Aryne Chemistry. Part XXXI.[1] Reactions of Arynes with αβ-Unsaturated Aldehydes

By **H. Heaney,* J. M. Jablonski,** and **C. T. McCarty,** Department of Chemistry, The University of Technology, Loughborough, Leicestershire LE11 3TU

The reaction of benzyne, generated from anthranilic acid, benzothiadiazole 1,1-dioxide, and diphenyliodonium-2-carboxylate, with cinnamaldehyde results in the formation of flav-3-ene. Similarly tetrachlorobenzyne, generated from tetrachloroanthranilic acid, tetrachlorobenzenediazonium-2-carboxylate hydrochloride, and 3,4,5,6-tetrachloro-2-(3,3-dimethyltriazeno)benzoic acid, affords 5,6,7,8-tetrachloroflav-3-ene. Reactions with other αβ-unsaturated aldehydes result in the formation of derivatives of 2*H*-chromen. The mechanism of the reaction has been studied using ^{14}C, ^{2}H, and alkyl groups as labels.

THE use of αβ-unsaturated aldehydes in Diels–Alder reactions is well known.[2] However, the reaction of an αβ-unsaturated carbonyl compound with an acetylene derivative appears to be restricted to one example using an *o*-quinone methide.[3] The structure of this product is not known with certainty. The reactions of arynes with αβ-unsaturated carbonyl compounds should provide a novel approach to the synthesis of six-membered oxygen heterocyclic ring systems. Certain of our results have appeared in preliminary communications.[4]

Our original reactions were carried out by the aprotic diazotisation of tetrachloroanthranilic acid.[5] When a solution of tetrachloroanthranilic acid in diethyl ether (or acetone or acetonitrile) was added to a solution of pentyl nitrite in dichloromethane and an αβ-unsaturated aldehyde, we isolated alkyl 2,3,4,5-tetrachlorophenyl ethers from the pentyl nitrite [6] and the diethyl ether,[7] together with crystalline products which were formed by the addition of 1 mol. equiv. of the αβ-unsaturated aldehyde (1)—(6) to tetrachlorobenzyne. Elemental analysis and mass spectrometry established the molecular formulae of the 1 : 1 adducts.

The absence of a carbonyl stretching frequency in the i.r. spectra of the products excluded a number of possible structures. The ^{1}H n.m.r. spectra (Table 1) of the products and the corresponding dihydro-derivatives, obtained by reduction with hydrogen in the presence of palladium on carbon, indicated that they did not

[1] Part XXX, B. Hankinson, H. Heaney, and R. P. Sharma, *J.C.S. Perkin I*, 1972, 2372.

[2] J. Colonge and G. Descotes, in '1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967, p. 217; A. S. Onishchenko, 'Diene Synthesis,' Israel Program for Scientific Translations, Jerusalem, 1964.

[3] K. Hultzch, *J. prakt. Chem.*, 1941, **158**, 275; 1941, **159**, 180; *Ber.*, 1941, **74**, 898; 903; 1539; *Angew. Chem.*, 1948, **60**, 179.

[4] (*a*) H. Heaney and J. M. Jablonski, *Chem. Comm.*, 1968, 1139; (*b*) H. Heaney and C. T. McCarty, *ibid.*, 1970, 123.

[5] H. Heaney and J. M. Jablonski, *J. Chem. Soc.* (*C*), 1968, 1895.

[6] H. Heaney, K. G. Mason, and J. M. Sketchley, *J. Chem. Soc.* (*C*), 1971, 567.

[7] J. P. N. Brewer, H. Heaney, and J. M. Jablonski, *Tetrahedron Letters*, 1968, 4455.

correspond to 1,4-cycloadducts. Chemical shift data is available for 2*H*-chromen [8] and 4*H*-chromen,[9] and spin–spin coupling constants [8] for the former compound. The compounds were evidently the 2*H*-benzo[*b*]pyran derivatives (7)—(12). Thus in for example 2*H*-chromen (19; R = H) the methylene protons resonate as a double doublet ($|J_{2,3}|$ 3·5 Hz) at τ 5·25 while in 4*H*-chromen (20) the methylene protons resonate at τ 6·66. In our compound (7) the methylene protons resonate at τ 5·05. The other data are collected in Table 1. It is noteworthy that spin–spin decoupling experiments showed that the multiplet at lowest field in the chroman derivative (14) was spin–spin coupled to the methyl group which was therefore located at C-2. The u.v. spectra (Table 2) of the compounds (7)—(11) showed the presence of a styrene-type chromophore. The structure of the 2*H*-chromen (10) was also confirmed by a conventional synthesis.[10] We prepared tetrachlorosalicylaldehyde (21) by the aprotic diazotisation of tetrachloroanthranilic acid in the presence of dimethylformamide [11] and hence obtained 5,6,7,8-tetrachlorobenzo[*b*]pyran-2-one (22) by a Perkin reaction.[12] The reaction of an excess of methylmagnesium iodide with the compound (22) gave an alcohol which was converted into the 2*H*-chromen (10) with methanolic hydrochloric acid.

TABLE 1

^{1}H N.m.r. spectra of chromans and 2*H*-chromens at 60 MHz (in $CDCl_3$)

	Chemical shifts (τ) (multiplicity)					Coupling constants (Hz)			
Compound	2-H	3-H	4-H	2-Me	Other	$J_{2,3}$	$J_{3,4}$	$J_{2,4}$	Other
(7)	5·05 (dd)	4·0 (dt)	3·15 (dt)			3·4	10·3	1·7	
(8)	4·91 (ddq)	4·19 (dd)	3·32 (dd)	8·5 (d)		3·4	10·3	1·7	R^1, R^2 6·4
(9)	5·15 (dq)		3·63 (s)	8·63 (d)	(3-Me) 8·12 (s)			1·7	R^1, R^2 6·4
(10)		4·27 (d)	3·36 (d)	8·54 (s)			10·8		
(11)	3·95 (s †)	3·9 (q †)	3·02 (q †)		(2-Ph) 2·77br (s)				
(11) *	4·05 (s †)	4·0 (q †)	3·15 (q †)		2·71br (s)				
(12)		4·10 (d)	3·26 (d)		(2-Ph) 2·77br (s)		10·8		
(13)	5·76 (t)	7·9 (m)	7·16 (t)			5·4	6·8		
(14)	5·78 (m)	8·0 (m)	7·2 (m)	8·52 (d)					R^1, R^2 6·0
(15)	5·7 (dq)	7·8 (m)	7·32 (m)	8·74 (d)	(3-Me) 9·04 (d)	3·0			R^1, R^2 6·5
									R^3, H 6·0
(16)		8·21 (t)	7·27 (t)	8·68 (s)			7·2		
(17)	4·78 (dd)	7·7 (m)	7·05 (m)		(2-Ph) 2·51br (s)	4·0 and 9·0			
(18)		7·65 (m)	7·05 (m)		(2-Ph) 2·65br (s)				

* Determined at 100 MHz; s = singlet; d = doublet; t = triplet; q = quartet; br = broad; dd = double doublet *etc.*
† Apparent multiplicity.

TABLE 2

U.v. spectra of 2*H*-chromens [$\lambda_{max.}$/nm ($\log_{10}\varepsilon$)] in ethanol

Compound	
(7)	233 (4·36), 237·5 (4·38), 246 (4·17), 281 (3·70), 291 (3·62)
(8)	233 (4·48), 237·5 (4·49), 245·5 (4·31), 280 (3·85), 290 (3·78)
(9)	232 (4·51), 238 (4·53), 246 (4·35), 281 (3·99), 292 (3·93)
(10)	231 (4·53), 237 (4·56), 245 (4·36), 278 (3·92), 290 (3·86)
(11)	234 (4·56), 238 (4·59), 247 (4·47), 282 (3·89), 289 (3·83)

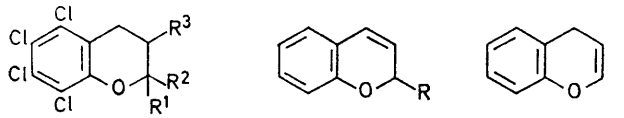
The decomposition of benzenediazonium-2-carboxylate, to give benzyne, is thought to occur by a stepwise mechanism in which the initial step involves the loss of nitrogen to give the dipolar intermediate (23).[13] The intermediate (23) has been trapped [13,14] with for example carbonyl compounds,[14a] and it was possible that our reactions were 'arynoid',[15] also involving a similar intermediate. We therefore studied the reaction of benzyne, generated from benzothiadiazole 1,1-dioxide,[16] diphenyliodonium-2-carboxylate,[17] and from anthranilic acid by aprotic diazotisation,[18] with cinnamaldehyde. In each case we isolated flavene (19; R = Ph) which was identified by a comparison of the ^{1}H n.m.r. spectrum with the published spectral data,[19] and by reduction to the crystalline flavan.[20] The mechanism of the frag-

[8] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 1964, 981; E. E. Schweizer, J. Liehr, and D. J. Monaco, *J. Org. Chem.*, 1968, **33**, 2416.
[9] W. E. Parham and L. D. Huestis, *J. Amer. Chem. Soc.*, 1962, **84**, 813.
[10] S. Wawzonek, in 'Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, New York, 1951, vol. 2, p. 173.
[11] S. Yaroslavsky, *Tetrahedron Letters*, 1965, 1503.
[12] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1956.
[13] R. Gompper, G. Seybold, and B. Schmolke, *Angew. Chem., Internat. Edn.*, 1968, **7**, 389; see however, T. J. Barton, A. J. Nelson, and J. Clardy, *J. Org. Chem.*, 1972, **37**, 895.
[14] (*a*) G. P. Chiusoli and C. Venturello, *Chem. Comm.*, 1969, 771; (*b*) D. C. Dittmer and E. S. Whitman, *J. Org. Chem.*, 1969, **34**, 2004; (*c*) S. F. Dyke, A. J. Floyd, and S. Ward, *Tetrahedron Letters*, 1969, 2837; *Tetrahedron*, 1970, **26**, 4005; (*d*) T. L. Gilchrist, F. J. Graveling, and C. W. Rees, *J. Chem. Soc.* (*C*), 1971, 977.
[15] D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Comm.*, 1967, 727; J. I. G. Cadogan, M. J. P. Harger, and J. T. Sharp, *Amer. Chem. Soc. Div. Petrol. Chem.*, 1969, 14, p. C 19; J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *Chem. Comm.*, 1970, 299; M. G. Reinecke and H. W. Adickes, *J. Amer. Chem. Soc.*, 1968, **90**, 511.
[16] G. Wittig and R. W. Hoffmann, *Chem. Ber.*, 1962, **95**, 2718.
[17] E. Le Goff, *J. Amer. Chem. Soc.*, 1962, **84**, 3786; F. M. Berringer and S. J. Huang, *J. Org. Chem.*, 1964, **29**, 445.
[18] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.
[19] J. W. Clarke-Lewis and D. C. Skingle, *Austral. J. Chem.*, 1968, **21**, 2059.
[20] W. Borsche and A. Geyer, *Ber.*, 1914, **47**, 1160; J. A. Van Allen, G. A. Reynolds, and T. H. Regan, *J. Org. Chem.*, 1967, **32**, 1897.

mentation of benzothiadiazole 1,1-dioxide almost certainly involves the concerted loss of nitrogen and sulphur dioxide [16] while the thermal decomposition of diphenyliodonium-2-carboxylate may involve an anionic inter-

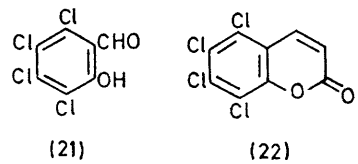
(1) $R^1=R^2=R^3=H$
(2) $R^1=R^3=H, R^2=Me$
(3) $R^1=H, R^2=R^3=Me$
(4) $R^1=R^2=Me, R^3=H$
(5) $R^1=R^3=H, R^3=Ph$
(6) $R^1=D, R^2=Ph, R^3=H$

(7) $R^1=R^2=R^3=H$
(8) $R^1=R^3=H, R^2=Me$
(9) $R^1=H, R^2=R^3=Me$
(10) $R^1=R^2=Me, R^3=H$
(11) $R^1=R^3=H, R^2=Ph$
(12) $R^1=D, R^2=Ph, R^3=H$

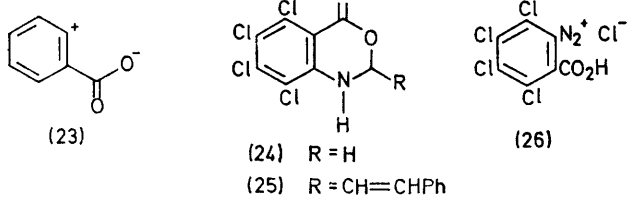


(13) $R^1=R^2=R^3=H$
(14) $R^1=R^3=H, R^2=Me$
(15) $R^1=H, R^2=R^3=Me$
(16) $R^1=R^2=Me, R^3=H$
(17) $R^1=R^3=H, R^2=Ph$
(18) $R^1=D, R^2=Ph, R^3=H$

(19) (20)



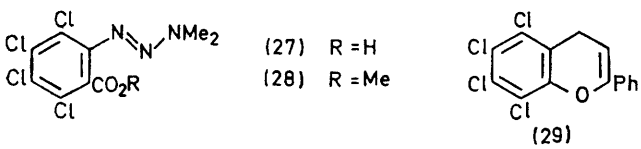
(21) (22)



(23)

(24) R = H
(25) R = CH=CHPh

(26)



(27) R = H
(28) R = Me

(29)

mediate.[21] These reactions therefore do involve benzyne.[22]

The yields obtained in our reactions of αβ-unsaturated aldehydes with tetrachlorobenzyne generated from tetrachloroanthranilic acid were not good and ranged from 4 to 37·5%. In certain of the reactions this was undoubtedly due to our using a low ratio of the aldehyde to the anthranilic acid. However, it is known that tetrachloroanthranilic acid reacts readily with formaldehyde, with the formation of 5,6,7,8-tetrachloro-2*H*-3,1-benzoxazin-4(1*H*)-one (24),[23a] and similar products have been prepared using anthranilic acid and a variety of aldehydes.[23b] We have shown [24] that a number of aldehydes, including cinnamaldehyde, react readily with tetrachloroanthranilic acid under the conditions used to generate tetrachlorobenzyne, and result in the formation of derivatives of (24), for example (25). We therefore investigated the reactions of cinnamaldehyde with tetrachlorobenzyne generated from other precursors.

We prepared tetrachlorobenzenediazonium-2-carboxylate hydrochloride (26) by the diazotisation of tetrachloroanthranilic acid with pentyl nitrite in tetrahydrofuran containing hydrogen chloride.* Benzenediazonium-2-carboxylate hydrochloride has been used as a source of benzenediazonium-2-carboxylate in which the hydrogen chloride was removed with propene oxide.[25] We found that compound (26) is much less stable † than the unchlorinated analogue and that when it was heated at 130° in an excess of *p*-xylene the expected adduct [5] of tetrachlorobenzyne was formed in 71% yield. Similarly, the hydrochloride (26) was heated at 60° in chloroform containing an excess of cinnamaldehyde and afforded compound (11) in 58% yield.

During the course of our present study preliminary accounts appeared which described the use of 2-(3,3-dimethyl-triazeno)benzoic acid as a benzyne precursor.[26] We have prepared 3,4,5,6-tetrachloro-2-(3,3-dimethyltriazeno)benzoic acid (27) by the addition of the compound (26) to an aqueous solution containing an excess of sodium carbonate and dimethylamine. The triazene (27) also decomposes to tetrachlorobenzyne. This was shown by heating the triazene (27) in *p*-xylene at 130° and which resulted in the formation of the adduct of tetrachlorobenzyne with *p*-xylene in 60% yield. When the compound (27) was heated at 120° in tetrachloroethylene containing an excess of cinnamaldehyde we obtained the compound (11) in 35% yield, while at 200° in the absence of a solvent we obtained 5,6,7,8-tetrachloro-4*H*-flaven (29) in 22% yield. That the compound (29) was formed from (11) was shown by the ready isomerisation of (11) ⟶ (29) in the presence of cinnamaldehyde at 200°. The conversion of (11) ⟶ (29) can be achieved more readily by chromatography on neutral alumina. The isomerisation is an intermolecular process as shown by the conversion of the deuterio-compound (12) ⟶ (29). When the reverse process was attempted

* Prof. L. Friedman has informed us that his group have also used this precursor.

† We have observed minor explosions with partially dried material.

[21] R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press, New York, 1967, p. 72.

[22] R. Huisgen and R. Knorr, *Tetrahedron Letters*, 1963, 1017; B. H. Klanderman and T. R. Criswell, *J. Amer. Chem. Soc.*, 1969, **91**, 510.

[23] (*a*) V. Villiger and L. Blangey, *Ber.*, 1909, **42**, 3549; (*b*) see for example, J. B. Ekeley and P. M. Dean, *J. Amer. Chem. Soc.*, 1912, **34**, 161.

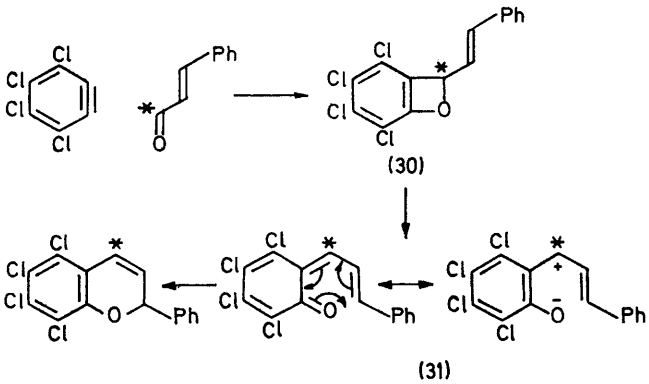
[24] H. Heaney and C. T. McCarty, unpublished observations.

[25] L. Friedman, personal communication; see also M. P. Cava and M. J. Mitchell, 'Selected Experiments in Organic Chemistry,' Benjamin, New York, 1966, p. 93.

[26] R. Gompper, E. Kutter, and G. Seybold, *Chem. Ber.*, 1968, **101**, 2340; J. Nakayama, O. Simamura, and M. Yoshida, *Chem. Comm.*, 1970, 1222; see also J. Elks and D. H. Hey, *J. Chem. Soc.*, 1943, 441.

using alumina which had been deactivated with deuterium oxide we obtained compound (29) which was shown, by mass spectrometry, to contain *ca.* 20% of deuterium. The n.m.r. spectrum confirmed the presence of deuterium C-4.

In our preliminary communication [4a] we suggested a mechanism (Scheme 1) which rationalised our early results. Our results obtained using the aldehydes (3)—(6) also support this mechanism. We now report results which confirm our earlier suggestion. Our basic assumption was that it was unlikely that the initial product was the 1,4-cycloadduct (*i.e.* the 4*H*-chromen) since it would have required that hydrogen migration occurs in the reaction with acrolein while methyl migration occurs with crotonaldehyde. The deuteriocinnamaldehyde (6) was prepared by the aldol condensation [27] using benzaldehyde labelled with deuterium in the formyl group and which was prepared using the morpholino-nitrile method.[28]



SCHEME 1

The key step in our suggested mechanism (Scheme 1) was the 1,2-cycloaddition leading to a benzoxet derivative [*e.g.* (30)]. *N*-Phenylbenzazetine has been isolated recently and was found to be thermally unstable. Products which arise from an *o*-quinimine methide were obtained.[29] Benzothiets and their dioxide [30,31] derivatives have also been prepared recently. However, as far as we are aware there are no known examples of the benzoxet ring system, although the benzoxetone system has been postulated as an intermediate.[10] If such an intermediate was formed and underwent ring opening, a quinone methide [*e.g.* (31)] would be formed which could undergo an electrocyclic ring closure to give the observed products. Precedent for this type of reaction exists. It has been suggested [32] that quinone methides of this type may be involved in the biosynthesis of the 2,2-dimethylchromen system. The photochromism of 2*H*-chromen and a number of derivatives has been studied and found to be reversible. Quinone methides were postulated as the coloured intermediates.[33] The nearest proven analogy to our proposed final cyclisation involves the photoisomerisation of *trans*- to *cis*-β-ionone followed by thermal electrocyclic ring closure.[34] Other communications have appeared recently in which products have been rationalised as involving similar intermediates.[35] During the course of our present study the 2*H*-chromen derivative (10) has been prepared by the reaction of 3,3-dimethylallyltriphenylphosphorane with tetrachloro-*o*-benzoquinone.[35h] This reaction is also assumed to involve the identical quinone methide which leads to the compound (10) in our reactions.

In order to prove that the formyl carbon atom eventually appears as the C-4 carbon atom in our products we carried out a reaction of tetrachlorobenzyne using cinnamaldehyde labelled with ^{14}C in the formyl group. The position of the radiolabel is indicated by an asterisk in Schemes 1 and 2. The required compound was prepared using the dihydro-oxazine method.[36] [1-^{14}C]Acetic acid was converted by standard methods [12] into [1-^{14}C]acetonitrile *via* [1-^{14}C]acetamide, and hence [37] into 2,4,4,6-tetramethyl-5,6-dihydro-[2-^{14}C]-1,3-oxazine. The overall yield of [1-^{14}C]cinnamaldehyde from [1-^{14}C]-acetic acid was 6%. The position of the label was confirmed by oxidation to [1-^{14}C]cinnamic acid and conversion to unlabelled β-bromostyrene.[38]

A large number of degradations of flavenes, 2*H*-chromens, and chromans are available,[39] but a number

[27] A. Scipioni, *Ann. Chim.* (*Italy*), 1951, **41**, 697 (*Chem. Abs.*, 1952, **46**, 8635).

[28] D. J. Bennett, G. W. Kirby, and V. A. Moss, *Chem. Comm.*, 1967, 218; *J. Chem. Soc.* (*C*), 1970, 2049.

[29] E. M. Burgess and L. McCullagh, *J. Amer. Chem. Soc.*, 1966, **88**, 1580.

[30] L. A. Paquette, *J. Org. Chem.*, 1965, **30**, 629.

[31] D. C. Dittmer and N. Takashina, *Tetrahedron Letters*, 1964, 3809; L. A. Paquette and T. R. Phillips, *J. Org. Chem.*, 1965, **30**, 3883.

[32] W. D. Ollis and I. O. Sutherland, 'Chemistry of Natural Phenolic Compounds,' Pergamon, Oxford, 1961, p. 84; A. B. Turner, *Quart. Rev.*, 1964, **18**, 347.

[33] R. S. Becker and J. Michl, *J. Amer. Chem. Soc.*, 1966, **88**, 5931; J. Kolc and R. S. Becker, *J. Phys. Chem.*, 1967, **71**, 4045; C. Schiele and G. Arnold, *Tetrahedron Letters*, 1967, 1191; J. B. Flannery, *J. Amer. Chem. Soc.*, 1968, **90**, 5660; L. D. Weis, T. R. Evans, and P. A. Leermakers, *ibid.*, 1968, **90**, 6109; J. Kolc and R. S. Becker, *Photochem. Photobiol.*, 1970, **12**, 383; L. Edwards, J. Kolc, and R. S. Becker, *ibid.*, 1971, **13**, 423.

[34] G. Büchi and N. C. Yang, *J. Amer. Chem. Soc.*, 1957, **79**, 2318; E. N. Marvell, G. Caple, T. A. Gosink, and G. Zimmer, *ibid.*, 1966, **88**, 619.

[35] (*a*) J. Zsindley and H. Schmid, *Helv. Chim. Acta*, 1968, **51**, 1510; (*b*) R. Hug, H.-J. Hansen, and H. Schmid, *Chimia* (*Switz.*), 1969, **23**, 108; (*c*) G. Cardillo, R. Gricchio, and L. Merlini, *Tetrahedron*, 1968, **24**, 4825; (*d*) D. W. Hutchinson and J. A. Tomlinson, *Tetrahedron Letters*, 1968, 5027; (*e*) E. E. Schweizer, D. M. Crouse, and D. L. Dalrymple, *Chem. Comm.*, 1969, 354; (*f*) R. M. Bowman, M. F. Grundon, and K. J. James, *ibid.*, 1970, 666; (*g*) G. W. Kirby, S. L. Tan, and B. C. Uff, *ibid.*, 1970, 1138; (*h*) G. Cardillo, L. Merlini, and S. Servi, *Ann. Chim.* (*Italy*), 1970, **60**, 564; (*i*) R. Hug, Gy. Fráter, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1971, **54**, 306; (*j*) E. E. Schweizer, T. Minami, and D. M. Crouse, *J. Org. Chem.*, 1971, **36**, 4028; (*k*) O. L. Chapman, M. R. Engel, J. P. Springer, and J. C. Clardy, *J. Amer. Chem. Soc.*, 1971, **93**, 6696.

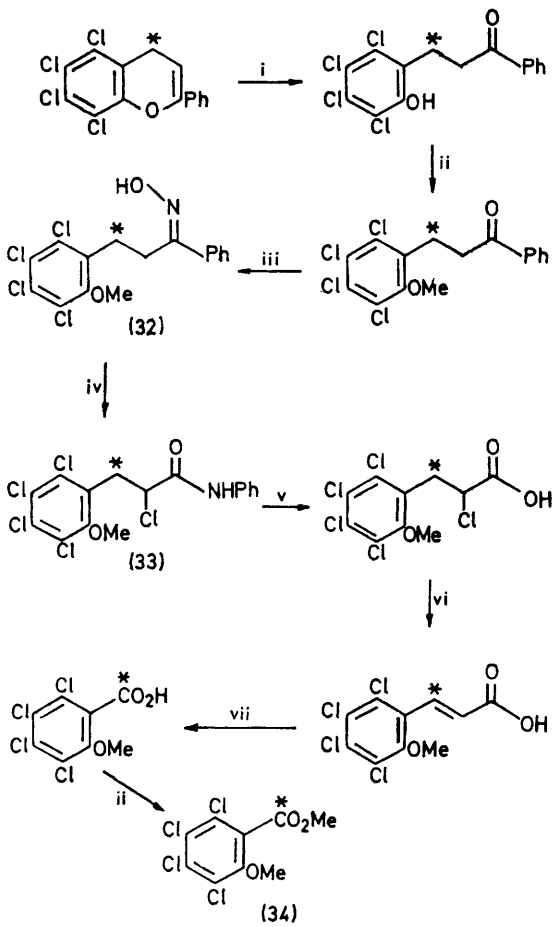
[36] A. I. Meyers, A. Nebeya, H. W. Adickes, J. M. Fitzpatrick, G. R. Malone, and I. R. Politzer, *J. Amer. Chem. Soc.*, 1969, **91**, 764; Prof. A. I. Meyers, personal communication.

[37] E. J. Tillmanns and J. Ritter, *J. Org. Chem.*, 1957, **22**, 839.

[38] S. J. Cristol and W. P. Norris, *J. Amer. Chem. Soc.*, 1953, **75**, 2645.

[39] *E.g.* M. Greenwood and M. Nierenstein, *J. Chem. Soc.*, 1920, **117**, 1594; P. Karrer, R. Widmer, A. Helfenstein, W. Hürliman, O. Nievergelt, and P. Monsarrat-Thoms, *Helv. Chim. Acta*, 1927, **10**, 729; R. L. Shriner and R. B. Moffett, *J. Amer. Chem. Soc.*, 1940, **62**, 2711; A. R. Alertsen, *Acta Chem. Scand.*, 1955, **9**, 1725; F. E. King, T. J. King, and L. C. Manning, *J. Chem. Soc.*, 1953, 3932.

of trial experiments showed that none of these enabled us to degrade our tetrachloro-compounds to a derivative of tetrachlorosalicylic acid in good yield. The previously reported [40] hydrolytic ring opening of 4*H*-flavens to the corresponding *o*-hydroxydihydrochalcones was successful with compound (29). A degradation to tetrachlorosalicylic acid, in 35% overall yield, was achieved using the route shown in Scheme 2. Two stages are worthy of further comment. When we prepared the oxime (32) we could only find evidence, by t.l.c., for the formation of one isomer,[41] the structure of which was established by Beckmann rearrangement followed by hydrolysis. We also found initially that the treatment of the oxime



SCHEME 2 Reagents: i, HCl–AcOH; ii, CH_2N_2; iii, NH_2OH; iv, PCl_5; v, aq. NaOH; vi, KOH–MeOH; vii, O_3–HCO_3H

(32) with four moles of phosphorus pentachloride resulted in the formation of a small amount of the α-chloro-amide (33) in addition to the expected amide. The α-chloro-amide was the only product when we used an excess of phosphorus pentachloride (15 mol. equiv.). When we interrupted a rearrangement reaction carried out with an excess of phosphorus pentachloride we only isolated the oxime (32) in addition to the α-chloro-amide. We were also unable to convert the amide into the α-chloro-amide using the same reaction conditions. We conclude from these experiments that either the α-chloro-oxime undergoes the Beckmann rearrangement very much more rapidly than does the oxime (32) or, perhaps more likely, than an intermediate involved in the rearrangement is chlorinated. The various compounds isolated in the sequence were counted (Table 3)

TABLE 3

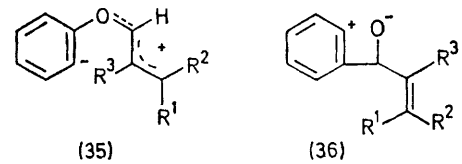
Specific activities of ^{14}C-labelled compounds

Compound	Activity (10^9 dis. min^{-1} mol^{-1})
Acetic acid *	2·64
Cinnamaldehyde semicarbazone	2·65
(11)	2·73
(29)	2·71
3-(3,4,5,6-Tetrachloro-2-methoxyphenyl)-propiophenone	2·71
(32)	2·78
trans-3-(3,4,5,6-Tetrachloro-2-methoxyphenyl)propenoic acid	2·78
(34)	2·54

* Calculated from the dilution of the purchased [1-^{14}C]acetic acid.

together with the final product, all of which had, within experimental error, the same specific activity as the cinnamaldehyde used in the reaction with tetrachlorobenzyne. We prepared tetrachlorosalicylic acid by the oxidation of tetrachlorosalicylaldehyde, and hence obtained methyl 2-methoxytetrachlorobenzoate, for comparison purposes.

The various labelling experiments show that a benzoxet must be involved in the reactions of arynes with αβ-unsaturated aldehydes, but the mechanism of its formation is obscure. It is unlikely that the formation of the benzoxet involves a stepwise addition of the αβ-unsaturated aldehyde to the aryne to form an intermediate (35) which has an appreciable life time. A stabilised betaine (35) would be expected to collapse at



least in part to give 4*H*-benzopyran derivatives, particularly when using for example ββ-dimethylacrolein. We looked at the reaction mixtures carefully but we could find no evidence for the presence of derivatives of 4*H*-benzopyran. It is possible, on the other hand, that a dipolar intermediate of the type (36) could be formed in which the aldehyde functions as an electrophile.[42] Reactions in which arynes function as nucleophiles have been discussed previously.[43]

A $_{\pi}2_s + {}_{\pi}2_s$ concerted cycloaddition of an aryne with a

[40] K. Freudenberg, H. Fokentscher, and W. Wenner, *Annalen*, 1925, **442**, 309; K. Freudenberg and M. Harder, *ibid.*, 1926, **451**, 213.

[41] T. P. Raikowa, *Ber.*, 1929, **62**, 1626; 2142; A. H. Blatt and J. F. Stone, *J. Amer. Chem. Soc.*, 1931, **53**, 4134.

[42] H. Heaney, J. M. Jablonski, C. T. McCarty, and A. P. Price *Amer. Chem. Soc. Div. Petrol. Chem.*, 1969, **14**, p. C 28.

[43] Ref. 21, p. 182.

carbonyl compound is not thermally allowed.[44] However, a $_{\pi}2_s + _{\pi}2_a$ process is allowed and would explain our results. Similarly an allowed concerted mechanism could be envisaged utilising non-bonded electrons from oxygen in a $_{\pi}2_s + _{\pi}2_s + _{n}2_s$ reaction. Our failure to obtain cycloadducts in attempted reactions of tetrachlorobenzyne with αβ-unsaturated ketones may be associated with a steric effect which precludes the formation of the necessary transition state in one of these latter two processes.

EXPERIMENTAL

I.r. spectra were determined for potassium bromide discs (for solids) except where stated, or as solutions in chloroform (for liquids) using Perkin-Elmer 237 or 257 grating spectrophotometers. U.v. spectra for ethanolic solutions (except where stated) were determined with a Unicam SP 800 spectrophotometer. ^{1}H N.m.r. spectra were determined at 60 MHz for solutions in deuteriochloroform (tetramethylsilane as internal standard) except where stated, using a Perkin-Elmer R10 spectrometer. Mass spectra were determined with an A.E.I. MS 12 spectrometer (the observed molecular weights of chlorinated compounds refer to the major molecular ion in the isotopic clusters).

Light petroleum refers to that fraction having b.p. 60—80°. M.p.s were determined using a Kofler hot stage and are uncorrected. Preparative layer chromatography was carried out using silica (Merck PF_{254}) on layers of 0·5 mm thickness.

Preparation of 2-Carboxytetrachlorobenzenediazonium Chloride.—Dry hydrogen chloride was passed into a solution of tetrachloroanthranilic acid (4·0 g) in dry tetrahydrofuran (60 ml) for *ca.* 12 h, the suspension was then cooled to −10 °C and pentyl nitrite (4 ml) was added dropwise. The mixture was then stirred for 15 min at −10 °C and the precipitate was filtered and washed with ether, ensuring that the solid never became dry on the sinter (*CAUTION*—the dry solid was found to *detonate* if heated or scratched). Air-dried material was used subsequently as *2-carboxytetrachlorobenzenediazonium chloride* (26) (4·8 g) [Found: Cl (ionic) 10·5. $C_7HCl_4N_2O_2^+ Cl^-$ requires 11·0%].

Preparation of 3,4,5,6-Tetrachloro-2-(3,3-dimethyltriazeno)benzoic Acid.—2-Carboxytetrachlorobenzenediazonium chloride (*ca.* 16 g) was added in small portions to a stirred solution of dimethylamine (35 ml) and sodium carbonate (20 g) in ice–water (500 ml). After 1 h the solution was allowed to warm to room temperature and neutralised with hydrochloric acid (5N). Extraction with ether gave the *triazene* (27) (14·8 g, *ca.* 90%), m.p. 155—160 °C (decomp.) (from benzene–light petroleum) [Found: C, 32·75; H, 2·3; N, 12·6%; *M* (mass spectrometry), 331. $C_9H_7Cl_4N_3O_2$ requires C, 32·65; H, 2·15; N, 12·7%; *M*, 331]; τ −2·70 (1H, s, exchangeable), 6·45br (3H, s), and 6·74br (3H, s); $\nu_{max.}$ 3330—2700 and 1705 cm^{-1}.

The addition of an excess of an ethereal solution of diazomethane to compound (27) (465 mg) gave the *triazene* (28) (450 mg, 91%), m.p. 88—89 °C (from light petroleum) [Found: C, 34·75; H, 2·7; N, 12·3%; *M* (mass spectrometry), 345. $C_{10}H_9Cl_4N_3O_2$ requires C, 34·8; H, 2·6; N, 12·2%; *M*, 345]; τ 6·18 (3H, s), 6·50br (3H, s), and 6·76br (3H, s); $\nu_{max.}$ 2940—2900 and 1742 cm^{-1}.

Reactions of Tetrachlorobenzyne with p-*Xylene.*—(*a*) Compound (26) (*ca.* 1·2 g) was suspended in *p*-xylene (20 ml) and heated at *ca.* 140 °C for 1 h. Removal of the excess of *p*-xylene and elution of the residue from alumina with light petroleum gave 5,6,7,8-tetrachloro-1,4-dihydro-2,10-dimethyl-1,4-ethenonaphthalene (0·86 g, *ca.* 71%), m.p. 128—129 °C (lit.,[5] m.p. 128—130 °C); i.r. and ^{1}H n.m.r. spectra identical with those of an authentic sample.

(*b*) Compound (27) (500 mg) similarly gave 5,6,7,8-tetrachloro-1,4-dihydro-2,10-dimethyl-1,4-ethenonaphthalene (280 mg, 60%).

Reactions of Tetrachlorobenzene with αβ-Unsaturated Aldehydes.—(a) *By aprotic diazotisation*[5] *of tetrachloroanthranilic acid.* (i) *With acrolein.* Tetrachloroanthranilic acid (5·6 g, 0·02 mol) in acetone (50 ml) was added dropwise to a solution of pentyl nitrite (5 ml) in dichloromethane (100 ml) containing freshly distilled acrolein (50 ml) at 40 °C. After 2 h the solvents were removed by distillation and the residue was placed on alumina (50 g). Elution with light petroleum gave (a) *3-methylbutyl 2,3,4,5-tetrachlorophenyl ether* (10%), m.p. 62 °C (from ethanol) (Found: C, 43·6; H, 3·95; Cl, 46·7. $C_{11}H_{12}Cl_4O$ requires C, 43·75; H, 4·0; Cl, 46·95%); τ 3·09 (1H, s), 5·8—6·2 (2H, m), 8·0—8·4 (3H, m), and 9·02 (6H, d, $|J|$ 6 Hz) and (b) *5,6,7,8-tetrachloro-2H-chromen* (7) (17%), m.p. 150 °C (from ethanol) [Found: C, 40·15; H, 1·4; Cl, 52·6%; *M* (mass spectrometry), 270. $C_9H_4Cl_4O$ requires C, 40·0; H, 1·5; Cl, 52·6%; *M*, 270]; $\nu_{max.}$ 3070, 2980, 1635, 1560, 1450, 1405, 760, and 685 cm^{-1}.

(ii) *With crotonaldehyde.* This gave *5,6,7,8-tetrachloro-2-methyl-2H-chromen* (8) (34%), m.p. 56 °C (from ethanol) [Found: C, 42·2; H, 2·55; Cl, 49·65%; *M* (mass spectrometry), 284. $C_{10}H_6Cl_4O$ requires C, 42·25; H, 2·15; Cl, 49·9%; *M*, 284]; $\nu_{max.}$ 3070, 2960, 1640, 1565, 1450, 1410, 770, and 700 cm^{-1}.

(ii) *With 2,3-dimethylacrolein.*[45] This gave after chromatography on silica, *5,6,7,8-tetrachloro-2,3-dimethyl-2H-chromen* (9) (4%), m.p. 80—81 °C (from methanol–benzene) [Found: C, 44·3; H, 2·8%; *M* (mass spectrometry), 298. $C_{11}H_8Cl_4O$ requires C, 44·35; H, 2·7%; *M*, 298]; $\nu_{max.}$ 2980, 1660, 1537, 1416, 735, and 660 cm^{-1}.

(iv) *With 3,3-dimethylacrolein.*[46] This gave 5,6,7,8-tetrachloro-2,2-dimethyl-2*H*-chromen (10) [35h] (11%), m.p. 58—59 °C (from light petroleum) [Found: C, 44·25; H, 2·75%; *M* (mass spectrometry), 298. Calc. for $C_{11}H_8Cl_4O$: C, 44·35; H, 2·7%; *M*, 298]; $\nu_{max.}$ 2985, 2940, 1640, 1566, 1400, and 795 cm^{-1}.

(v) *With cinnamaldehyde.* This gave, after chromatography on silica, *5,6,7,8-tetrachloroflav-3-ene* (11) (37·5%), m.p. 98—99° (from ethanol) [Found: C, 52·3; H, 2·35%; *M* (mass spectrometry), 346. $C_{15}H_8Cl_4O$ requires C, 52·05; H, 2·35%; *M*, 346]; $\nu_{max.}$ 2860, 1637, 1564, 1413, 758, and 705 cm^{-1}.

A reaction using [3-^{2}H]cinnamaldehyde,[27,28] gave compound (12), *M* (mass spectrometry), 347 (94%), 346 (6%).

(b) *From 2-carboxytetrachlorobenzenediazonium chloride.* 2-Carboxytetrachlorobenzenediazonium chloride (*ca.* 0·4 g) was added to a solution of cinnamaldehyde (1·0 g) in chloroform (30 ml) and the mixture was heated under reflux for 15 min during which time the solid went into solution. After the removal of the solvent and excess of

[44] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781; M. Jones and R. H. Levin, *J. Amer. Chem. Soc.*, 1969, **91**, 6411; and references therein.

[45] M. B. Green and W. J. Hickinbottom, *J. Chem. Soc.*, 1957, 3262.

[46] G. Saucy, R. Marbet, H. Lindlar, and O. Isler, *Helv. Chim. Acta*, 1959, **42**, 1945.

cinnamaldehyde under reduced pressure the residue was eluted from silica to give compound (11) (*ca.* 58%).

(c) *From 3,4,5,6-tetrachloro-2-(3,3-dimethyltriazeno)benzoic acid.* A solution of the triazene (2·4 g) and cinnamaldehyde (2·0 g) in tetrachloroethylene (30 ml) was heated under reflux for 1 h. Removal of the solvent and excess of cinnamaldehyde under reduced pressure gave, after chromatography on silica, compound (11) (35%).

A similar reaction carried out in the absence of solvent at the reflux temperature of cinnamaldehyde gave *5,6,7,8-tetrachloroflav-2-ene* (29) (22%), m.p. 184—186 °C (from chloroform) [Found: C, 51·7; H, 2·55%; *M* (mass spectrometry), 346. $C_{15}H_8Cl_4O$ requires C, 52·05; H, 2·35%; *M*, 346]; τ (+80 °C) 2·2—2·75 (5H, m), 4·47 (1H, t, $|J| \simeq 5$ Hz), and 6·5 (2H, d, $|J| \simeq 5$ Hz); $\lambda_{max.}$ (MeOH) 222 ($\log_{10}$ ε 3·58), 240 (3·48), 247 (3·36), and 306 (2·22) nm; $\nu_{max.}$ 2880, 1688, 1554, 1408, 1190, 1059, 784, 754, 748, 707, and 684 cm^{-1}.

Rearrangements of 5,6,7,8-Tetrachloroflav-3-ene.—(a) *In cinnamaldehyde.* Compound (11) in cinnamaldehyde was heated under reflux for 5 min and gave compound (29) (50%).

(b) *On alumina.* Compound (11) (200 mg) was dissolved in ether (5 ml) and placed on an alumina column (100 g; Brockman activity 1). Elution with light petroleum gave a mixture which was separated by preparative layer chromatography and gave (R_F 0·25) compound (29) (160 mg, 80%) and (R_F 0·17) compound (11) (34 mg, 17%).

Similarly compound (12) gave compound (29) which was shown not to contain deuterium by mass spectrometry.

Compound (11) when subjected to chromatography on alumina which had been deactivated with deuterium oxide gave compound (29) which was shown by ^1H n.m.r. spectroscopy and mass spectrometry to contain 4-^2H (19%).

Reductions.—(i) Compound (7) (100 mg) in ethanol (50 ml) was reduced with hydrogen at atmospheric pressure in the presence of palladium–carbon. After the removal of the catalyst and solvent the residue gave *5,6,7,8-tetrachlorochroman* (13) (100%), m.p. 102 °C (from ethanol) (Found: C, 39·8; H, 2·7; Cl, 51·85. $C_9H_6Cl_4O$ requires C, 39·75; H, 2·2; Cl, 52·1%); $\lambda_{max.}$ (hexane) 226 ($\log_{10}$ ε 4·10) nm.

(ii) Similarly compound (8) gave *5,6,7,8-tetrachloro-2-methylchroman* (14) (100%), m.p. 82 °C (from ethanol) (Found: C, 42·2; H, 3·2; Cl, 49·3. $C_{10}H_8Cl_4O$ requires C, 42·0; H, 2·8; Cl, 49·6%); $\lambda_{max.}$ (hexane) 226 (log ε 4·10) nm.

(iii) Similarly compound (9) gave *5,6,7,8-tetrachloro-2,3-dimethylchroman* (15) (83%), m.p. 64—66 °C [from methanol–benzene (3 : 1)] [Found: C, 44·15; H, 3·45%; *M* (mass spectrometry), 300. $C_{11}H_{10}Cl_4O$ requires C, 44·05; H, 3·35%; *M*, 300].

(iv) Similarly compound (10) gave *5,6,7,8-tetrachloro-2,2-dimethylchroman* (16) (95%), m.p. 104—105 °C (from ethanol) [Found: C, 43·9; H, 3·25%; *M* (mass spectrometry), 300. $C_{11}H_{10}Cl_4O$ requires C, 44·05; H, 3·35%; *M*, 300].

(v) Similarly compound (11) gave *5,6,7,8-tetrachloroflavan* (17) (97%), m.p. 121—122 °C (from methanol) [Found: C, 51·8; H, 3·05%; *M* (mass spectrometry), 348. $C_{15}H_{10}Cl_4O$ requires C, 51·7; H, 2·9%; *M*, 348].

(vi) Similarly compound (12) gave compound (18) which was shown by mass spectrometry and ^1H n.m.r. spectroscopy to contain 2-^2H (94%).

(vii) Similarly compound (29) gave compound (17) (86%), m.p. and mixed m.p. 121—122 °C, i.r. and ^1H n.m.r. spectra identical with those of an authentic sample.

Preparation of Tetrachlorosalicylaldehyde.—A solution of tetrachloroanthranilic acid (5·5 g) in dry dimethylformamide (25 ml) and a solution of pentyl nitrite (3·5 ml) in dry dimethylformamide (12·5 ml) were added concurrently to a flask maintained at 40 °C. After a further 0·5 h the solvent was removed under reduced pressure and the residue was placed on a column of silica and eluted with benzene to give *tetrachlorosalicylaldehyde* (21) (1·4 g) (25%), as pale yellow needles, m.p. 178—180 °C (from ether) [Found: C, 32·15; H, 0·8%; *M* (mass spectrometry), 260. $C_7H_2Cl_4O_2$ requires C, 32·4; H, 0·8%; *M*, 260]; $\lambda_{max.}$ (MeOH) 241 ($\log_{10}$ ε 3·81), 278 (3·70), 303 (3·28), 326 (3·28), and 352 (3·14) nm; $\nu_{max.}$ ($CHCl_3$) 1655, 1600, 1587, 1413, 1390, 1374, 1280, 1270, 1187, 1000, and 938 cm^{-1}.

Preparation of 5,6,7,8-Tetrachloro-2,2-dimethyl-2H-chromen.—A solution of tetrachlorosalicylaldehyde (1·1 g) in acetic anhydride (10 ml) containing trimethylamine (4 ml) was heated under reflux for 3 h. Conventional work-up and purification by preparative layer chromatography gave *5,6,7,8-tetrachlorocoumarin* (22) (0·375 g), 31%), m.p. 189—190 °C [from benzene–light petroleum (1 : 1)] [Found: C, 38·15; H, 0·8%; *M* (mass spectrometry), 284. $C_9H_2Cl_4O_2$ requires C, 38·05; H, 0·7%; *M*, 284]; τ 2·64 (2H, ABq, $|J|$ 10·5 Hz); $\lambda_{max.}$ (MeOH) 232 ($\log_{10}$ ε 4·19), 291 (4·14), and 333 (3·58) nm; $\nu_{max.}$ 1792, 1762, 1750, 1715, 1613, 1565, 1393, 1377, 1226, 1180, 1102, 1012, 970, 890, 835, 755, and 680 cm^{-1}. 5,6,7,8-Tetrachlorocoumarin (350 mg) in benzene (30 ml) was added to an excess of a solution of methylmagnesium iodide [from methyl iodide (700 mg)] in ether and heated under reflux for 1·5 h. After the addition of hydrochloric acid (2N) and the removal of the solvents the residue was heated under reflux for 3 h in methanol (20 ml) containing hydrochloric acid (10 ml; 2N). Conventional work-up and preparative layer chromatography gave 5,6,7,8-tetrachloro-2,2-dimethyl-2*H*-chromen (10) (60 mg, 14%), m.p. 58—59 °C(from light petroleum), identical by i.r., u.v., n.m.r., and mass spectrometry with the product obtained from the reaction of tetrachlorobenzyne with 3,3-dimethylacrolein.

Reaction of Tetrachloroanthranilic Acid with Cinnamaldehyde.—A solution of tetrachloroanthranilic acid (2·75 g) and cinnamaldehyde (1·32 g) was heated under reflux in diethyl ether for 24 h. Evaporation of the solvent gave *5,6,7,8-tetrachloro-2-styryl-2H-3,1-benzoxazin-4(1H)-one* (25) (1·75 g, 45%), m.p. 175—177 °C (from benzene) [Found: C, 49·3; H, 2·4; N, 3·55%; *M* (mass spectrometry), 389. $C_{16}H_9NO_2Cl_4$ requires C, 49·4; H, 2·35; N, 3·6%; *M*, 389]; $\nu_{max.}$ 3400, 1735, 1580, 1455, 1400, 1330, 1250, 1215, 1200, 1145, 975, 860, 785, and 680 cm^{-1}.

Reactions of Benzyne with Cinnamaldehyde.—(a) *By the aprotic diazotisation of anthranilic acid.* A solution of anthranilic acid (6·65 g) in ether (40 ml) and dichloromethane (80 ml) was added dropwise during 0·5 h to a stirred solution of cinnamaldehyde (26·4 g) and pentyl nitrite (3 ml) in dichloromethane (50 ml) which was maintained at 40 °C. Removal of the solvents after a further 0·5 h gave an oil which was purified by column chromatography on alumina and finally by preparative layer chromatography to give 2*H*-flaven (19; R = Ph) (1·2 g, 15%), n.m.r. spectrum identical with that published.[19] Reduction in ethanolic solution with hydrogen in the presence of palladium–carbon gave flavan, m.p. 43—45 °C (lit.,[20] 44—45 °C) (Found: C, 85·8; H, 6·85. Calc. for $C_{15}H_{14}O$: C, 85·7; H, 6·7%).

(b) *From benzothiadiazole 1,1-dioxide.*[47] Cinnamaldehyde

[47] G. Whittig and R. W. Hoffmann, *Org. Synth.*, 1967, **47**, 4.

(5·0 g) was added to an ethereal solution of benzothiadiazole 1,1-dioxide [from *o*-nitrobenzenesulphinic acid (1·87 g)] at −20 °C and the mixture was allowed to warm to room temperature. After 12 h the solvent and excess of cinnamaldehyde was removed and the residue gave, as above, 2*H*-flaven (0·28 g, 15%), i.r. and n.m.r. spectra identical with those from the above sample.

(c) *From diphenyliodonium-2-carboxylate.* Diphenyliodonium-2-carboxylate (1·5 g) was heated in cinnamaldehyde (15 ml) at 180 °C for 10 min. Chromatography on alumina followed by preparative layer chromatography gave iodobenzene (53%) and 2*H*-flaven (5·7%).

Degradation of 5,6,7,8-Tetrachloroflav-2-ene.—5,6,7,8-Tetrachloroflav-2-ene (29) (623 mg) was heated under reflux in acetic acid (20 ml) containing hydrochloric acid (5 ml) until a homogeneous solution was obtained (45 min). Water (50 ml) was added to the cold solution which was then extracted with chloroform (3 × 20 ml) and gave, after the removal of acetic acid, 3-(3,4,5,6-*tetrachloro*-2-*hydroxyphenyl*)*propiophenone* (650 mg, 99%), m.p. 184—185 °C (from benzene) [Found: C, 49·55; H, 3·1%; *M* (mass spectrometry), 364. $C_{15}H_{10}Cl_4O_2$ requires C, 49·5; H, 2·9%; *M*, 364]; τ 1·10 (1H, s), 1·9—2·6 (5H, m), and 6·35—6·95 (4H, m); $\lambda_{max.}$ (MeOH) 241 ($\log_{10}$ ε 4·33), 290 (2·44), 299 (2·45), and 318 (2·17) nm; $\nu_{max.}$ 3500, 3360—3060, 1666, 1597, 1448, 1390, 1175, and 956 cm^{-1}.

The phenol (200 mg) in ether (20 ml) and methanol (0·5 ml) was added to an excess of an ethereal solution of diazomethane to give the *methoxy-compound* (196 mg, 94%), m.p. 84—85 °C (from methanol) [Found: C, 50·8; H, 3·35%; *M* (mass spectrometry), 378. $C_{16}H_{12}Cl_4O_2$ requires C, 50·85; H, 3·2%; *M*, 378]; τ 1·9—2·6 (5H, m), 6·14 (3H, s), and 6·77 (4H, s); $\lambda_{max.}$ (MeOH) 240 ($\log_{10}$ ε 3·30) and 283 (2·15) nm; $\nu_{max.}$ 2960, 2920, 2865, 1678, 1601, 1454, 1388, 1378, 1367, 1215, 1027, 746, and 689 cm^{-1}.

The ketone (924 mg) in hot ethanol (30 ml) and benzene (5 ml) was treated with hydroxylamine hydrochloride (930 mg) and pyridine (1·5 ml) and the mixture was heated under reflux for 10 min. Concentration of the solution gave 3-(3,4,5,6-*tetrachloro*-2-*methoxyphenyl*)*propiophenone anti-oxime* (32) (900 mg, 95%), m.p. 175—176 °C (from chloroform) [Found: C, 49·0; H, 3·45; N, 3·5%; *M* (mass spectrometry), 393. $C_{16}H_{13}Cl_4NO_2$ requires C, 48·9; H, 3·35; N, 3·55%; *M*, 393]; τ −1·22 (1H, s), 2·1—2·6 (5H, m), 6·11 (3H, s), and 7·01 (4H, s).

The oxime (32) (490 mg) was dissolved in ether, phosphorus pentachloride (1·0 g, 4 equiv.) was added, and the mixture was heated under reflux for 1 h. After washing the cooled mixture with water the residue was shown, by analytical t.l.c. to contain two products which were separated by preparative layer chromatography and gave (*a*) R_F 0·3, 2-*chloro*-N-*phenyl*-3-(3,4,5,6-*tetrachloro*-2-*methoxyphenyl*)*propionamide* (33) (229 mg, 43%), m.p. 156—161 °C (from benzene–light petroleum) [Found: C, 45·3; H, 2·75; N, 3·2%; *M* (mass spectrometry), 426. $C_{16}H_{11}Cl_5NO_2$ requires C, 45·05; H, 2·6; N, 3·3%; *M*, 426]; τ −0·08 (1H, s), 2·2—3·0 (5H, m), 5·07 (1H, q, $|J_{AX} + J_{BX}|$ 15 Hz), 6·08 (3H, s), 6·2—6·65 (2H, m, AB of ABX); $\nu_{max.}$ 3290, 2940, 2860, 1675, 750, and 690 cm^{-1}; and (*b*) R_F 0·05, *N*-phenyl-3-(3,4,5,6-tetrachloro-2-methoxyphenyl)propionamide (275 mg, 56%), m.p. 211—212 °C (from benzene–light petroleum), *M* (mass spectrometry), 393; τ 0·2—0·4 (1H), 2·2—3·0 (5H, m), 6·08 (3H, s), 6·6—7·0 (2H, m), and 7·2—7·6 (2H, m); $\nu_{max.}$ 3290, 2940, 2860, 1646, 753, and 688 cm^{-1}.

When the oxime (32) was treated as above with phosphorus pentachloride (14 equiv.) the amide (33) was obtained in 92% yield.

The amide (33) (300 mg) was heated under reflux in acetic acid (20 ml) and hydrochloric acid (10 ml) for 1·5 h. The cooled solution was then neutralised with sodium hydrogen carbonate and extracted with chloroform. Concentration of the extract gave aniline (45 mg) (comparison of i.r. spectra and conversion to acetanilide). The aqueous phase on acidification and extraction with chloroform gave 2-chloro-3-(3,4,5,6-tetrachloro-2-methoxyphenyl)-propionic acid, as an oil (144 mg, 62%); τ 0·1—0·2 (1H), 5·24 (1H, t, $|J|$ 7·0 Hz), 6·08 (3H, s), and 6·44 (2H, d, $|J|$ 7·0 Hz); $\nu_{max.}$ 3300—2500 and 1740 cm^{-1}. The oil (90 mg) was heated under reflux in methanol (30 ml) containing potassium hydroxide (200 mg) for 1·5 h and gave after acidification trans-3-(3,4,5,6-*tetrachloro*-2-*methoxyphenyl*)-*propenoic acid* (78 mg, 98%), m.p. 205—206 °C (from benzene) [Found: C, 38·1; H, 2·0%; *M* (mass spectrometry), 316. $C_{10}H_6Cl_4O_3$ requires C, 38·0; H, 1·9%; *M*, 316]; τ 2·4—2·7 (1H, exchangeable), 2·77 [2H, ABq (δ = 0·98 p.p.m.), $|J|$ 17·0 Hz], and 6·21 (3H, s); $\nu_{max.}$ 3300—2800 and 1700 cm^{-1}.

Similarly, hydrolysis of the 2-dechloro-analogue of (33) gave aniline and 3-(3,4,5,6-*tetrachloro*-2-*methoxyphenyl*)-*propanoic acid* (50%), m.p. 160—163 °C (from benzene) [Found: C, 37·9; H, 2·3%; *M* (mass spectrometry), 318. $C_{10}H_8Cl_4O_3$ requires C, 37·75; H, 2·55%; *M*, 318]; τ [$(CD_3)_2SO$] 0·8—1·2 (1H, exchangeable), 6·12 (3H, s), 6·6—7·0 (2H, m), and 7·2—7·7 (2H, m); $\nu_{max.}$ 3300—2500 and 1710 cm^{-1}.

Ozone-enriched oxygen was passed for 5 min through a solution of the *trans*-propenoic acid (312 mg) in methanol (25 ml) and chloroform (10 ml) at 0 °C. Removal of the solvents afforded an oil which was dissolved in formic acid (10 ml) and hydrogen peroxide (5 ml; 100 vol) was added. The mixture was heated gently and then more vigorously for 10 min and allowed to cool. Water (10 ml) was then added and the precipitate which formed was extracted into chloroform and gave 2-methoxy-3,4,5,6-tetrachlorobenzoic acid (150 mg, 52%); τ 3·1—3·7 (1H, exchangeable) and 6·05 (3H, s); $\nu_{max.}$ 3500—2800 and 1730 cm^{-1}. This was methylated with an excess of an ethereal solution of diazomethane to give *methyl 2-methoxytetrachlorobenzoate* (34) (141 mg, 95%), m.p. 88—90 °C (from light petroleum) [Found: C, 35·45; H, 2·1%; *M* (mass spectrometry), 304. $C_9H_6Cl_4O_3$ requires C, 35·55; H, 2·0%; *M*, 304]; τ 6·05 (s); $\nu_{max.}$ 2960, 2865, and 1750 cm^{-1}.

Tetrachlorosalicylaldehyde (100 mg) was methylated with an excess of an ethereal solution of diazomethane and gave 2-methoxytetrachlorobenzaldehyde, τ 0·21 (1H, s) and 6·21 (3H, s); $\nu_{max.}$ 2950, 2860, and 1718 cm^{-1} which was oxidised with chromium(III) oxide in acetic acid and gave after the usual work-up and methylation methyl 2-methoxytetrachlorobenzoate, m.p. and mixed m.p. 88—90 °C, i.r. spectrum identical with that of an authentic sample.

We thank the University and the S.R.C. for studentships (to J. M. J. and C. T. McC. respectively). We also thank the P.C.M.U. and S.R.C. for certain n.m.r. spectra.

[2/1261 *Received, 5th June,* 1972]