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CYCLIC DIMER OF 1,2-DIBENZOYLACETYLENE[1]

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1,2-dibenzoylacetylene has been found to be cyclodimerized and rearranged thermally. Similar products have been obtained from the bis-para- chloro and bis-para-bromo benzoyl acetylenes. The proposed structure which we believe proceeds via a cyclobutadiene intermediate is shown in the figure.

Acetylene and substituted acetylenes have been found to be cyclooligomerized by heat,[2] irradiation,[3] or some metal catalysts.[4] In many cases cyclobutadiene derivatives have been proposed as intermediates, and the recent isolation of a number of metal-cyclobutadiene complexes support this view. We wish to report a thermal cyclodimerization and rearrangement which is proposed to proceed via a cyclobutadiene intermediate.

When 1,2-dibenzoylacetylene is heated to 150-200° for several hours, either by itself or in a high-boiling solvent such as decalin or dichlorobenzene, thin yellow platlets are deposited, m.p. 206°. The elemental analysis and mass spectrum leave no doubt that the product is a dimer, $C_{32}H_{20}O_4$. Similar products are obtained from the bis-para-chloro- and bis-para-bromo benzoylacetylenes. The principal peaks of the mass spectrum are shown in Table 1. Except for the unexplained peak at m/e 169, the major fragments result from loss of phenyl and benzoyl groups. Sufficient rearrangement has occurred upon dimerization to prevent easy reformation of the monomer, as only a small ion is observed at m/e 234. The infrared spectrum exhibits not only two carbonyl peaks at 1620 and 1650 cm^{-1}, but an OH stretching vibration at 3640 cm^{-1}. There is apparently only one hydroxyl group, as the compound will form only a monoacetate (characterized by elemental analysis and mass spectroscopy), in which the 3640 cm^{-1} peak is no longer present. Treatment of the dimer with refluxing hydrazine hydrate yields an azine $C_{32}H_{20}O_2N_2$, m.p. 240°, which has no bands assignable to NH or CO groups, showing that the dimer has two and only two carbonyl groups. The mass spectrum of the azine is also shown in Table 1: it shows no fragments due to loss of a benzoyl group, and, like the dimer, no fragmentation into the monomer.

TABLE 1

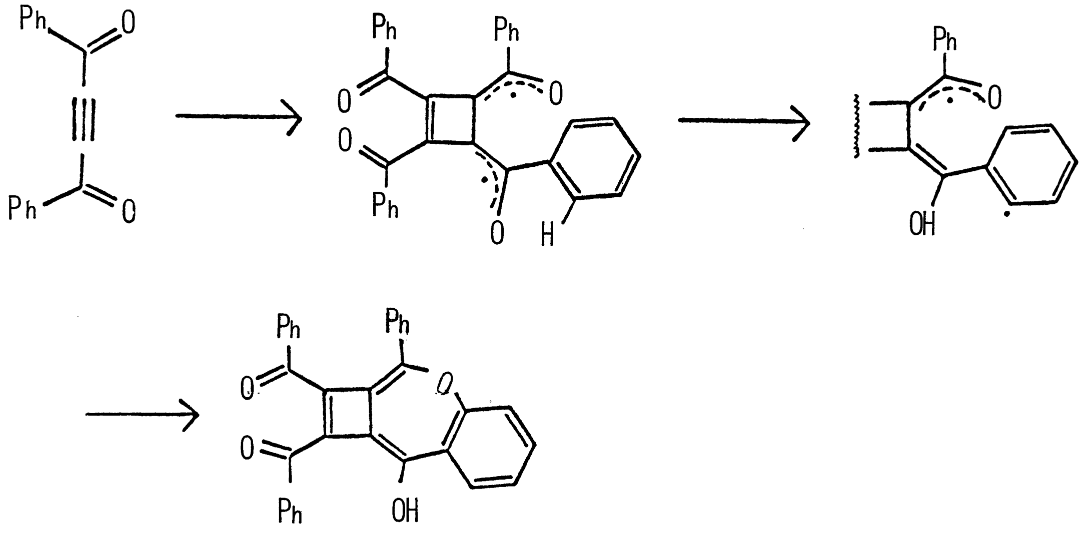
Mass Spectra* of I and the Azine of I

	Dimer			Azine	
m/e	Intensity	Assignment	m/e	Intensity	Assignment
470	5	P + 2	466	1	P + 2
469	26	P + 1	465	5.5	P + 1
468	74	P	464	14.5	P
451	4	P - OH	447	19.5	P - OH
391	25	P - C_6H_5	448	7	P - H_2O
363	4	P - C_6H_5CO	387	4	P - C_6H_5
			359	0.5	P - C_6H_5CO
313	7	P - 2 x C_6H_5	302	5.5	
			300	3.5	
276	5				
234	2	P/2	279	13	
202	4		232	3	P/2
201	5		167	21.5	
200	4		149	63	
196	9		113	15	
105	20	C_6H_5CO	105	10	
77	5	C_6H_5	97	15	
			95	15	
51	5		85	16	

* Sample temperature 185°, 75v ionization potential.

Since there are no further C=O or OH groups, the fourth oxygen atom of the dimer must be an ether linkage. In addition, one of the phenyl rings is disubstituted, as one aromatic proton has become part of the OH group in the dimer. The proposed structure of the dimer, I, and the mechanism of its formation are shown in the Figure 1.

FIGURE 1



I

Bis-methylene cyclobutenes are sufficiently thermally stable to be stable under these conditions, as bis-methylene cyclobutene itself is formed from 1,5-hexadiyne by heating to 300° for 96 sec.

The dimer was sufficiently insoluble that only very weak nmr spectra could be obtained, which show only a number of multiplets in the aromatic region and yield no further structural information. Attempts to obtain crystals of this material suitable for single-crystal x-ray diffraction analysis are in progress.

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