Tetrahedron Letters,Vol.22,No.48,pp 4831-4834,1981 0040-4039/81/484831-04$02.00/C
Printed in Great Britain
©1981 Pergamon Press Ltd.

ACID-CATALYSED REACTIONS OF 3,5-DIALKYL-SPIRO[2.5]OCTA-2,5-DIEN-4-ONES

By R.S. Ward* and K.S. Thatcher.

Chemistry Department, University College of Swansea, Singleton Park,
Swansea SA2 8PP.

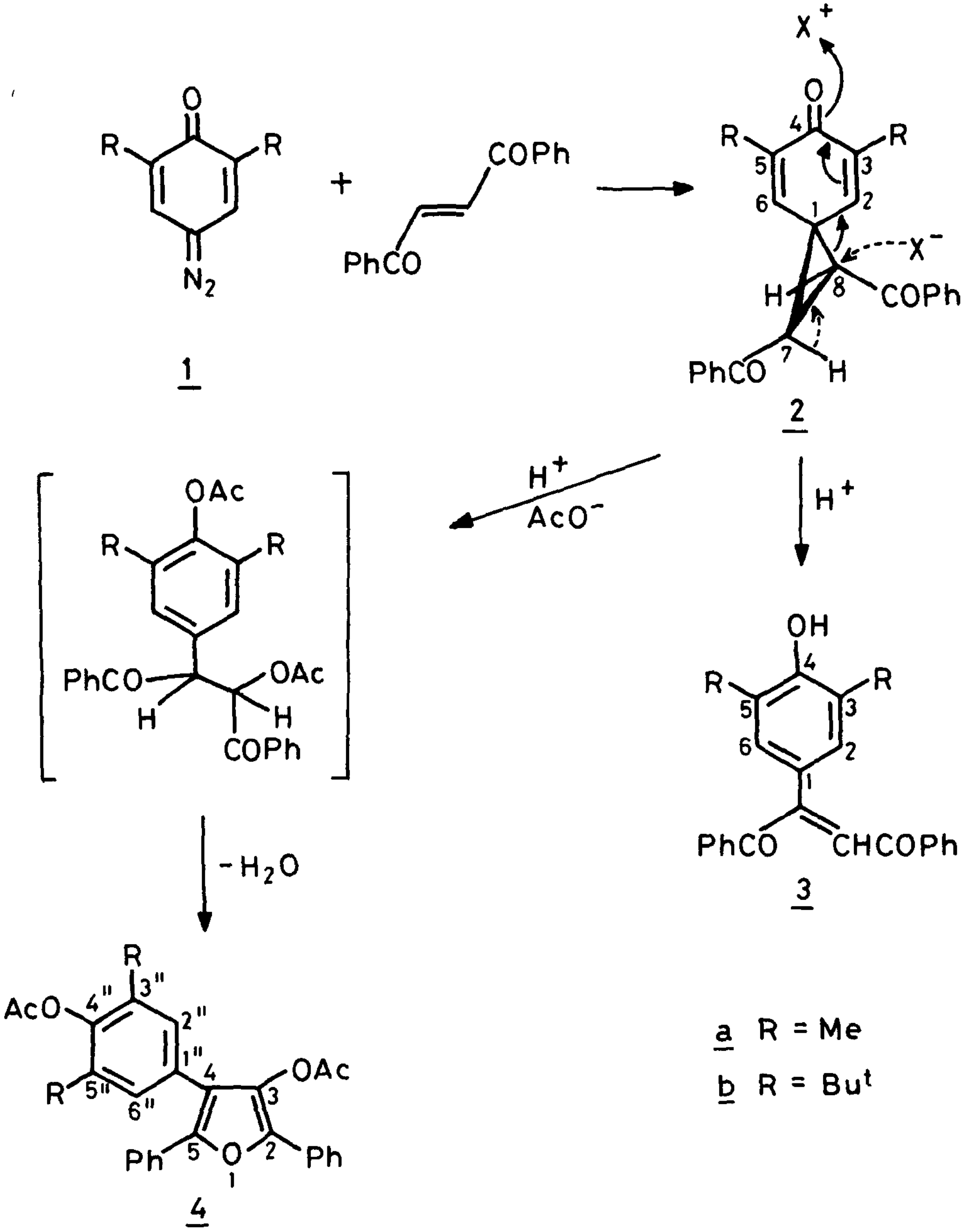
SUMMARY. Acid-catalysed ring opening of the spirodienones (2a) and (2b) using p-toluenesulphonic acid affords the styrene derivatives (3a) and (3b), while treatment with acetic anhydride/H_2SO_4 affords the furan derivatives (4a) and (4b).

Considerable attention has over the years been directed towards investigating the rearrangement reactions of spirodienones.[1-6] As a contribution to our understanding of the mechanisms of such reactions we have studied the acid-catalysed reactions of the spirocyclopropyl-cyclohexa-2,5-dienones (2a)[7] and (2b), which were prepared using a known procedure by reacting 3,5-dialkylbenzene-1,4-diazooxides (1a)[8] and (1b)[9] with trans-dibenzoylethylene.

Treatment of (2a) with p-toluenesulphonic acid in refluxing toluene gave an orange crystalline solid (40% yield), m.p. 218-20^o, M^{+} 356.1410 ($C_{24}H_{20}O_3$), ν_{max}^{KBr} 3480, 1673 and 1636 cm^{-1}. The ^1H n.m.r. spectrum of this compound was consistent with structure (3a), as indeed was the ^{13}C n.m.r. spectrum (Table 1) which showed two carbonyl carbon atoms at 187.7 and 197.3 p.p.m. in addition to the expected signals due to the aromatic, olefinic and methyl carbon atoms. The ^1H and ^{13}C n.m.r. spectra further showed that the phenolic ring was symmetrically substituted since only one methyl signal was observed in each case.

Treatment of (2b) with p-toluenesulphonic acid under the same conditions gave an analogous product (3b), m.p. 196-8^o, M^{+} 440.2350 ($C_{30}H_{32}O_3$), ν_{max}^{KBr} 3520 and 1662 cm^{-1}.

In contrast, when (2a) and (2b) were allowed to react with acetic anhydride containing a trace of sulphuric acid at room temperature two entirely different products were obtained. Thus, (2a) gave a white crystalline solid (40% yield), m.p. 177-8°, $M^{+\cdot}$ 440.1624 ($C_{28}H_{24}O_5$), ν_{max}^{KBr} 1761, 1638 cm^{-1}. The infrared spectrum showed the presence of an acetate group but gave no indication of the presence of benzoyl or dienone groups. This was confirmed by the ^{13}C n.m.r. spectrum (Table 1) which gave n



peaks below 168.5 p.p.m. The presence of two acetyl groups was indicated by both the ^{1}H and ^{13}C n.m.r. spectra and was also confirmed by the mass spectrum which contained prominent ions at m/e 398 and 356 corresponding to the successive loss of two molecules of ketene. Structure (4a) is therefore assigned to this product. A similar product (4b), m.p. 148-150°, M^{+} 524.2563 ($C_{34}H_{36}O_{5}$), ν_{max}^{KBr} 1752, 1700 cm^{-1}, was also obtained from (2b).

Table 1. ^{13}C n.m.r. data.

	(2a)[a]	(2b)[a]	(3a)[b]	(3b)[a]
1	41.34	41.22	124.85	126.13
2/6	138.50	135.08	128.98	124.67
3/5	139.28	151.41	124.90	137.73
4	186.30	185.38	155.75	156.58
7	39.02	39.61	156.51	157.42
8			117.25	117.98
CO	193.22	193.52	187.70 197.30	188.08 198.34
1'	136.86	137.06	136.11 137.10	136.60
2'6'	128.48	128.41	127.93 128.02	128.37
3'/5'	128.90	128.84	128.49 128.75	128.55
4'	133.94	133.81	133.01 133.21	132.93
Me	16.49	-	16.58	-
Bu^{t}	- -	29.28 35.35	- -	30.01 34.39

	(4a)[a]	(4b)[a]
1''	130.59	130.64
2''/6''	129.65	127.64
3''/5''	130.74	142.85
4''	146.63	146.81
3	135.14	134.91
4	119.28	119.84
2	140.86	141.07
5	148.05	147.59
1'	128.41 129.36	128.49 129.42
2'6'	124.14 125.63	124.17 125.92
3'/5'	128.75 128.75	128.73 128.73
4'	127.53 127.74	127.64 127.79
Me	16.35	-
Bu^{t}	- -	31.50 35.52
OAc	168.53 20.46 20.61	168.52 170.70 20.66 22.65

[a] $CDCl_3$

[b] d_6-DMSO

These reactions demonstrate the preference for ring opening rather than dienone-phenol rearrangement in spiro[2.5]octa-2,5-dienones[1,6] and also illustrate a divergence in reaction pathway depending upon whether or not a nucleophilic counterion is present.

References

1. S. Winstein and R. Baird, J.Amer.Chem.Soc., 1957, 69, 4238 and 1963, 85, 567.
2. N.L. Wendler, in "Molecular Rearrangements", ed. P. de Mayo, Wiley-Interscience, New York, 1964, p.1028.
3. A.J. Waring, Adv. Alicycl.Chem., 1966, 1, 129.
4. A.M. Choudhury, K. Schofield and R.S. Ward, J.Chem.Soc. (C), 1970, 2543.
5. R.S. Ward, Chem. in Britain, 1973, 9, 444.
6. L.H. Schwartz, R.V. Flor and V.P. Gullo, J.Org.Chem., 1974, 39, 219.
7. J.C. Fleming and H. Schechter, J.Org.Chem., 1969, 34, 3962.
8. W. Ried and R. Dietrich, Chem.Ber., 1961, 94, 387.
9. G.F. Koser and W.H. Pirkle, J.Org.Chem., 1967, 32, 1992.

(Received in UK 21 September 1981)