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THE DIMER OF 1,3-DIBENZOYLALLENE

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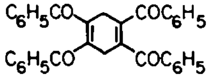
Abstract—Structure XIII is deduced for the yellow dimer of 1,3-dibenzoylallene (I).

In a thesis presented in 1958,[1] Gaudemar-Bardone recorded the first synthesis of a symmetrical allenic diketone, 1,3-dibenzoylallene (I). As one might expect, the compound is relatively sensitive to heat and oxidation and reacts readily with various nucleophiles at the central carbon atom. Less predictably this substance dimerizes rather easily upon simple evaporation of its acetone or ethanol solutions to give a stable orange product. We found this latter property interesting and somewhat curious but were reluctant to accept the dihydrobenzene structure (II) suggested for the dimer. The proposal is not only difficult to reconcile with the reported failure of the dimer to aromatize to a tetrabenzoylbenzene under a variety of conditions, but it also has mechanistic implications which we would prefer not to accept. Demonstration of the structure of this compound could add to the meager information available concerning the properties of the monomer, and we have accordingly investigated its chemical and physical properties.

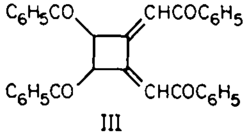
$C_6H_5COCH{=}C{=}CHCOC_6H_5$

I

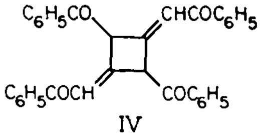


II

In our hands 1,3-dibenzoylallene dimerizes in concentrated acetone solution at temps from 5° to 56°. The reaction is accompanied by considerable resinification and is unaffected by the presence or absence of light. While the reaction occasionally failed to produce any dimer at all, yields were generally 40–50% and were independent of variations in conditions. The dimer precipitates from the reaction mixture as largish orange prisms; recrystallization from ethanol or dichloromethane–ethanol furnishes fine yellow to orange needles, m.p. 201–201·5° (rep. m.p. 204°[1]). In the UV this compound shows three high intensity maxima at 247 (34,800), 286 (21,500) and 398 mμ (25,900)[2]. Its NMR spectrum[3,4] contains aromatic absorption at 7·5 ppm (20 H, multiplet) and three singlets at 4·32 (2H), 5·63 (1H) and 8·73 ppm (1H).



III



IV

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[1] F. Gaudemar-Bardone, *Ann. Chim. Paris* XIII 3, 52 (1958).

[2] Measured in 95% EtOH.

[3] NMR spectra were measured with a Varian Assoc. Model A-60 spectrometer; chemical shifts are expressed in ppm downfield from external tetramethylsilane.

[4] Measured in perdeuterodimethyl sulfoxide. Similar results were obtained in $CDCl_3$.

In considering structures for this substance, we favoured two possible modes of dimerization. The first is a simple cycloaddition reaction leading to a four-membered ring. Head-to-head dimerization would yield III, while head-to-tail addition would give IV; in either case, the final product might well be the cyclobutene double bond isomer.[5] The above spectral data fail to accord with expectation for such structures and are sufficient to eliminate them from further consideration.[8] Alternatively, the dimerization could be a Diels-Alder reaction utilizing the α,β-unsaturated carbonyl system of one molecule as diene with a carbon-carbon double bond of the second molecule as dienophile, and furnishing initially V or VI.[9] In either case, one would probably expect a prototropic shift to the more stabilized γ-pyrone methide, VII or VIII. While both V and VI may be ruled out, since neither should give a two proton NMR signal, possibilities VII and VIII require further consideration. No good UV model is available for these chromophores, but the reported spectrum of the simpler IX ($\lambda\lambda_{max}$ 243 (7240) and 358 mμ (26,300))[2,10] indicates that VII or VIII could well absorb at 398 mμ. The NMR spectrum of IX[10] also encourages closer investigation of these structures, for the signal of the vinylic proton adjacent to the acetyl group in IX appears at an unusually low field (7·6 ppm). The remaining two signals found for the dimer are similarly reasonable for VII and VIII. The nuclear protons of IX are at 5·65 and 5·23 ppm while a variety of γ-pyrones give signals for such protons at 5·4–6·4 ppm.[11] The methylene signal at 4·22 ppm is unexceptional for these structures.

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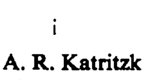
[5] Formation of such structures would find ample analogy in the dimerization of allene itself (cf. Ref. 6) and in the cycloaddition of allenes to dienophiles (cf. Ref. 7). In each of these cases cyclobutanes are formed, although under more energetic conditions.

[6] Y. M. Slobodin and A. P. Khitrov, *Zh. Obshch. Khim.* **33**, 153 (1963); J. K. Williams and W. H. Sharkey, *J. Amer. Chem. Soc.* **81**, 4269 (1959); A. T. Blomquist and J. A. Verdol, *Ibid.* **78**, 109 (1956). The original observation is that of S. V. Lebedev, *J. Russ. Phys. Chem. Soc.* **45**, 1249 (1913), esp. p. 1357 ff.

[7] K. Alder and O. Ackermann, *Chem. Ber.* **90**, 1697 (1957); H. N. Cripps, J. K. Williams and W. H. Sharkey, *J. Amer. Chem. Soc.* **80**, 751 (1958).

[8] The longest wavelength ultraviolet absorption expected from these structures should be that of the 1,4-dibenzoylbutadiene system of III. 1,4-Dibenzoylbuta-1,3-diene itself shows a single λ_{max} at 307 mμ (29,600). Cf. H. H. von Ziegler, C. H. Eugster and P. Karrer, *Helv. Chim. Acta* **38**, 613 (1955).

[9a] That α,β-unsaturated ketones and aldehydes can function as diene components is well known, simple examples being the dimerization of acrolein at elevated temps (K. Alder and E. Rüden, *Ber. Dtch. Chem. Ges.* **74**, 920 (1941)), and the spontaneous self-addition of 2-methylenecyclohexanone (C. Mannich, *Ibid.* **74**, 557, 565 (1941)). There are a number of examples of allenic double bonds serving as dienophiles (cf. E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.* 4073 (1956)). [b] A further example involving a cumulated bond system is the dimerization of the acylketene i to the acylpyronone ii. (H. Stetter and K. Kiehs, *Chem. Ber.* **98**, 1181 (1965). Additional examples are included in this report.)

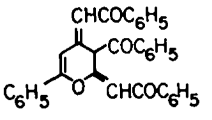


i

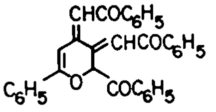
ii

[10] A. T. Balaban, P. T. Frangopol, A. R. Katritzky and C. D. Nenitzescu, *J. Chem. Soc.* 3889 (1962).

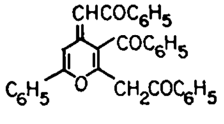
[11] M. A. Butt and J. A. Elvidge, *J. Chem. Soc.* 4483 (1963); A. K. Ganguly, T. R. Govindachari and P. A. Mohamed, *Tetrahedron* **21**, 93 (1965).



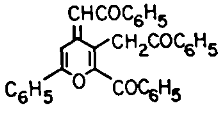
V



VI

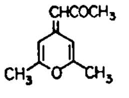


VII

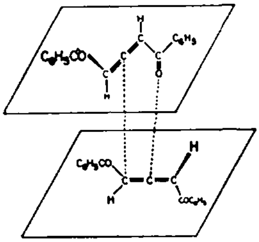


VIII

Confirmation of a pyrone methide structure for the allene dimer was provided by reaction with strong acid. Both VII and VIII are vinylogous γ-pyrones and should be weakly basic. Compound IX, for example, yields a number of crystalline salts, some of which are hydrolyzed in water.[10] Treatment of the dimer in acetic acid solution with excess perchloric acid furnished a beautiful red-orange salt. Elemental analysis indicated the addition of one mole of perchloric acid, and the salt was instantly dissociated in ethanol or acetic acid by addition of water to give a yellow mixture from which the dimer could be isolated.



IX



X

Evidence outlined below indicates that of the two isomeric methides, VII is the correct structure. First, examination of molecular models points to X as the sterically most favourable orientation of two molecules of dibenzoylallene for Diels-Alder addition, an arrangement which leads to VII after prototropic shift. The orientation necessary for VIII requires one of the addends to be rotated 180° in its plane, leading to overlap of the two hydrogen atoms outside the planes during reaction.

Other evidence bearing on the structure of the dimer derives from its behaviour in base. The action of a variety of bases on the compound produces instantaneously the reversible, vivid red color noted by Gaudemar-Bardone[1]. For NMR measurements we conveniently treated a solution of the dimer in dimethyl sulfoxide with one equivalent of butyl-lithium. The NMR spectrum shows aromatic protons at 7·3 ppm (20 H, multiplet) and three one-proton singlets at 5·19, 5·43 and 9·09 ppm, indicating that the base has removed one of the methylene protons to give an anion stabilized by extended conjugation. Subsequent neutralization of the anion with hydrogen chloride returns the dimer in good yield. The UV spectrum of the anion[12] has reversible maxima at 247 (29,200), 388 (22,400) and 522 mμ (50,400). A shift to such long

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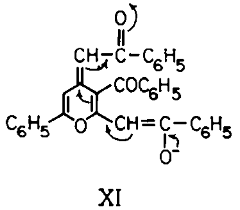
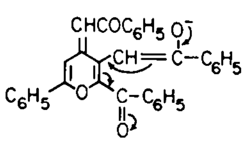
[12] Measured in 95% EtOH 0·01M in NaOH.

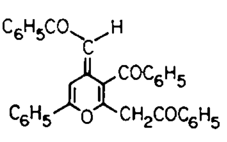
wavelengths as this last maximum on anion formation is unusual and probably best explained by VII which yields the extended anion XI, rather than VIII, which would give anion XII.[13]



XI



XII



XIII

Finally, the shifts in NMR absorption on passing from dimer to anion confirm structure VII. Both the low field singlet and the high field methylene signal move to lower field on anion formation (8·73 → 9·09 and 4·32 → 5·19 ppm), changes reflecting the increase in negative character of the oxygen atoms near these protons (cf. XI). The third signal, that of the ring proton not involved in the extended anion system, actually shifts *upfield* on ionization (5·63 → 5·43 ppm). These observations receive no explanation in VIII, in which neither of the original single protons of the dimer is involved in the conjugated system of the anion.

Structure VII may be expanded by further consideration of X. The uninvolved benzoyl group of the diene (upper plane) should be on the side away from the dienophile.[14] If the above considerations are correct, we may represent the full structure of the dimer of 1,3-dibenzoylallene as XIII. Finally, it is worth noting that both this result and those of Stetter with the dimers of acylketenes[9b] arise from orientation in Diels-Alder dimerization contrary to that generally observed for simple unsaturated carbonyl compounds. These reactions customarily lead to α-acyldihydropyrans.[15]

EXPERIMENTAL

Dimerization of 1,3-*dibenzoylallene.* The reaction was conveniently carried out under N_2 in acetone (from $KMnO_4$) solution containing the allene at a concentration of 100 mg/ml. The reaction is insensitive to the presence or absence of light and yields 40–50% dimer at temps from 5–56°. Crude dimer was filtered from the reaction mixture after 2–3 days at room temp or 9–10 days at 5°. Recrystallization from EtOH gave yellow to orange needles, m.p. 201–201·5° (rep. m.p. 204°[1]).

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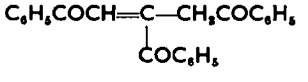
[13] The anion from 1,2,3-tribenzoylpropene iii has its maximum at 487 mμ (40,600) (P. Yates, D. G. Farnum and G. H. Stout, *J. Amer. Chem. Soc.* **80**, 196 (1958)). Aside from the nature of the cross conjugation, the principal difference in X is the ring oxygen substituent on the chromophore. Such a negatively substituted oxygen should probably cause no more than a 10–12 mμ shift. On the other hand, the extension of conjugation by an additional double bond in anion IX could account satisfactorily for the observed absorption.



$C_6H_5COCH{=}\underset{\displaystyle COC_6H_5}{\underset{|}{C}}{-}CH_2COC_6H_5$

iii

[14] Compare the similar and thoroughly effective shielding by carboxyl of one side of the pentadiendioic acid molecule in its reaction (*as dienophile*) with cyclopentadiene. W. C. Agosta, *J. Amer. Chem. Soc.* **86**, 2638 (1964).

[15] See Refs in footnote 9*a* and also further examples cited by K. Alder in *Newer Methods of Preparative Organic Chemistry* (translated and revised from the German) esp. p. 501 ff. Interscience, New York **1**, 381 (1948).

Salt of 1,3-*dibenzoylallene dimer with perchloric acid.* A solution of 30 mg of dimer in 2·6 ml hot acetic acid was treated with 3·0 ml 70% perchloric acid. The solution immediately turned from red-orange to bright red and red needles precipitated as the solution slowly cooled. The solution was centrifuged and the supernatant discarded. The product was washed with 38% aqueous alcohol and dried *in vacuo*, m.p. 178–180° dec, 23 mg (64%). (Found: C, 68·72; H, 4·04; Calc. for $C_{34}H_{25}O_8Cl$: C, 68·40; H, 4·22%.)

Recovery of dimer from its salt with perchloric acid. A suspension of 49 mg of dimer perchlorate in 5 ml of acetic acid was treated with 3 ml water. The resulting yellow solid was filtered to give 40 mg (98%). Four recrystallizations from EtOH gave 6·7 mg (16%) dimer, m.p. 200–201°, IR spectrum (KBr) identical with that of authentic dimer. Chromatography of the mother liquors from the above furnished only traces of dimer.

Formation of dimer anion and reconversion to dimer. A suspension of 96 mg of dimer in 2·0 ml of dimethyl sulfoxide was treated with 0·125 ml (1·0 eq.) of a solution of BuLi in hexane. The solution instantly became deep red and within 10 min all dimer had apparently dissolved. The solvent was evaporated below 40° at 0·1 mm press with pumping continued for 64 hr after all solvent was apparently removed. The dark red residue was dissolved in 0·5 ml of perdeuterodimethyl sulfoxide for NMR measurement. After this determination, the solution was once again taken to dryness *in vacuo*. The residue was dissolved in EtOH and acidified by passing dry HCl briefly over the surface. There was an immediate precipitate which was filtered and twice recrystallized from EtOH to give 71 mg (74%) dimer, m.p. 200·5–201·5°. The IR spectrum (KBr) was identical with that of authentic dimer.