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PHOTOADDITION OF METHYL PHENYLPROPIOLATE TO BENZENE.

PHOTOCHEMICAL PREPARATION OF 1-CARBOXYMETHYL-8-PHENYLCYCLOOCTATETRAENE

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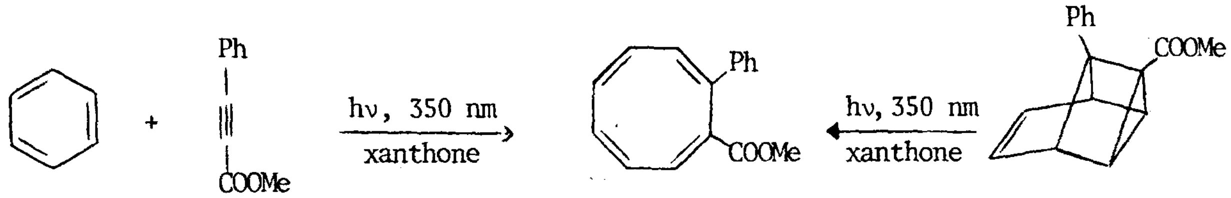
In the course of a recent series of studies of photoadditions of methyl phenylpropiolate 1 to fused heteroaromatic derivatives,[1,2] it became necessary to synthesize 1-carboxymethyl-2-phenylcyclooctatetraene 2. As we have recently reported[4] direct irradiation of 1 in benzene through Pyrex, gives methyl 5-phenyltetracyclo$[3.3.0.0^{2,4}.0^{3,6}]$oct-7-ene-4-carboxylate 3 (mp 74-75°)[4], rather than the previously reported cyclooctatetraene.[3]

Thus 1 (6.25×10^{-3}m) in benzene produces 3 (65-70%) when irradiated with a 450 W medium pressure mercury lamp through Pyrex for 72 hrs. Through quartz, however, at 95% conversion, 2 (38%) is produced as well as 3 (62%). Direct irradiation of 3 gave cyclooctatetraene 2 (24%), along with methyl phenylpropiolate (35%), when 3 was irradiated through quartz. At 253.7 nm with low pressure mercury resonance lamps the ratio 3/2 drops further. At 72% conversion 2, about (40%) is found among the products as well as 3 (32%).

The desired cyclooctatetraene 2 could be obtained exclusively (92%), however, from triplet sensitized irradiation of 3 at 350 nm with high energy sensitizers or from the sensitized reaction of 1 with benzene (eq. 1). In fact, this is the experimental method of choice for preparing the cyclooctatetraene. At incomplete conversions of 1, however, small amounts of 3 also could be detected in the crude reaction mixture.

The preparation of 2 was carried out in the following way. A solution of 490 mg (2.06 mmol) of 3, and 300 mg (1.53 mmol) of xanthone in 650 ml nitrogen degassed benzene was irradiated in a Rayonet reactor equipped with 16 350 nm lamps for 40 hrs. When the starting material had been completely consumed, as shown by nmr, the solvent was removed on a rotary evaporator. The chromatographed product 2 (452 mg, 92%) exhibited the same spectroscopic properties as a sample obtained by pyrolysis[4] of 3 at 180°.

A solution of 620 mg (3.87 mmol) of 1 and 500 mg (2.55 mmol) of xanthone in 650 ml nitrogen degassed benzene was irradiated as above for 68 hrs. After work-up as above, 588 mg of 2 (65%) was isolated.



1 2 3 (1)

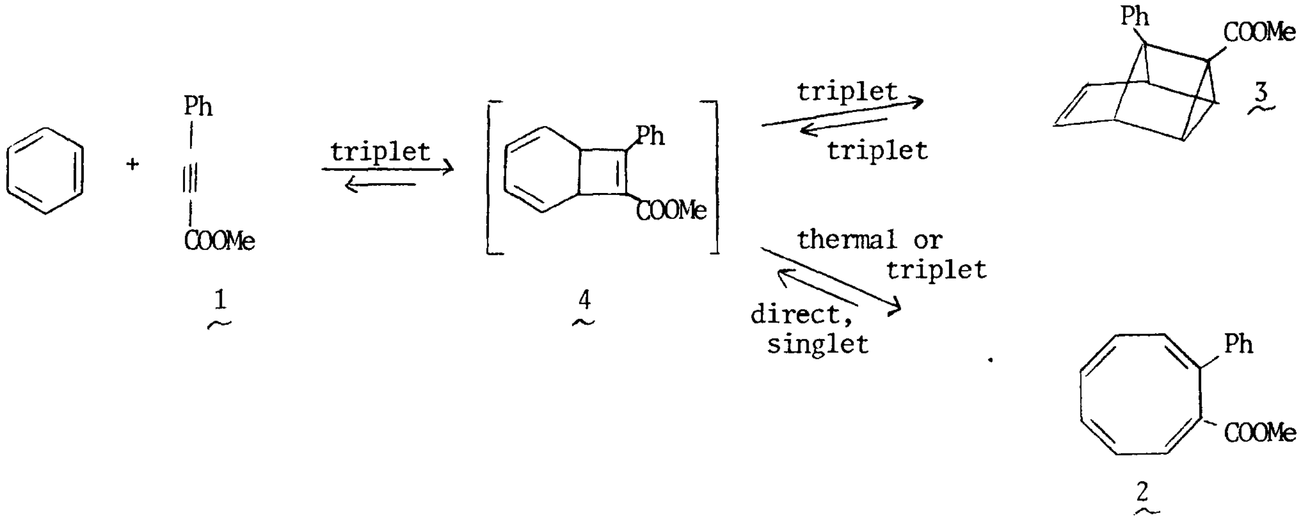
On irradiation of a solution of 1 in benzene in presence of the sensitizer benzophenone at 350 nm both 2 and 3 are obtained. The 2/3 ratio strongly depends on the amount of sensitizer used. At relatively high concentrations of benzophenone the amount of 2 increased, suggesting that the reverse reaction 2→3 (via 4) is not operative. Control experiments confirmed this result. Under the conditions described above 3 appears to be photostable upon irradiation, Table I.

Table I. Direct and sensitized irradiations of 1, 2, and 3 under different conditions.

Conc. starting material x 10^{3}M		Method	Time Hrs.	Sens. x 10^{3}M	Relative product ratio (%) 1	2	3
1	7.5	A	15	----	no reaction	---	---
1	7.5	A	15	1.5[a]	5	90	5
1	19.2	A	27	3.9[a]	41	50	9
1	7.5	A	21	7.5[b]	10	43	47
1	6.3	B	72	----	19[c]	none	55[c]
1	10.2	B	20	----	72	---	28
1	10.2	C	6	----	trace	38	62
1	31.2	C	15	----	45	15	40
1	1.9	D	5	----	28	39	33
2	1.0	B	42	----	none	none	90[c]
2	1.0	C	22	----	14	37	49
3	2.5	A	76	3.0[a]	---	95	5
3	3.2	A	40	2.3[a]	none	92[c]	none
3	2.5	A	48	3.3[b]	---	---	no reaction
3	1.2	C	20	----	35	24	41

a. xanthone as sensitizer
b. benzophenone as sensitizer
c. isolated yields; method A: Rayonet reactor fitted with 16 350 nm lamps; method B: immersion well apparatus through Pyrex with 450 W medium pressure mercury lamp; method C: identical as method B but through quartz.

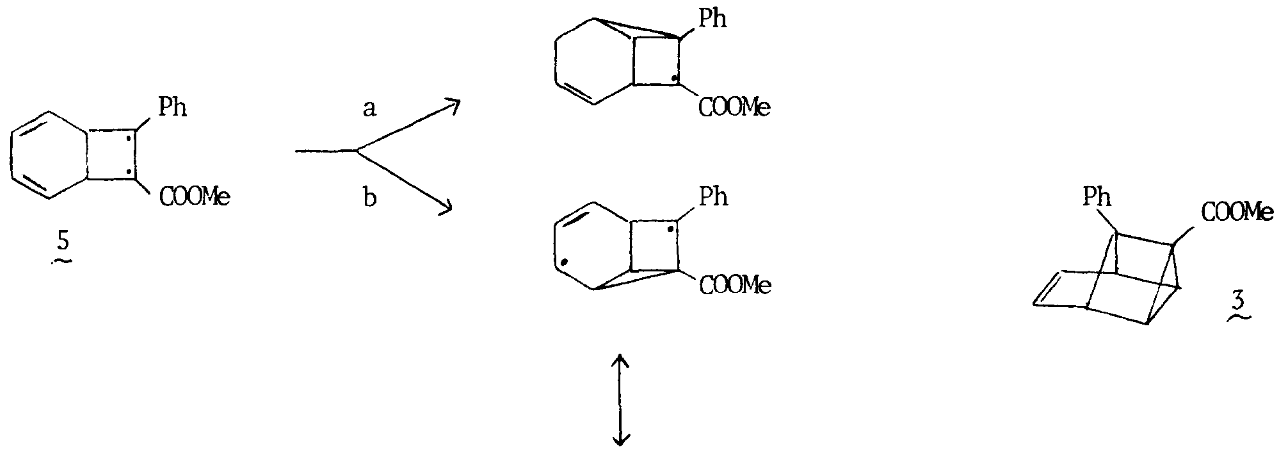
The photoaddition of 1 to benzene likely proceeds by way of a bicyclo[4.2.0]octa-2,4,7-triene 4. Such an intermediate has been isolated in the photoaddition of phenylacetylenes to hexafluorobenzene.[5] Unless 4 rearranges to 3 by an energy transfer process, 4 must live long enough to absorb a second photon in competition with residual 1 in the direct irradiation.

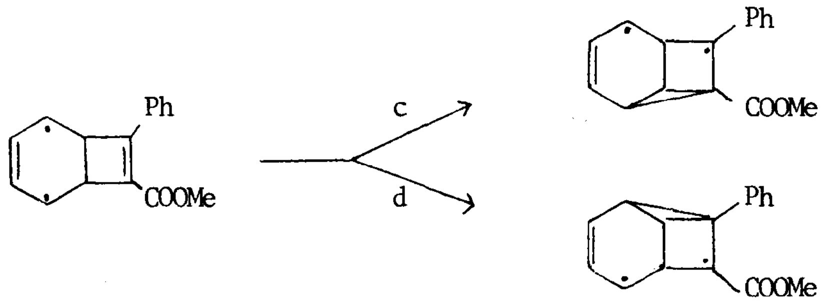


This photochemical process must also compete with the thermal and/or photochemical ring opening leading to 2. Surprisingly, no 2 could be detected at low conversions from 1 or at 50°, where we expect the thermal ring opening of 4 to be very efficient. Therefore, all the cyclooctatetraene thermally and/or photochemically formed must be very efficiently converted into 3 under the reaction conditions.

From the sensitized experiments it is clear that 4 is formed from triplet 1 (E_T < 69 kcal mol^{-1}) and ground state benzene, in accordance with quenching studies for the addition of t-butylphenylacetylene to hexafluorobenzene.[5] Since 4 absorbs no light directly, the formation of 3 from 4 also proceeds via a triplet state.

We suggest the following pathway for obtaining 4→3, based on the presumption that an appreciable concentration of 4 accumulates.[6] Triplet 4 (E_T < 69 kcal mol^{-1}) can undergo bond formation in four different ways (a-d). In view of biradical stability arguments a and d are unlikely.





Since di-π-methane rearrangements of the biradicals 5 and 6 lead to semibullvalenes,[7] by energetically less favorable processes 3 is the preferred product.

Low temperature experiments designed to elucidate further these processes are in progress.

Acknowledgment

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