N-Oxides and Related Compounds. Part L.[1] Reactions of Pyridinium and Sulphonium Ylides with Pyrylium Salts

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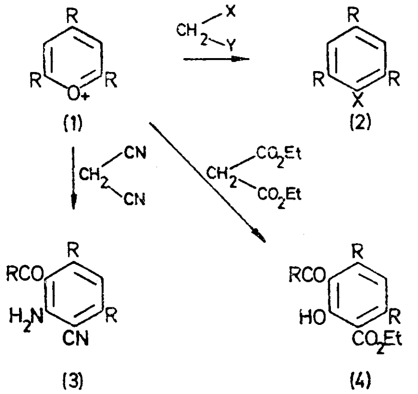
2,4,6-Triphenylpyrylium perchlorate reacts with pyridinium acylylides to form arylpyridinium perchlorates by a ring-opening–ring-closure mechanism, and with sulphonium ylides to afford furans. Spectral data are discussed.

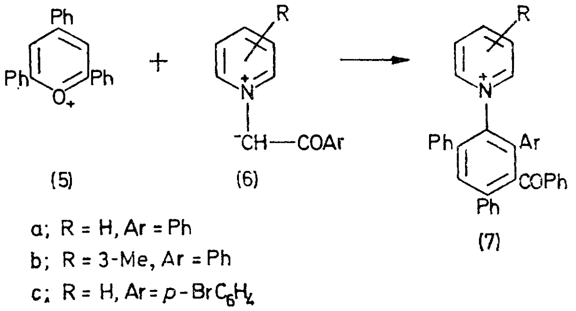
NUMEROUS reactions of pyrylium salts with amino-compounds yield pyridine derivatives.[2-6] Several types of active methylene compounds similarly afford benzenes: thus, nitromethane yields nitrobenzenes.[7] β-oxo-esters give benzoate esters,[8] acetylacetone gives acetophenones,[8] and cyanoacetic ester benzonitriles.[8] An analogous reaction with benzyl-lithium or benzylmagnesium chloride affords a biphenyl.[8,9] In all the foregoing cases the reaction can be represented by (1) ⟶ (2) in Scheme 1. However, reactions with malonic ester[10] and malononitrile can take a different course [(1) ⟶ (3) or (4)] in which two carbon atoms from the nucleophile are incorporated into the new ring.



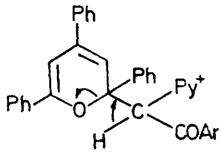
SCHEME 1

Only one previous disclosure[11] was found concerning reactions of pyrylium salts with ylides; we now report our results with pyridinium, sulphonium, and phosphonium ylides.

Reactions with Pyridinium Ylides.—2,4,6-Triphenylpyrylium perchlorate (5) reacted with the pyridinium acylylides (6a—c) to give the arylpyridinium perchlorates (7a—c). The products are considered to be formed *via* intermediates of types (8) and (9), and were identified on the basis of analysis and spectral data. Particularly significant were the one-proton singlets in the n.m.r. spectra at δ 7.91 ± 0.02 for the 5-protons of the phenyl groups and the benzoyl carbonyl i.r. absorption at 1 670 ± 2 cm^{-1}. In the original ylides (6a—c), ν(C=O) varied in the range 1 710—1 695 cm^{-1}; the invariability of the corresponding absorption in the products indicates that the acyl group is benzoyl derived from the pyrylium ring rather than the original (substituted) aroyl group of the acylylide.



SCHEME 2



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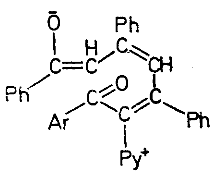

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Reactions with Sulphonium Ylides.—2,4,6-Triphenylpyrylium perchlorate (5) reacted with the sulphonium ylides (10a—c) to yield the furans (13a—c) (Table 1). The reaction is considered to involve the intermediates (11) and (12), and the products are assigned the furan formulae (14) rather than the alternative oxepin structures (13) on the basis of a single crystal *X*-ray study[12] of compound (14c).† The formation of the furan ring from (12) was unexpected, and the precise details of the mechanism are not known. The furans (14a—c) show broad carbonyl absorption at *ca.* 1 650 cm^{-1} (KBr or

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† In our preliminary communication [1] we incorrectly referred to an *X*-ray study of compound (14a).

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[7] (*a*) K. Dimroth and G. Bräuninger, *Angew. Chem.*, 1956, **68**, 519; (*b*) K. Dimroth, G. Bräuninger, and G. Neubauer, *Chem. Ber.*, 1957, **90**, 1634; (*c*) K. Dimroth, G. Neubauer, H. Möllenkamp, and G. Oosterloo, *ibid.*, p. 1668.

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[11] G. Märkl, *Angew. Chem.*, 1962, **74**, 696.

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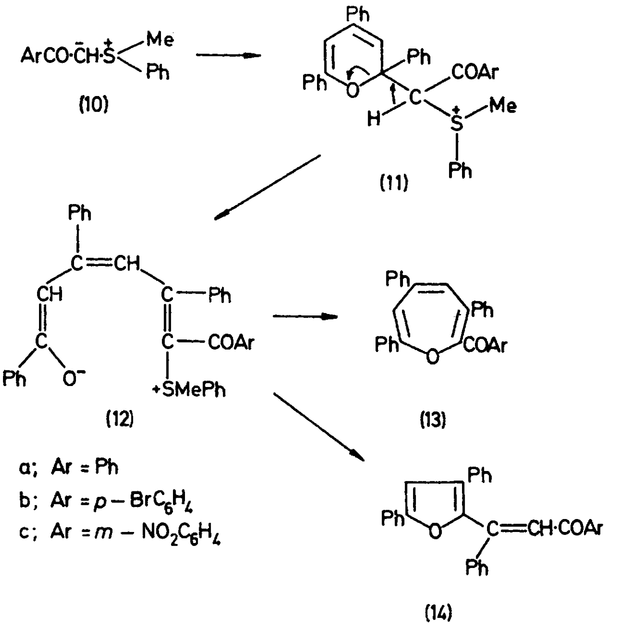
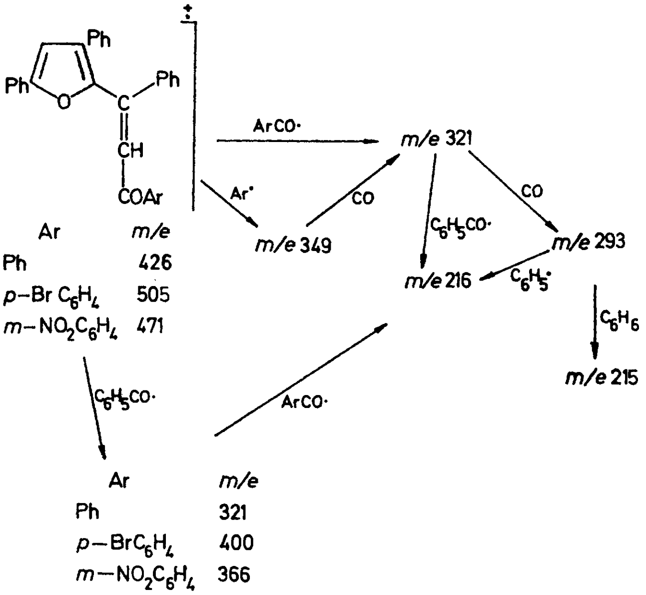
$CHCl_3$); *cf.* chalcone[13] ν(C=O) 1 669 cm^{-1} and 3-(2-furyl)acrylophenone[13] 1 669 cm^{-1}. In the polysubstituted systems it is difficult to distinguish the characteristic furan ring stretching modes,[14] but strong absorptions are observed near 1 550 and 1 200 cm^{-1}.

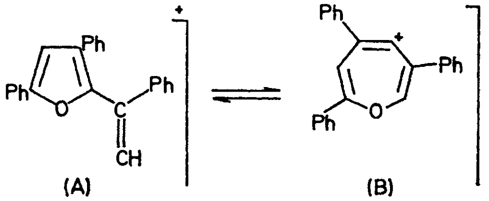


SCHEME 3



SCHEME 4

The general mass-spectral fragmentation pattern for the furans is outlined in Scheme 4. The M and $M + 1$ ions were observed in all three cases and the ion at m/e 321 was the base peak. Unfortunately, the mass spectral evidence does not provide conclusive proof for either the furan or the oxepin structure, since the loss of COAr from structure (14) would give ion (A) which could rearrange to (B) (Scheme 5). No ions were observed corresponding to 2,4-diphenylfuran or to a pyrylium salt. The latter was an expected rearrangement product from either structure. The mass spectra contain M^{2+} peaks for the parent ions and metastable ions corresponding to the loss of –COAr from the oxepin molecule.

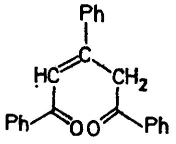


SCHEME 5

N.m.r. spectra are complicated by the large number of aromatic protons. A one-proton singlet at 6.80 ± 0.02 is due either to the styryl proton (–CPh=CH·COAr) or the 4-proton of the furan ring. Attempts to identify the other expected singlet by use of lanthanide shift reagents failed.

U.v. measurements (solvent 95% ethanol; Table 2) show absorption maxima analogous to those of the related substituted acrylophenones.

Reaction with a Phosphonium Ylide.—2,4,6-Triphenylpyrylium perchlorate (5) reacted with triphenylphosphonium phenacylide to give the anhydro-base (15). This diketone probably arises from attack of moisture on the triphenylphosphonium intermediate analogous to (12). A similar intermediate was isolated by Märkl[11] from the corresponding methoxycarbonyl ylide.



(15)

EXPERIMENTAL

Methylphenacylphenylsulphonium Perchlorate.—Methyl phenyl sulphide (6.2 g, 0.05 mol), dichloroethane (50 ml), phenacyl bromide (8.95 g, 0.05 mol), and silver perchlorate–acetonitrile complex (18.6 g, 0.05 mol)[15] were stirred for 12 h at 20 °C. Silver bromide was filtered off and washed with hot acetonitrile (20 ml). Solvent was evaporated from the combined filtrate (15 mmHg; 40 °C) to give the sulphonium[16] salt, which crystallised from acetone–ether. 4-Bromophenacyl-, 3-nitrophenacyl-, and 4-methoxyphenacyl-sulphonium salts were prepared similarly (Table 3).

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TABLE 1

Furans (14)

Ar	Crystal form	Yield (%)	M.p. (°C)	Found (%)			Mol. formula	Required (%)			I.r.[a]	
				C	H	Other		C	H	Other	$\nu_{max.}$(CO)	$\nu_{max.}$ (vinyl ether)
Ph	Yellow needles	87	112—113	87.1	5.3		$C_{31}H_{22}O_2$	87.3	5.2		1 645 ± 2	1 212(A), 1 016s
p-BrPh	Yellow needles	85	166—168	73.6	4.4	15.9(Br)	$C_{31}H_{21}BrO_2$	73.7	4.2	15.8(Br)	1 650 ± 2	1 211(A), 1 010s
m-NO_2Ph	Yellow prisms	73	170—172	79.0	4.7	3.0(N)	$C_{31}H_{21}NO_4$	79.0	4.5	3.0(N)	1 655 ± 2	1 207(A), 1 085s[b]

[a] KBr disc; cm^{-1}. [b] NO_2 1 525 and 1 347 cm^{-1}.

TABLE 2

U.v. maxima for furans and substituted acrylophenones ($R^1R^2C{=}CH{-}COAr$)

R^1	R^2	Ar	λ/nm (ε)	λ/nm (ε)	λ/nm (ε)
Ph	H	Ph	228[a] (9 800)		308[a] (24 300)
Ph	Ph	Ph	231[a] (16 100)	250[a] (13 500)	298[a] (10 500)
2-Furyl	H	Ph		260[b] (8 872)	340[b] (29 480)
2-(3,5-Diphenyl)furyl	Ph	Ph	225 (21 000)	273sh (26 200)	382 (6 600)
		p-BrC_6H_4	226 (27 200)	275sh (31 200)	392 (8 300)
		m-$NO_2C_6H_4$	226 (25 500)	262sh (29 000)	377 (7 400)

[a] Taken from D. S. Noyce and M. J. Jorgenson, *J. Amer. Chem. Soc.*, 1962, **84**, 4312. [b] Taken from V. F. Lavrushin, S. V. Tsukerman, and A. I. Artemenko, *J. Gen. Chem.* (*U.S.S.R.*), 1962, **32**, 2516 (*Zhur. obshchei Khim.*, 1962, **32**, 2551).

TABLE 3

Phenacylpyridinium perchlorates [*cf.* (6)]

cf. (6)		Crystal form	Yield (%)	M.p. (°C)	Found (%)			Mol. formula	Calc. (%)			N.m.r.[a]		I.r.[b]
R	Ar				C	H	N		C	H	N	CH_2 (s)	Ar (m)	$\nu_{max.}$(CO)
H	Ph	Needles	75	184—185	52.5	4.3	4.7	$C_{13}H_{12}ClNO_5$	52.4	4.0	4.7	6.39	7.46—8.84	1 700 ± 2
H	*p*-BrC_6H_4	Needles	82	227—228	41.4	3.1	3.7	$C_{13}H_{11}BrClNO_5$	41.4	2.9	3.7	6.48	7.71—8.93	1 695 ± 2
H	*m*-$NO_2C_6H_4$[c]	Prisms	80	187—189	45.1	3.3	8.5	$C_{13}H_{11}ClN_2O_7$	45.5	3.2	8.2	6.68	7.76—9.0	1 695 ± 2
3-Me	Ph	Needles	75	164—166	53.8	4.6	4.5	$C_{14}H_{14}ClNO_5$	53.9	4.5	4.5	6.45	7.50—8.64[d]	1 710 ± 2

[a] 60 MHz; solvent $CF_3{\cdot}CO_2H$; δ values from internal Me_4Si. [b] KBr disc; cm^{-1}. [c] Bromide salt obtained as prisms from ethanol, m.p. 242—244° (decomp.) (Found: C, 48.1; H, 3.6; N, 8.7. $C_{13}H_{11}BrN_2O_3$ requires C, 48.3; H, 3.4; N, 8.7%). [d] 3-CH_3: 2.67(s).

TABLE 4

Methylphenacylphenylsulphonium perchlorates [*cf.* (10)]

Ar [*cf.* (10)]	Crystal form	Yield (%)	M.p. (°C)	Found (%)		Mol. formula	Calc. (%)		N.m.r.[a]			I.r.[b]
				C	H		C	H	CH_3 (s)	CH_2 (s)	Ar (m)	$\nu_{max.}$ (CO)
Ph	Needles	88	143—145	52.5	4.8	$C_{15}H_{15}ClO_5S$[c]	52.5	4.4	3.40	5.56	7.51—8.20	1 680 ± 2
p-BrC_6H_4	Plates	86	175—177	42.3	3.5	$C_{15}H_{14}BrClO_5S$	42.7	3.3	3.43	5.54	7.58—8.17	1 685 ± 2
p-$MeOC_6H_4$	Plates	85	142—143	51.5	4.7	$C_{16}H_{17}ClO_6S$	51.5	4.6	3.42	5.20[d]	6.98—8.13	1 660 ± 2
m-$NO_2C_6H_4$[e]	Needles	82	139—140	46.0	3.8	$C_{15}H_{14}ClNO_7S$	46.4	3.6	3.51	5.71	7.7—8.8	1 693 ± 2[f]

[a] 60M Hz; solvent $CF_3{\cdot}CO_2H$; δ values from Me_4Si. [b] KBr disc; cm^{-1}. [c] Fluoroborate salt known (see ref. 16). [d] *p*-CH_3O: 3.93(s). [e] Found: N, 3.6 (Calc. 3.6%). [f] NO_2: 1 521 and 1 351 cm^{-1}.

TABLE 5

N-Phenylpyridinium salts (7)

R	Ar	Crystal form	Yield (%)	M.p. (°C)	Found (%)			Mol. formula	Calc. (%)			N.m.r.[a]		I.r.[b]
					C	H	N		C	H	N	5H (s)	ArH (m)	$\nu_{max.}$ (CO)
H	Ph	Plates	40	170—172	72.7	4.8	2.6	$C_{36}H_{26}ClNO_5$	73.5	4.4	2.4	7.91 ±0.02	6.97—8.76	1 671 ± 2
H	*p*-BrC_6H_4	Plates	35	242—244	64.2	4.0	2.1	$C_{36}H_{25}BrClNO_5$	64.9	3.8	2.3	7.91 ±0.02	7.09—8.82	1 671 ± 2
3-Me	Ph	Needles	52	178—180	73.5	4.8	2.2	$C_{37}H_{28}ClNO_5$	73.8	4.7	2.3	7.91 ±0.02	7.10—8.45[c]	1 668 ± 2

[a] 100 MHz; solvent $CF_3{\cdot}CO_2H$; δ values from Me_4Si. [b] KBr disc; cm^{-1}. [c] 3-Me: 2.34(s).

1-*Phenacylpyridinium Perchlorate.*—Pyridine (7.9 g, 0.1 mol), ethanol (50 ml), and phenacyl bromide (19.9 g, 0.1 mol) were heated under reflux for 2 h. Ether was added to the cooled mixture. The intermediate bromide separated and was dissolved in the minimum of water, and saturated sodium perchlorate was added. The perchlorate which separated was recrystallised from acetone–ether. 1-Phenacyl-3- and -4-methylpyridinium perchlorates and 1-(4-bromophenacyl)-, and 1-(3-nitrophenacyl)-pyridinium perchlorates were prepared similarly (Table 4).

Preparation of Ylides.—Crude quaternary bromides were converted into the corresponding ylides by treating their aqueous solutions with aqueous 10% sodium carbonate. The ylide was extracted with chloroform; filtration through anhydrous sodium carbonate and evaporation gave the crude ylide which was dried at 0.2 mmHg and 25 °C for 1 h before use. Perchlorates were converted into ylides by using chloroform and shaking until all the solid dissolved.

Substituted Diphenylfurans.—2,4,6-Triphenylpyrylium perchlorate (4.08 g, 0.01 mol), the sulphonium ylide (0.02 mol), and chloroform (175 ml) were heated under reflux for 3 h. After cooling, the resulting crystalline solid (methylphenacylphenylsulphonium perchlorate), (3.2 g) was filtered off and the filtrate evaporated. The residual red oil was extracted with light petroleum (evaporation of the extract yielded methyl phenyl sulphide). The yellow *furans* insoluble in light petroleum were crystallised from benzene–light petroleum (b.p. 40—60°) (Table 1).

1-(3-*Benzoyl*-2,4,6-*triphenyl*)*phenylpyridinium Perchlorates.*—The pyridinium ylide (0.006 mol), chloroform (40 ml), and 2,4,6-triphenylpyrylium perchlorate (1.225 g, 0.003 mol) were heated under reflux for 3 h. The mixture was cooled and the separated solid collected. Several recrystallisations from acetone–ether gave the *products* (Table 5).

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