

AN ANOMALOUS HUNSDIECKER REACTION OF

3,3-DIPHENYLPROPIONIC ACID

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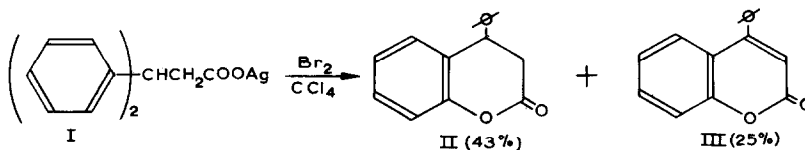
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The mechanism of halide formation by the reaction of halogens with silver salts of carboxylic acids, commonly known as the Hunsdiecker reaction, is believed to proceed via the intermediacy of free radicals, which are derived from an acylhypohalite intermediate, formed in the initial step of the reaction<sup>1</sup>.

Recently, however, a case of an anomalous Hunsdiecker reaction has been reported in which the products do not arise from a process involving a decarboxylative halogenation<sup>2,a,b</sup>. Thus, it was observed, that when silver 3,3,3,-triphenylpropionate was treated with bromine the main products of the reaction were the phenyl esters of 2-bromo-3,3-diphenylacrylic and 3,3-diphenylacrylic acids, for the formation of which the authors have suggested a C - O rearrangement involving a 1 - 4 phenyl migration.

1. C. V. Wilson, Organic Reactions Vol. IX. J. Wiley, New York. 1957, p.332.
2. (a) J. W. Wilt and D. D. Oathoudt, J. Org. Chem. 23, 218 (1958).  
(b) J. W. Wilt and J. L. Finnerty, ibid. 26, 2173 (1961).

In this communication we wish to report our results on the attempted Hunsdiecker reaction of 3,3-diphenylpropionic acid which appears to involve yet another type of skeletal transformation. Treatment of the silver salt I with bromine, under typical Hunsdiecker conditions, resulted in a mixture of neutral products which were separated by gas chromatography. The two main fractions of the reaction mixture were recognised as lactones and have been assigned the structures II and III based upon the evidence presented in the sequel.



The identification of II was achieved by a comparison of its retention time and its infra-red, mass and NMR spectra with those of an authentic sample of 4-phenyl-3,4-dihydrocoumarin<sup>3</sup>. The NMR spectrum of II showed a multiplet for the nine aromatic protons at 2.61 - 3.25  $\tau$  and a typical pattern for an  $\text{AX}_2$  system for the remaining three protons, with a triplet centered at 5.80  $\tau$  and a doublet at 7.11 and 7.21  $\tau$ ;  $J_{\text{AX}} = 5.9$  cps. The mass spectrum of II (Fig. 1) showed the molecular ion peak at  $m/e = 224$ , however, the most prominent peak of the spectrum appeared at  $m/e = 181$ . A possible formulation of a stable fragment of 43 mass units less than the parent molecule may conceivably involve a loss of ketene unit,

3. J. Simpson and H. Stephen, J. Chem. Soc. 1382 (1956).

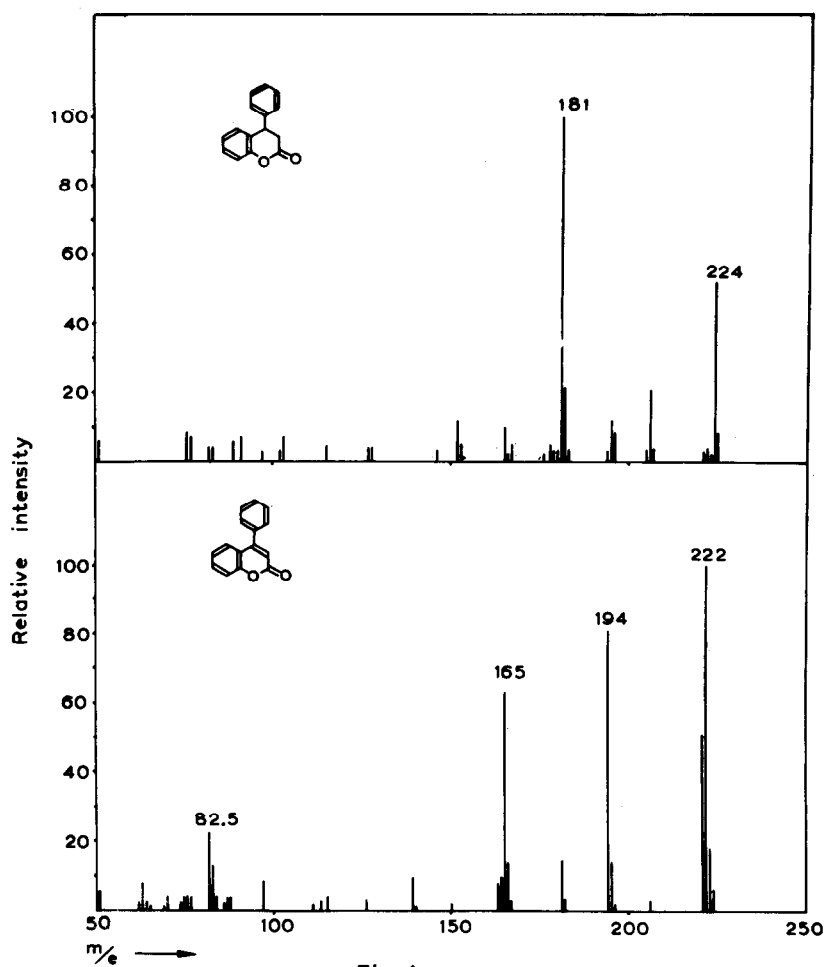
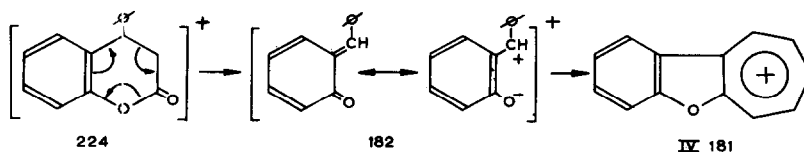


Fig. 1

in an expected manner<sup>4</sup>, followed by rearrangement and loss of a hydrogen atom, to form the highly stabilised intermediate IV.

4. K. Biemann, Mass Spectrometry, Organic Chemical Applications, McGraw-Hill, 1962, p.111.

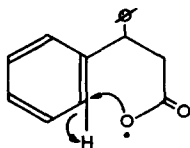


The structure of lactone III was adduced from its chemical behaviour upon alkaline hydrolysis, its infra-red spectrum (strong carbonyl band at  $1729\text{ cm}^{-1}$  for the  $\alpha,\beta$ -unsaturated phenolic lactone system) and its micro-analysis (Found: C,81.32; H,4.59.  $\text{C}_{15}\text{H}_{10}\text{O}_2$  requires: C,81.06; H,4.54.). In agreement with this assignment the NMR spectrum showed nine aromatic protons (2.41 - 2.98  $\tau$ ) and one ethylenic proton as a singlet at 3.83  $\tau$ . Further corroborative evidence was obtained from the mass spectrum of III (Fig. 1) which showed a strong molecular ion peak at 222 and revealed that the main fragmentation pathway involves the initial expulsion of a carbon monoxide molecule with the resultant fragment probably cyclising to the stable 3-phenyl-benzofuran system ( $m/e = 194$ ). Further fragmentation appears to follow the loss of a CHO unit to give the fully aromatic fluorenyl cation ( $m/e = 165$ ).

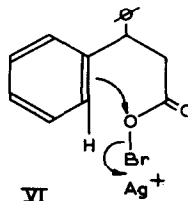
The formation of lactone II, which seems to be the obvious precursor of III, can arise from an intramolecular radical cyclisation process of the type V, of which several examples have been recently reported <sup>5,a,b,c</sup>, or

5. (a) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.* **25**, 880 (1960).
- (b) P. J. Bunyan and D. H. Hey, *J. Chem. Soc.* 2771 (1962).
- (c) A. Roedig, G. Märkl and M. Schlosser, *Chem. Ber.* **95**, 2243 (1962).

alternately, via an ionic mechanism involving the loss of a bromide ion from the acylhypobromite intermediate, accompanied by a concerted or stepwise participation of the  $\pi$ -electrons of the phenyl group (VI). Investigation of the mechanism of lactone formation and a comparison of the fate of the radical species V when produced by different processes, is in progress.



V



VI

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