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SOME REACTIONS OF 1,2,3-TRIBENZOYLCYCLOPROPENE

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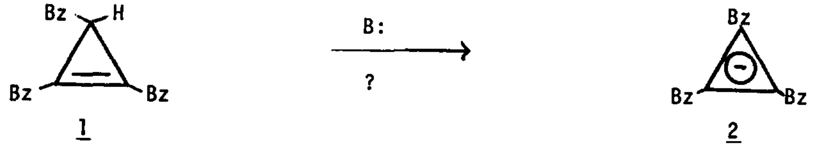
The cyclopropenyl anion is the simplest antiaromatic system. Evidence has been accumulated[1] that this anion is destabilized by conjugation and strain, and that most substituted derivatives are of very high energy indeed. However, a reasonable extrapolation of substituent effects to this system suggests that compounds such as 1,2,3-tribenzoylcyclopropene (1) should have a pK_a low enough to make the corresponding anion 2 accessible. One approach to the whole system would involve generating the cyclopropene 1 with base, followed by further removal of the proton with base to furnish the symmetrical tribenzoylcyclopropenyl anion 2. Accordingly, we have prepared the bromotribenzoylcyclopropane 3, mp 165.5-166°,[2] in 57% yield and the chlorotribenzoylcyclopropane 4, mp 147-148°,[2] in 35% yield, by reaction of the trans-1,2-dibenzoylhaloethylene with dimethylsulfonium phenacylide.[3] Both compounds readily eliminated[4] hydrogen halide to generate the cyclopropene 1, but in every case this cyclopropene then underwent further complex changes.

3: X = Br
4: X = Cl



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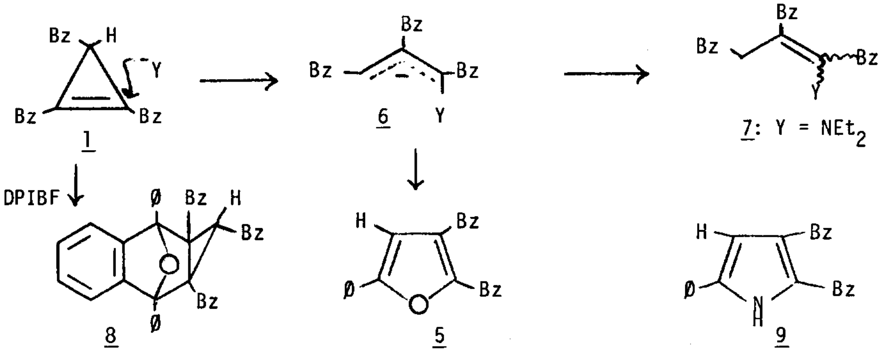
2

Bz = benzoyl

For instance, on heating with triethylamine in benzene, 3 afforded 2,3-dibenzoyl-5-phenylfuran (5), mp 151.5-152°,[2] in 80% yield. With hydrazine, 5 afforded the expected triphenylfuranopyridazine, mp 239-240.5°.[2] Treatment of 3 with $LiNEt_2$ in Et_2NH at room temperature produced a deep red color (6); on quenching and chromatography the product was the furan 5 and a mixture of the cis- and trans-isomers of 1-diethylamino-1,2,3-tribenzoylpropene (7). The structure of 7 followed from its spectroscopic properties and from a direct synthesis starting with 1,2,3-tribenzoylpropene (treatment with NBS, then diethylamine). On standing in base, compound 7 was converted to the furan 5. A careful study revealed that in Et_2NH alone the halide 3 disappears over the course of 4 min, the aminopropene 7 builds to a maximum and then disappears again in favor of furan 5, which is the only component after 15 min. With EtO^- in EtOH 3 is converted to the ethoxytribenzoylpropene mixture and thence to the furan 5.

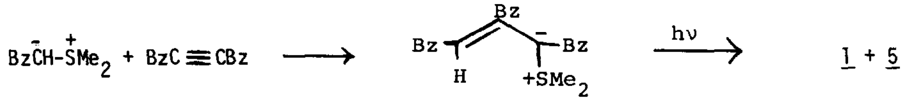


The mechanism shown implies a base-induced elimination from 3 to form the cyclopropene 1 as the first step, and indeed this can be demonstrated by performing the elimination in the presence of diphenylisobenzofuran (DPIBF). With a mixture of DPIBF and Et_2NH in tetrahydrofuran 3 is converted to furan 5 and to 8, mp 265.5-266.5°,[2] the DPIBF adduct of 1. The ratio of furan to adduct was directly proportional to the ratio of Et_2NH to DPIBF; thus the two products are derived from competition for a common intermediate, undoubtedly 1. Similar trapping experiments in deuterated solvents under a variety of conditions afford 8, without deuterium. Thus 1 does not exchange before trapping.

In contrast to the halo derivative 3, tribenzoylcyclopropane is quite stable to base. On refluxing for 2 hr in Et_2ND it is recovered structurally unchanged although 50% deuterated on the cyclopropane ring, but on reflux with NaH it does undergo ring opening to tribenzoylpropene. The deuteration without ring opening suggests that ring opening in the attack of Y^- on 1 occurs before full development of the enolate.

We have also examined hindered bases. To a solution of 3 and DPIBF in THF at -78° was added various amounts of a solution of $NaN(SiMe_3)_2$. Quenching afforded a ∿50% yield of the adduct 8. By contrast, if the DPIBF was added to the reaction mixture only after 3 had stood with the base at -78° for 3 min, then no adduct was formed. Apparently even this very hindered base attacks 1, and more readily than it reacts with 3 so that the use of smaller amounts of base simply resulted in recovered 3 along with the transformation of 1. After workup the major material isolated was the pyrrole 9, which must be formed in a fashion similar to that shown for the furan. The same pyrrole 9, mp 193-194°,[2] was obtained in good yield if 3 was treated with NH_3 in THF at room temperature. Similarly, reaction of 3 with sodium triphenylmethide and DPIBF gave adduct 8 only if the DPIBF was present at the time of base addition. Otherwise, a series of products were formed from addition of triphenylmethide to 1. Potassium 4-methyl-2,6-di-t-butylphenoxide[5] also added to 1, and 1,8-bis(dimethylamino)naphthalene converted 4 to 5. Treatment of 3 with NaH afforded adduct 8 only if DPIBF was initially present. In its absence a 40% yield of a dimeric compound is produced, mp 286-290°,[2] which is apparently hexabenzoylbenzene, m/e 702.

Cyclopropenes have also been generated[6] by photolysis of sulfonium allyides. We prepared the allyide 10, mp 160-161°,[2] (dec), by reaction of dimethylsulfonium phenacylide with dibenzoylacetylene in chloroform. When this was photolyzed in CH_2Cl_2 at room temperature, starting material disappeared rapidly and furan 5 was obtained in 57% yield. Photolysis in the presence of DPIBF did not produce adduct 8, but if the photolysis of 10 was performed at -78°, and DPIBF was then added, adduct 8 was obtained in 3-7% yield, along with 31% of furan 5. Thus, the tribenzoylcyclopropene 1 is in fact present in low concentrations and stable in this reaction mixture. If the solution is allowed to warm to 0° before DPIBF is added then no adduct 8 is formed.



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It is thus apparent that 1,2,3,-tribenzoylcyclopropene 1 can be generated under a variety of conditions. It can even be demonstrated to have a limited independent stability at low temperature in the photolysis experiments. However, all bases examined were able to attack the very strained double bond and thus lead to further transformation products of 1. The only possible exception is NaH, but even here there is no evidence for the production of tribenzoylcyclopropenyl anion instead. Thus, while the hydrogen in tribenzoylcyclopropene might indeed have some reactivity towards appropriate bases, in all the systems we have examined the double bond is instead the preferred point of attack.[7]

References

1. For a review, cf. R. Breslow, Accts. Chem. Res., **6**, 393 (1973).
2. Satisfactory analyses, nmr, mass, uv, and infrared spectra support the assigned structure.
3. B.M. Trost, J. Amer. Chem. Soc., **89**, 138 (1967).
4. Cf. K.B. Wiberg, R.K. Barnes, and J. Albin, J. Amer. Chem. Soc., **79**, 4994 (1957) for an early example of such a process.
5. Cf. H.C. Brown, H. Nambu, and M.M. Rogic, J. Amer. Chem. Soc., **91**, 6852 (1969).
6. B.M. Trost and R.W. LaRochelle, J. Amer. Chem. Soc., **92**, 5804 (1970).
7. Taken in part from the Ph.D. theses of T.P. Higgs (1971) and J.M. Pecoraro (1973). Support of this work by NIH is gratefully acknowledged.