

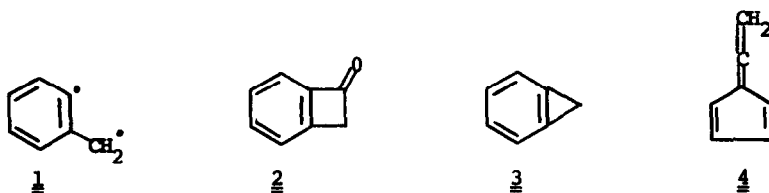
BENZOCYCLOBUTENONE : PYROLYSIS AND PHOTOCHEMISTRY

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Over the past few years we have studied a variety of  $C_7H_6$  intermediates,<sup>1</sup> one of which was the 1,3-diradical 1 generated from pyrolysis of benzocyclobutenone (2)<sup>1b</sup>; we found that 1 either collapsed to give benzocyclopropene (3) or rearranged to fulvenallene (4). In order to gain more insight into these reactions, especially with respect to synthetic control of the product distribution, we have now investigated the photochemical generation of 1 from benzocyclobutenone (2) in the gas phase via mercury photosensitization. In addition, we have reinvestigated the irradiation of 2 in alcoholic solution and have found that an unexpected ring cleavage occurs along with the previously reported formation of toluates.<sup>2</sup>



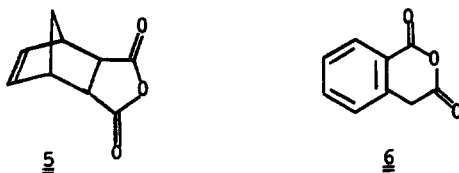
The mercury sensitized irradiation of 2 was carried out at reduced pressures (~54 $\mu$ ) in a quartz, tubular flow system as previously described.<sup>3</sup> About 70% of 2 was recovered along with benzocyclopropene (3) and fulvenallene (4)<sup>1b</sup> (1% and 5% yields, respectively, based on converted 2). Considerable deposition of polymer occurred on the reactor walls. 2 was quantitatively recovered when the gas phase irradiation was conducted in the absence of mercury.

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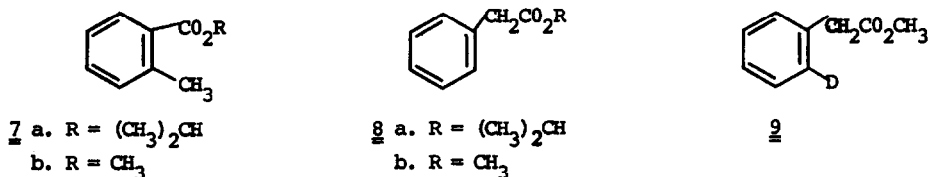
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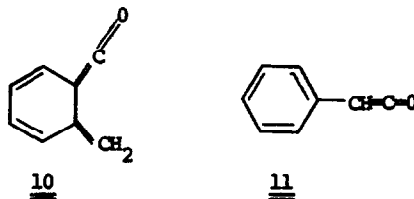
These results can be compared with the pyrolytic decarbonylation of 2. Pyrolysis of 2 at flash vacuum pyrolysis conditions<sup>1a,4</sup> at low pressures (ca. 0.05 Torr), short contact times (ca. 10 msec), and an oven temperature of 750° gave, after a vacuum line work-up, recovered 2 (69%), 3 (4.5%) and 4 (15%). An unsuccessful attempt was made to increase the yield of benzocyclopropene by carrying out the pyrolysis at increased pressures in the hope that the initially formed 3 would be stabilized.<sup>1e,f</sup> However, we were not able to find conditions where the yield of 3 could be increased although at higher temperatures ( $\geq 900^\circ$ ) the yield of 4 could be increased to 50 - 70%.

The availability of benzocyclobutenone (from the reaction of benzyne and vinylidene chloride followed by hydrolysis)<sup>5</sup> enhances the synthetic attractiveness of this route to 3 and 4 compared to the pyrolysis of the anhydrides 5<sup>1</sup> or 6<sup>5</sup>.



In contrast, when 0.3 M solutions of 2 in isopropanol or methanol were irradiated through Pyrex, we obtained the toluates 7 as the major product and, surprisingly, the phenyl acetates 8 as minor products (7a, 85%; 8a, 15%; 7b, 93%; 8b, 7%). These results imply that methylene ketene 10 and phenyl ketene 11 are key intermediates. However, the latter was ruled out by experiments where methanol-O-D was used as the solvent. Deuterated methyl phenylacetate was obtained whose nmr clearly indicated that all the deuterium was introduced in the aromatic ring, presumably at the ortho position (9); (nmr (CDCl<sub>3</sub>)  $\delta$  7.26 (s, 4),  $\delta$  3.66 (s, 3)  $\delta$  3.60 (s, 2). The nmr of the toluate product showed that deuterium was incorporated in the ortho methyl group as expected for 10; (nmr (CDCl<sub>3</sub>)  $\delta$  7.8-8.1 (m, 1),  $\delta$  7.0-7.16 (m, 3),  $\delta$  3.82 (s, 3),  $\delta$  2.55 (t, 2, J=2Hz). Finally, the recovered benzocyclobutenone did not incorporate deuterium.





The source of the unexpected phenylacetate product obtained in alcoholic solvent may involve a photochemically-induced solvolytic ring cleavage where nucleophilic alcohol attacks the carbonyl function in the excited ketone. It is interesting that aqueous sodium hydroxide cleaves benzocyclobutenone to give both *o*-toluic acid and phenylacetic acid.<sup>7</sup> Consequently, at least some toluate may be formed by a photosolvolytic ring cleavage by-passing 10.

It is well known that mercury photosensitization of carbonyl compounds leads predominantly to triplet state intermediates even though excited singlet states have been claimed as minor intermediates.<sup>8</sup> By analogy, it is likely that triplet biradical 1 is predominantly generated when 2 is irradiated in the presence of mercury, even though a singlet state intermediate may be a minor co-product. Thus, the interesting possibility of the rearrangement of triplet 1, which is probably the ground state, to triplet fulvenallene is raised in the photolytic experiments. Finally, if the pyrolytic decarbonylation does involve initial formation of methylene ketene 10, the latter is thermally unstable at the pyrolysis conditions.<sup>9</sup> Thus, no dimers from 10 were obtained from the pyrolysate after rapid quenching at liquid nitrogen temperatures.

#### References

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