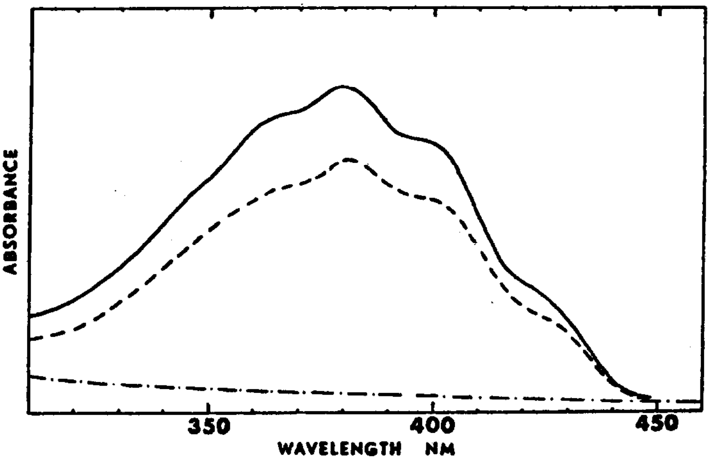
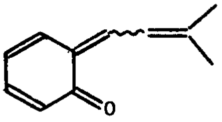


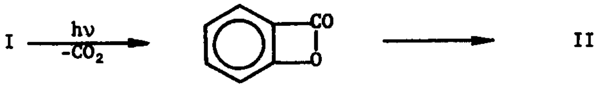
FIGURE 1. Full line: the first absorption band of keto-ketene II from phthaloyl peroxide I.
Broken line: the same band of II obtained by photolysis of III.
Baseline is also shown. 2-Methyltetrahydrofuran, 77°K.

closely related structure such as V.[4] The ketene II undergoes further photochemical transformations, which are presently under study. A plausible rationalization of the formation of II from



V

I involves the elusive β-lactone VI:



VI

According to some speculations, VI and II may play a role in the thermal generation of benzyne from benzenediazonium 2-carboxylate and from I.[5] So far, we have no conclusive spectral evidence for the independent existence of VI and it appears that its ring-opening to II is fast even at 77°K. An experiment at 4°K is in preparation.

One of the other products of matrix irradiation of I is apparently benzyne, since some biphenylene is formed upon melting (identified by its characteristic UV spectrum and by glc). No biphenylene is present before melting. However, we have not yet been able to identify conclusively absorption bands of benzyne[6] in the mixture.

The course of the photochemical reactions of I is remarkably sensitive to matrix polarity. Upon cooling to 77°K, a solution of I in 3-methylpentane or methylcyclohexane deposits much of I in the form of microcrystals, as evidenced by strong light-scattering and changes in the absorption spectrum. Irradiation of such samples gives very little if any II, but leads to formation of some biphenylene even before sample melting, and much more after sample melting. Benzyne is apparently formed now in a much cleaner reaction, but partially dimerizes inside the molecular aggregates of I. Further studies of additional glass-forming solvents and other benzyne precursors are in progress.

Similar striking effects of matrix polarity on the course of low-temperature photochemical reactions may account for some of the reported discrepancies between results of different authors.[3,7]

Acknowledgment

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