Tetrahedron. Vol. 30, pp. 2331 to 2335. Pergamon Press 1974. Printed in Great Britain

THE DEHYDROCHLORINATION OF SUCCINYL CHLORIDES[a]

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(*Received in the UK* 22 *February* 1974; *Accepted for publication* 18 *March* 1974)

Abstract—The dehydrochlorination of substituted succinyl chlorides has been investigated as a possible source of bisketens. The characterised products are bifurandiones and/or pyrano[3.2-b]pyran-2,6-diones. The mass spectral fragmentations of these compounds are discussed.

Bisketens of type **1** are putative intermediates in a variety of reactions. Thus pyrolysis of molecules such as **2** to benzocyclobutenedione (**3**) probably proceeds *via* formation of the bisketen (**1**).[1] This species is also apparently an intermediate in the photochemical conversion of **3** into the dimers **4**, **5** and **6**.[2] The formation of these three dimers is readily rationalised by appropriate couplings of the open-chain bisketen (**1**) and the derived cyclic carbene (**7**). Evidence for the intermediacy of both species has been provided by trapping experiments. Bisketens (**8**) have been generated by low temperature photolysis of cyclobutenediones and detected spectroscopically.[3] Irradiation of methanol solutions of various substituted cyclobutenediones gives the corresponding dimethyl succinates[3,4] but in aqueous solution dimethylcyclobutenedione gives tetramethylbifurandione.[5] Bisketens may also be formed in the thermal decomposition of 2,3-diazabenzo-1,4-quinones,[6] and are possible intermediates in the dicobalt octacarbonyl mediated carbonylation of acetylenes to bifurandiones.[7] Except in two little publicised instances, mentioned hereafter, the generation of bisketens by dehydrochlorination of succinyl chlorides does not appear to have received prior attention.

Treatment of 1,2-dihydrophthaloyl chloride with triethylamine in benzene gave, after work-up, a small amount of biphthalylidene (**4**) and, principally, benzoic acid. The latter product results from the novel elimination of the elements of formyl chloride. Neither of the dimers **5** or **6** could be detected in the reaction mixture. Dehydrochlorination of succinyl and methylsuccinyl chlorides under a variety of conditions failed to provide any well-defined products. However, α-phenylsuccinyl chloride gave a very small yield of a diphenylbifurandione m.p. 295–7°, which is clearly identical with one of those obtained by carbonylation of phenylacetylene.[8] The latter reaction also produces two other isomers m.p. 176–8° and 207–10°. Only the isomer m.p. 207–10° has an IR absorption band at 1655 cm^{-1}, which indicates the possession of a *cis* configuration about the interannular double-bond. Consideration of the UV spectral data summarised in the Table leads us to the indicated structural assignments. It should be noted that geometrically isomeric bifurandiones have almost identical spectral absorptions, and also that the 4,4′-diphenyl groups in tetraphenylbifurandione (**9b**) will be twisted out of the plane of the molecule and thus make a limited contribution to the chromophore.

Better yields of dimers were obtained with α,α'-disubstituted succinoyl chlorides. Both α,α'-dichloro and α,α'-diphenyl-succinoyl halides gave solely the tetrasubstituted bifurandiones (**9b** and **9c**). The tetraphenyl compound had apparently been obtained previously[9] by this route but no structure was assigned at that time. α,α'-Dimethylsuccinyl chloride gave an equimolar mixture of the bifurandione (**9d**) and the pyronopyrone (**10a**), while hexahydrophthaloyl chloride gave a trace of the bifurandione and principally the pyronopyrone (**10b**). We subsequently discovered that **10b** had been prepared previously by this method and its structure established by extensive degradative studies.[10] In view of the proclivity of the bifurandione (**9e**) to undergo acid-catalysed isomerisation to **10b**,[11] a quantity of **9e** was added to the hexahydrophthaloyl chloride prior to dehydrochlorination. The added **9e** was subsequently recovered indicating that the pyronopyrone (**10b**) is the primary reaction product.

Numerous unsuccessful efforts were made to intercept the supposed bisketens and derived cyclic carbenes by carrying out the dehydrochlorination reactions in the presence of various olefinic compounds such as had been used in similar studies.[2] While this may merely reflect the obtention of these species in a different electronic state to those ob-

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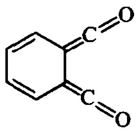
[a] A preliminary account of part of this work has already appeared: C. W. Bird and D. Y. Wong, *Tetrahedron Letters* 4433 (1970).

Table

Bifurandione	λ_{max}	$\nu_{max}^{(C=C)}$	Orientation assigned
Diphenyl m.p. 295–70°	407 nm	—	*trans*-3,3′-
Diphenyl m.p. 176–8°	381 nm	—	*trans*-3,4′-
Diphenyl m.p. 207–10°	381 nm	1655 cm^{-1}	*cis*-3,4′-
trans-3,3′,4–4′-Tetra phenyl	403 nm	—	—
trans-Unsubstituted	340 nm	—	—
cis-Unsubstituted	334 nm	1668 cm^{-1}	—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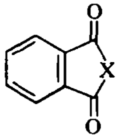
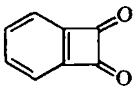



2: $\mathrm{X = CO;\ N.N = \overset{\overset{O}{\|}}{S}Ph_2}$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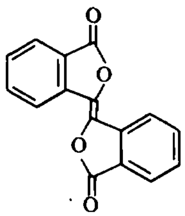
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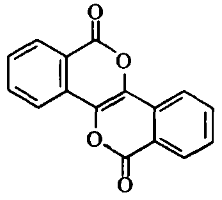
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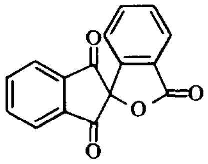
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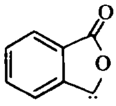
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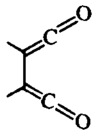
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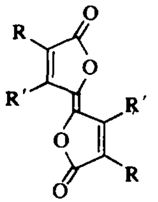
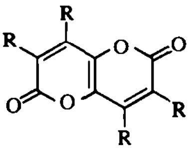




9a: R = Ph, R′ = H
b: R = R′ = Ph
c: R = R′ = Cl
d: R = R′ = Me
e: RR′ = $-(CH_2)_4-$

10a: R = Me
b: RR = $-(CH_2)_4-$

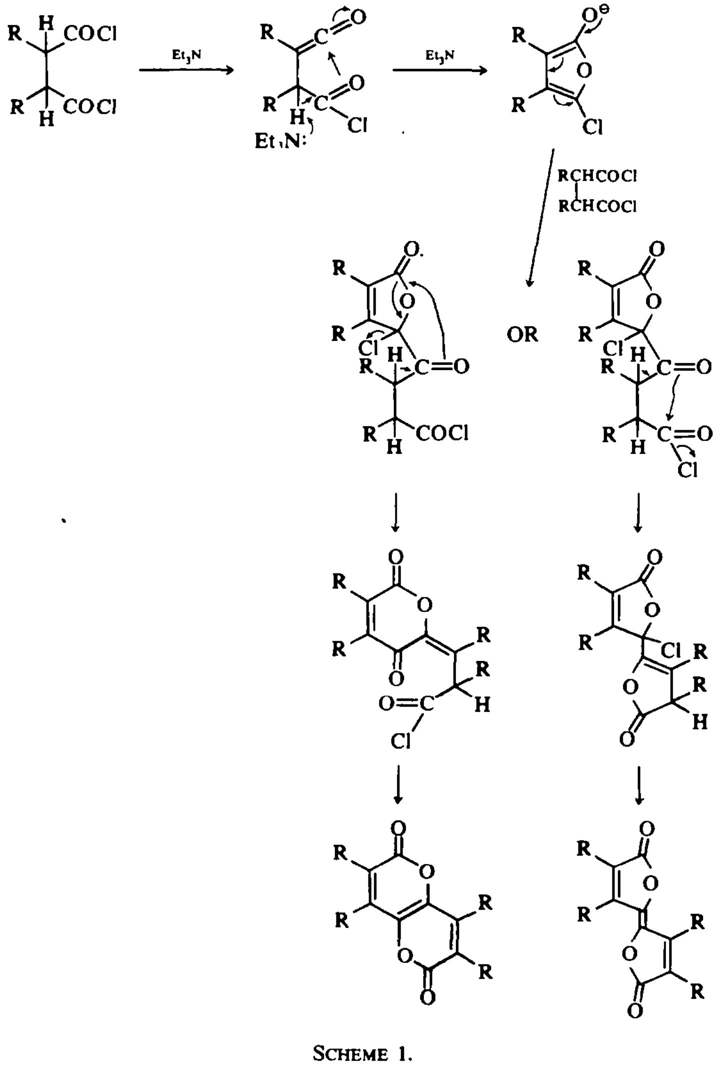
tained by photochemical means, it is also possible, *cf* Scheme 1, to formulate the generation of bifurandiones and pyronopyrones in these dehydrochlorination reactions without invoking intermediary bisketens.

The mass spectra of these compounds proved to be of particular diagnostic value during this study. In the case of practically every compound the base peak is due to the molecular ion, and isomeric bifurandiones and pyronopyrones exhibit identical fragmentation patterns. A general fragmentation pathway is summarised in Scheme 2. The postulated processes are supported by the observation of appropriate metastable ions in the mass spectra of one or more compounds. A particularly notable feature is the successive expulsion of four carbon monoxide residues, as has also been noted[12] for biphthalylidene (4) and the isomer 5. In the fragmentation process leading to loss of a substituent group from the σ-benzoquinone ion it is assumed that the group at position 3 is the one expelled, by analogy with observations[13] on 1,2-naphthoquinones.

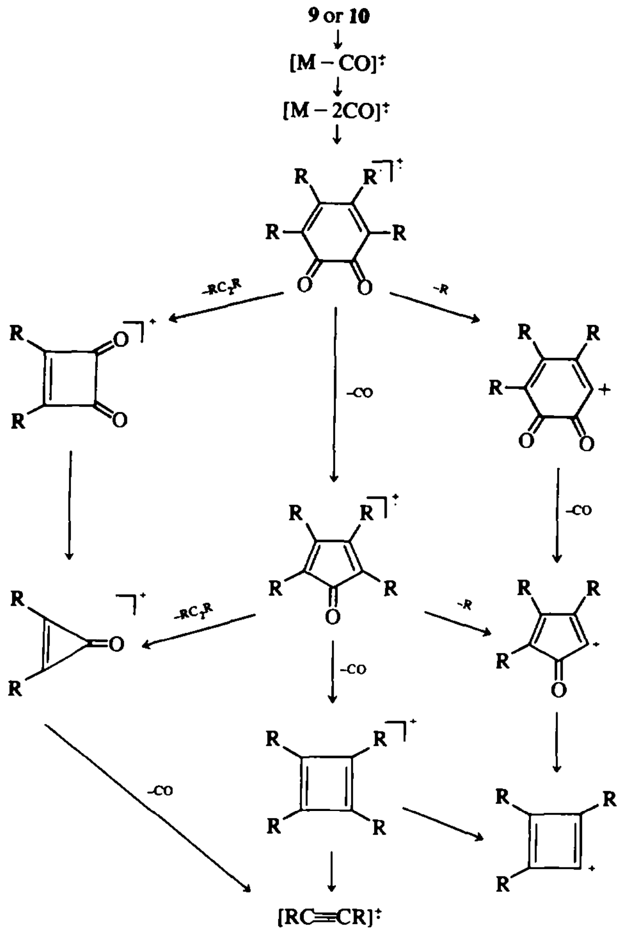
EXPERIMENTAL

IR spectra were recorded for Nujol mulls on a Unicam SP 200 spectrophotometer and UV spectra for acetonitrile solns on a Unicam SP 800 instrument. Mass spectra were recorded by the P.C.M.U. Harwell using an MS 9 instrument.

Dehydrochlorination of succinyl chlorides. The succinyl chlorides were prepared by treatment of the corresponding acids with PCl_5 in benzene,[14] as thionyl chloride gave the anhydride. Triethylamine (2·5 mole) was added slowly to a benzene soln of the succinyl chloride (1 mole). The stirred mixture was then heated under reflux for 2 to 3 h, cooled and filtered. The filtrate was chromatographed



SCHEME 1.



SCHEME 2.

on silica gel in benzene and the products eluted with benzene containing increasing proportions of EtOAC. The results with individual succinyl halides were as follows:

(a) 1,2-Dihydrophthaloyl chloride gave benzoic acid (32%) and biphthalylidene (3%) m.p. 350–352° from xylene identical with an authentic sample.[15]

(b) 2,3-Diphenylsuccinyl chloride gave 3,4,3′,4′-tetraphenylbifurandione (22%) m.p. 390° from EtOH identical with an authentic specimen.[11] *m/e* 468(96), 440(11), 412(23), 384(11), 356(2), 335(3), 307(7), 279(8), 234(20), 178(100), 177(18), 176(34), 152(25), 151(21), 150(12), 139(11), 126(12), 105(19), 77(14), m* 433, 415, 386, 364, 358, 176, 136, 130.

(c) 2,3-Dimethylsuccinyl chloride yielded 3,4,3′,4′-tetramethylbifurandione (3%) m.p. 238–239° from EtOH identical with an authentic sample,[11] and 3,4,7,8 - tetramethylpyrano[3,2-b]pyran - 2,6 - dione (3%) m.p. 222–223° from EtOH (Found: M, 220·0739 $C_{12}H_{12}O_4$ requires: M, 220·0736) λ_{max} 347 nm (14,200), 365 nm (16,900), 383 nm (11,500), ν_{max} 1700 cm^{-1}. This compound was identical with the compound assigned this structure[5] and obtained by irradiation of an aqueous suspension of 3,4 - dimethylcyclobut - 3 - ene - 1,2 - dione. The isomeric tetramethylbifurandione and pyranopyrandione had identical mass spectra *m/e* 220 (100), 192 (27), 164(49), 163(65), 149(18), 136(7), 121(9), 110(30), 82(15), 54(28), 53(21), 39(18). m* 168, 162·5, 140, 135·5, 113, 107·5, 61·2, 35·6.

(d) 2,3-Dichlorosuccinyl chloride provided 3,4,3′,4′ - tetrachlorobifurandione (19%) m.p. 289–291° (from xylene) (Found: C, 32·1; Cl, 43·5. Calc. for $C_8Cl_4O_4$: C, 31·8; Cl, 43·7%) λ_{max} 272 nm (8,720), 280 nm (9,400), 292 nm (6,000), 414 nm (8,400). ν_{max} 1750 cm^{-1}. *m/e* 304(50), 302(100), 300(80), 267(6), 265(5), 248(8), 246(28), 244(24), 241(26), 239(75), 237(85), 222(12), 220(50), 218(95), 216(78), 213(15), 211(35), 209(37), 194(6), 192(24), 190(40), 188(34), 185(27), 183(58), 181(62), 157(17), 155(50), 153(58), 132(6), 130(11), 122(12), 120(40), 118(63), 113(10), 111(32), 106(13), 95(21), 91(19), 87(20), 85(20), 85(18), 83(37), 71(10), 65(25), 63(62), 60(15).

(e) Hexahydrophthaloyl chloride gave 3,4 : 3′,4′ - bis(tetramethylene)bifuradione (1%) m.p. 308–310° (from EtOH) and 3,4 : 7,8 - bis(tetramethylene)pyrano[3,2 - b]pyran - 2,6 - dione (6%) m.p. 318–320° from EtOH, identified by comparison with authentic samples. The isomeric products had identical mass spectra, *m/e* 272(100), 268(4), 244(23), 216(25), 215(4), 188(15), 160(5), 136(6), 109(13), 108(20), 107(12), 81(7), 80(31), 79(45), 78(14), 77(33), 53(11), 52(31), 51(15), 39(14), m* 243, 219, 210, 192, 172, 164, 160, 145, 136, 108, 95·5, 86, 78·5, 60·5, 59·5, 58·5.

(f) Phenylsuccinyl chloride yielded 3,3'-diphenylbifurandione (1%) m.p. 305–308° from EtOH (Lit.[8] m.p. 295–7°). (Found: M, 316·0732. Calculated for $C_{20}H_{12}O_4$; M, 316·0736) λ_{max} 408 nm(32,000), ν_{max} 1765 cm^{-1}. *m/e* 316(100), 288(22), 260(17), 232(33), 231(12), 204(11), 203(9), 158(25), 144(6), 130(36), 103(18), 102(96), 101(7), 77(3), m* 263, 235, 230, 207, 187, 180, 117·5, 107, 56·6.

Acknowledgement—One of us (D. Y. W.) gratefully acknowledges the award of a College Postgraduate Scholarship.

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