Carbonyl and Thiocarbonyl Compounds. Part XIV.[1] Reactions of Tetrachloro-*o*-benzoquinone with 3-(2-Furyl)- and 3-(2-Thienyl)-acrylophenones

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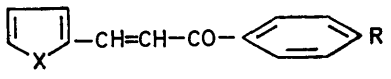
Tetrachloro-*o*-benzoquinone readily undergoes 1.4-cycloaddition with the furyl residue of 3-(2-furyl)acrylophenones to give the 1 : 1 adducts (2). Further addition to the electrophilic double bond of the side chain to give the 2 : 1 adducts (6a—c) requires drastic conditions. In contrast, addition to the side chain of the 3-(2-thienyl)acrylophenones (1d—f) readily gives the 1 : 1 adducts (3a—c), with the thiophen ring unmodified. Adducts (3a—c) form hydrazones and oximes, and the latter react with isocyanates affording oxime carbamates (3k—m) of possible pesticidal importance. The adducts (2a—c) react with benzylmagnesium chloride to give the expected β-benzyl adducts (6a—c), whereas with phenylmagnesium bromide concomitant cleavage of the dioxan ring occurs to give the 3-(2-furyl)-3-phenylpropiophenones (7a—c).

DURING studies on the dienophilic character of five-membered heterocycles we have shown [2] that tetrahalogeno-*o*-benzoquinones react readily with 2-vinylfurans to give adducts of the type (2) under mild conditions with retention of the vinyl side chain [*e.g.* (2a) from (1a)].

[1] Part XIII, N. Latif and S. Abdel Meguid, *J. Chem. Soc.* (*C*), 1971, 1095.

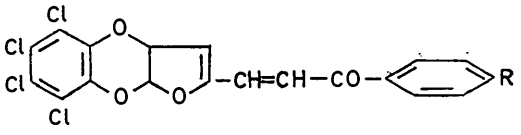
[2] N. Latif, N. S. Girgis, and F. Michail, *Tetrahedron*, 1970, **26**, 5765.

We now report that the thiophen analogue (1d) reacts with tetrachloro-*o*-benzoquinone under similar conditions



(1)

a; X = O, R = H
b; X = O, R = OMe
c; X = O, R = Cl
d; X = S, R = H
e; X = S, R = OMe
f; X = S, R = Cl

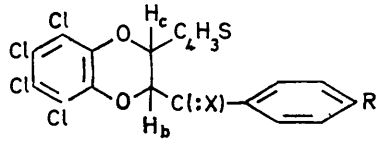


(2)

a; R = H
b; R = OMe
c; R = Cl

to give 5,6,7,8-tetrachloro-2,3-dihydro-3-(2-thienyl)-1,4-benzodioxin-2-yl phenyl ketone (3a) without modification of the thiophen ring. Thermal 1,4-cyclo-additions of *o*-quinones with open-chain αβ-unsaturated ketones have not been reported previously except recently, in connection with naphthalene chalcones.[3]

The adduct (3a) shows $\nu_{C=O}$ 1700 cm^{-1} like acetophenone. Its u.v. spectrum exhibits strong aroyl absorption [$\lambda_{max.}$ (cyclohexane) 235 nm (ε 31,100)],* as a shoulder on the long-wave side of a strong band at 217 nm (ε 63,400). A band similar to the latter has been recently reported in the spectra of polyhalogeno-1,4-benzodioxins and 1,3-benzodioxoles and ascribed to band I of benzene, red shifted owing to full substitution by auxochromes.[1,2] The n.m.r. spectrum of (3a) includes a pair of doublets at δ 5·85 and 6·05 due to H_b and H_c (*J* 5 Hz).



(3)

	X	R		X	R
a;	O	H	b;	O	OMe
c;	O	Cl	d;	N·NHCOPh	H
e;	N·NHPh	H	f;	N·NHPh	OMe
g;	N·NHPh	Cl	h;	N·OH	H
i;	N·OH	OMe	j;	N·OH	Cl
k;	N·O·CO·NHMe	H	l;	N·O·CO·NHMe	OMe
m;	N·O·CO·NHMe	Cl			

The adduct (3a) does not form a quinoxaline derivative with *o*-phenylenediamine; however, it condenses with benzoyl- and phenyl-hydrazine affording the hydrazones (3d and e), and gives a mono-oxime (3 h) which reacts readily with methyl isocyanate to give the *N*-methylcarbamate (3k).

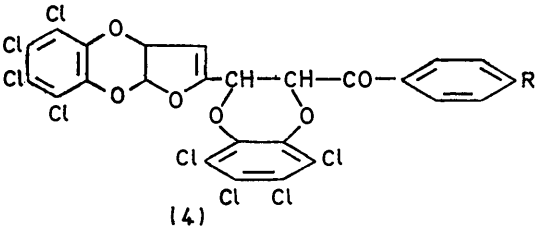
The substituted 3-(2-thienyl)acrylophenones (1d and e) react similarly with tetrachloro-*o*-benzoquinone to give the 1 : 1 adducts (3b and c). The n.m.r. spectrum of (3b) shows a methoxy-singlet at δ 3·8 and a pair of doublets at δ 5·75 and 5·95 (*J* 5 Hz) for the vicinal dioxan ring protons. This 5 Hz coupling in (3a and b) favours the *cis*-configuration. The adducts (3b and c) also give phenylhydrazones (3f and g), oximes (3i and j), and oxime carbamates (3l and m), respectively. The structural features of the carbamates are such as to make them suitable for testing as insecticides which may act as their own synergists.[4,5]

In contrast to the thiophen analogues, tetrachloro-*o*-benzoquinone does not add to the vinyl side chain of the 3-(2-furyl)acrylophenones (1a—c) except under drastic conditions (prolonged boiling in toluene), when the 2 : 1 adducts (4a—c) are formed, presumably through initial attack of the quinone on the electron-rich 4,5-double bond of the furyl residue, followed by cycloaddition on the side chain. This view is supported by the fact that the adducts (4a—c) are also obtained by the action of the quinone on the 1 : 1 adducts (2a—c) in boiling toluene. These 1 : 1 adducts are obtained readily from the furylacrylophenones (1a—c) under much milder conditions.

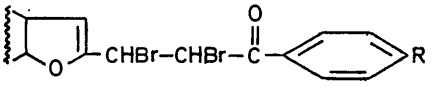
The higher reactivity of the side chain of the thienylacrylophenones than of the furyl analogues is presumably due mainly to the higher electron density at the double bond of the former as a result of extended conjugation involving the *n*-electrons of the sulphur atom. The resistance of the thiophen ring to attack by the quinone is presumably due to its pronounced aromatic character.

The i.r. and u.v. spectra of the adducts (4a—c) are similar to those of acetophenones. The u.v. spectra include the very strong absorption in the 215—220 nm region ascribed to band I of benzene but with almost double the extinction value of the adducts (2), owing to the presence of two polyhalogenobenzodioxin units.

The 1 : 1 adducts (2a—c) [(2a) has been reported previously [2]] readily form dibromides (5a—c). Their



(4)



(5)

a; R = H, b; R = OMe, c ; R = Cl

i.r. and u.v. spectra support the presence of the β-unsaturated side chain. The n.m.r. spectrum of (2b) includes a pair of doublets at δ 7 and 7·45 (*J* 15 Hz) for the coupled vinyl protons of the side chain. The high *J*

* The high ε value is presumably due to the presence of the thienyl residue [thiophen absorbs at 231 nm (ε 7100) in iso-octane].

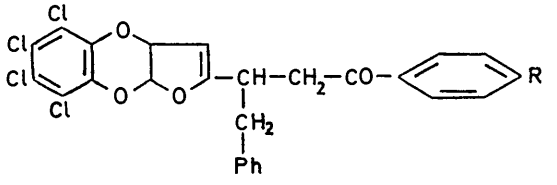
[3] N. Latif and Kh. El Bayouki, Third International Congress of Pesticide Chemistry, Helsinki, 1974, Abstracts p. 446.

[4] T. R. Fukuto, R. L. Metkalf, R. L. Jones, and R. O. Meyer, *J. Agric. Food Chem.*, 1969, **17**, 923.

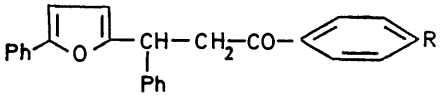
[5] R. L. Metkalf, T. R. Fukuto, and E. R. Metkalf, *J. Agric. Food Chem.*, 1966, **14**, 555.

value supports the *trans*-configuration. The signals for dioxin ring protons appear as a doublet and quartet at δ 5·45 and 6·75, with J 3 Hz, suggesting a *cis*-relationship. The other furan ring proton resonates as a doublet at δ 6·4 (J 7 Hz).

Reactions of the Cycloadducts with Organomagnesium Halides.—The 1 : 1 adducts (2a—c) react with benzylmagnesium chloride to give the expected butyrophenones (6a—c). However phenylmagnesium bromide cleaves the dioxan ring under mild conditions affording the propiophenones (7a—c) along with tetrachlorocatechol.



(6)



(7)

a; R = H, b; R = OMe, c; R = Cl

The n.m.r. spectra of (7a and b) exhibit ABX patterns for the ·CH·CH_2· group of protons. For example (7a) shows δ 3·72 (septet, J_{AB} 17, $J_{AX} = J_{BX}$ 8 Hz, CH_2) and 4·85 (t, CH). Signals for the furyl protons appear as a pair of doublets at 6·05 and 6·5 (J 4 Hz).

Presumably compounds (7a—c) are produced through 1,4-addition of the Grignard reagent to the unsaturated side chain of (2a—c) and attack of the reagent on the highly electrophilic C-5 of the furyl residue.

EXPERIMENTAL

N.m.r. spectra were recorded at 60 MHz with Varian T-60 and EM-360 spectrophotometers; Me_4Si was used as internal standard.* U.v. and i.r. data and elemental analyses are available as Supplementary Publication No. SUP 21324 (7 pp.).†

Reaction of Tetrachloro-o-benzoquinone with the Acrylophenones (1a—f).—A solution of the acrylophenone (0·05 mol) and the quinone (0·1 mol) in the appropriate solvent (150 ml) was refluxed for the required period, filtered hot, and evaporated to dryness. The oily residue was triturated with ether and the separated solid was crystallised from the appropriate solvent to give the cycloadducts (2a—c), (3a—c), and (4a—c) (Table 1).

Reactions of the 2-Benzoyl-2,3-dihydro-3-(2-thienyl)-1,4-benzodioxins (3a—c) *with Hydrazines and Hydroxylamine Hydrochloride.*—The reagent (0·015 mol) was added to a suspension of the adduct (0·01 mol) in the appropriate solvent (25 ml) [pyridine (0·5 ml) was also added in the case of hydroxylamine hydrochloride], and the mixture was refluxed for 4 h, filtered hot, concentrated, and cooled. The separated solid was crystallised from the appropriate solvent to give the hydrazones and oximes (3d—j) (Table 2). The products are reconverted into the parent benzodioxins on acidic hydrolysis.

Preparation of the Oxime Carbamates.—A solution of the oxime (0·01 mol), methyl isocyanate (0·01 mol), and a few drops of triethylamine in dry benzene (15 ml) was refluxed for 6 h, concentrated, and cooled after addition of a few ml of cyclohexane. The solid obtained was crystallised from the appropriate solvent to give the oxime carbamate (3k—m) (Table 2).

Reaction of Tetrachloro-o-benzoquinone with the 1 : 1 *Adducts* (2a—c).—A solution of the adduct (0·01 mol) and *o*-chloranil (0·01 mol) in dry toluene (30 ml) was refluxed for 20 h. The mixture was worked up as above to give the corresponding 2 : 1 adducts (4), identified by m.p. and mixed m.p.

Bromination of the 1 : 1 *Adducts* (2a—c).—Bromine (0·02 mol) in glacial acetic acid (10 ml) was added dropwise at 0—5 °C to a solution of the adduct (0·01 mol) in acetic acid (25 ml); after 1 h the dibromide (5) had separated out (Table 3).

Reaction of Benzyl- and Phenyl-magnesium Halides with the 1 : 1 *Adducts* (2a—c).—The adduct (0·01 mol) was added in portions at room temperature to an ethereal solution of the Grignard reagent (0·03 mol). The mixture was left for

TABLE 1

1 : 1 and 2 : 1 Adducts

Product	Reaction medium	Reflux time (h)	M.p. (°C)	Cryst. solvent *	Yield (%)
(2a)	PhH	1	194	PhH	75
(2b)	PhH	1	179—180	PhH	70
(2c)	PhH	1	206—207	PhH	73
(3a)	PhH	20	175	Ch	39
(3b)	PhH	20	158	Ch	38
(3c)	PhH	20	157—158	Ch	40
(4a)	PhMe	20	206—207	PhH–Ch	60
(4b)	PhMe	20	236—237	PhH–Ch	75
(4c)	PhMe	20	258—259	PhH–Ch	60

* Ch = cyclohexane.

TABLE 2

Hydrazones, oximes, and oxime carbamates

Product	Reaction medium	M.p. (°C)	Cryst. solvent *	Yield (%)
(3d)	BuOH	245	MeOH	60
(3e)	EtOH	178	EtOH	70
(3f)	EtOH	174—176	Ch	70
(3g)	EtOH	171—172	EtOH	68
(3h)	EtOH	181—182	Ch	72
(3i)	EtOH	180—182	Ch	70
(3j)	EtOH	175—176	Ch	65
(3k)	PhH	205—206	PhH–Ch	72
(3l)	PhH	158—160	Ch	68
(3m)	PhH	182—184	Ch	65

* Ch = cyclohexane.

TABLE 3

Bromination and Grignard reaction products

Product	M.p. (°C)	Yield (%)	Cryst. solvent *
(5a)	215	65	PhH
(5b)	205—206	60	PhH
(5c)	210—211	65	PhH
(6a)	90	70	H
(6b)	89—91	40	Ch
(6c)	83—85	45	Ch
(7a)	157—158	58	H
(7b)	155—156	60	H
(7c)	119—120	60	H

* Ch = cyclohexane; H = hexane.

* We thank Dr. T. Wirthlin, Varian, Switzerland, for determining the n.m.r. spectra.

† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

30 min, decomposed with ice and ammonium chloride, and then extracted with ether. The extract was washed with water, dried,* and evaporated to dryness. The residue was triturated with n-hexane and the separated solid was crystallised from the appropriate solvent to give the 3-(tetrachloro-3a,9a-dihydrofuro[2,3-b][1,4]benzodioxin-2-yl)-4-phenylbutyrophenone (6) or the 3-phenyl-3-(5-phenyl-2-furyl)propiophenone (7) (Table 3).

* In the reactions of phenylmagnesium bromide, the extract was washed with aqueous potassium hydroxide (5%); acidification of the washings then gave tetrachlorocatechol (identified as its diacetate).

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