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SPIRODIENYL DERIVATIVES AND BENZENONIUM IONS[1]

Edwin C. Friedrich and S. Winstein

Department of Chemistry, University of California, Los Angeles, Calif.

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IN this communication we report some results of an investigation of the reactions of the spirodienyl p-nitrobenzoates I-OPNB, II-OPNB and VII-OPNB, which furnish direct information regarding the behavior of the spirobenzenonium ion intermediates IV and VIII. The first of these had already been encountered[2] in acetolysis and formolysis of 4-phenyl-1-butyl p-bromobenzenesulfonate (III-OBs) since these receive some contribution from Ar$_1$-5-assisted ionization. Intermediate VIII, however, was not similarly accessible from 5-phenyl-1-pentyl p-bromobenzenesulfonate, since in this case Ar$_1$-6-assisted ionization does not compete appreciably with anchimerically unassisted solvolysis. Intermediates such as IV and VIII are also of interest in connexion with the dienol-benzene rearrangement.[3]

The necessary spirodienols I-OH, II-OH and VII-OH were prepared by reduction of the corresponding spirodienones, the two related to I-OH[4] and VII-OH[5] being already known. Spirodienone XIII corresponding to II-OH was prepared from tetramethylene fulvene (XI) by pyrolysis of its epoxide XII,

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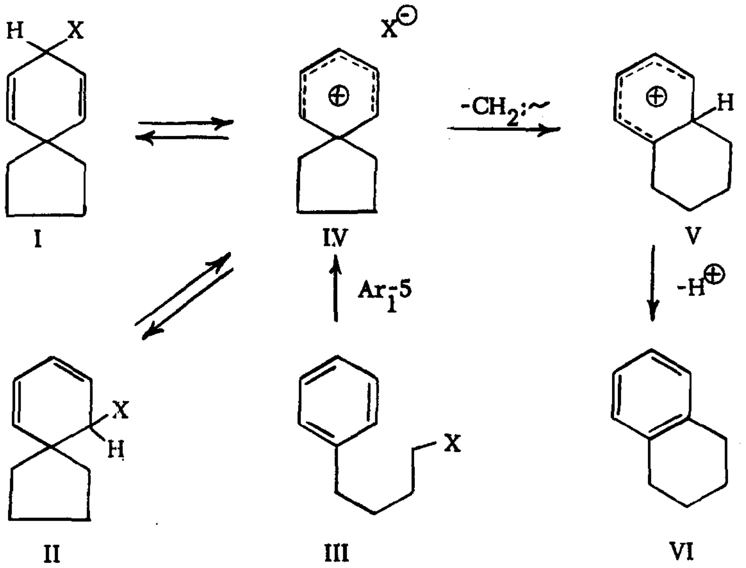
[1] Research sponsored by the U.S. Army Research Office (Durham).

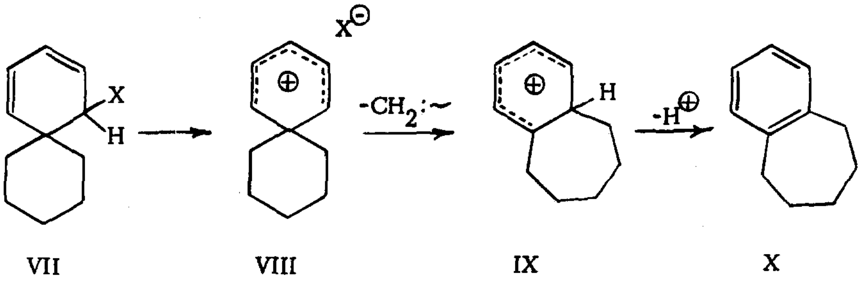
[2] R. Heck and S. Winstein, J. Amer. Chem. Soc. 79, 3105 (1957).

[3a] H. Plieninger and G. Keilich, Angew. Chem. 68, 618 (1956); [b] K. von Auwers and W. Julicher, Ber. Dtsch. Chem. Ges. 55, 2167 (1922); [c] K. von Auwers and K. Ziegler, Liebigs Ann. 425, 217 (1921); [d] H. Plieninger and G. Keilich, Chem. Ber. 91, 1891 (1958).

[4] R. Baird and S. Winstein, J. Amer. Chem. Soc. 84, 788 (1962).

[5] K. Alder, F.H. Flock and H. Lessenich, Chem. Ber. 90, 1709 (1957).





which was isolated as a dimer[6] (melting range 130-140°). The crude spirodienone XIII (λ_{max} in 95% EtOH, 306 mμ; ε = 3700) dimerized quite rapidly on standing to a white crystalline material,[6] m.p. 135-137°, with infrared carbonyl stretching absorptions at 1712 and 1685 cm^{-1} and a single U.V. absorption maximum at 230 mμ (ε = 6900, 95% EtOH).

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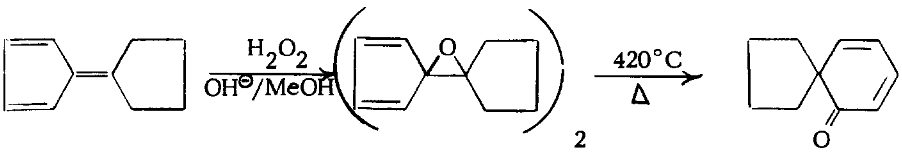
[6] This and the other designated compounds gave satisfactory elemental analyses.



XI XII XIII

In reduction of the dienones to dienols, there is a pronounced tendency toward saturation of the olefinic groups. Thus, treatment of I-ketone with sodium borohydride in basic methanol-water gave only 14 per cent of the desired spirodienol, the remainder of the product being a mixture of spiromonoenol and saturated spirodecanol.[7] The use of lithium aluminum hydride in ether at -78°[8] gave, in addition to the desired spirodienol, as much as 30 per cent of the spiromonoenone (C=O stretch at 1670 cm^{-1}), m.p. of orange 2,4-dinitrophenylhydrazone,[6] 148.6-149.0°. Employing lithium aluminum hydride in ether at room temperature, however, leads to satisfactory yields of each of the desired dienols. Each of them gave sharp-melting *p*-nitrobenzoates[6] which produced quantitative yields of tetralin (VI) or benzosuberan (X) on melting or heating in dry acetone.

As summarized in Table 1, the spirodienyl *p*-nitrobenzoates display exceedingly high first-order rate constants for acid production in 90 per cent aqueous acetone. Thus, the unconjugated five-ring spiro(4:5)deca-1,4-dienyl ester I-OPNB is more reactive than its monoallylic counterpart XIV by a factor of ca. 10^8. The monoallylic spirodecenyl ester XIV solvolyzes at essentially the same rate as does the *cis*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate reported by Goering and Silversmith.[9]

The behavior of the spirodienyl esters in solvolysis sheds light on

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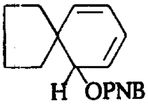
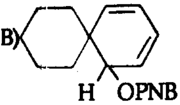
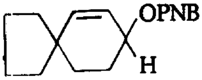
[7] N.W. Atwater, *J. Amer. Chem. Soc.* **83**, 3072 (1961).

[8a] F.A. Hochstein and W.G. Brown, *J. Amer. Chem. Soc.* **70**, 3484 (1948); [b] V.M. Mićović and M.L. Mihailović, *Lithium Aluminum Hydride in Organic Chemistry* p. 22. Belgrade (1955); [c] F. Bohlmann, *Chem. Ber.* **85**, 1144 (1952).

[9] H.L. Goering and E.F. Silversmith, *J. Amer. Chem. Soc.* **77**, 6249 (1955).

TABLE 1

First-order Rate Constants for Acid Production by Some p-Nitrobenzoates in 90 per cent Aqueous Acetone at 25.0°C

Compound	m.p. (°C)	$10^4k(\mathrm{sec}^{-1})$	Rel. k
(I-OPNB) 	72-73	11.0[a]	5.8×10^7
(II-OPNB) 	62-63	(2.50±0.06)	1.3×10^7
(VII-OPNB) 	93-94	(0.400±0.015)	0.21×10^7
XIV 	47-50[b]	1.9×10^{-7}[c]	1

[a] Drifts downward during a run due to rearrangement to the less reactive conjugated isomer ($k_r = 1.10 \times 10^{-4}$ sec^{-1}).

[b] Sample contained 40 per cent of the saturated spiro(4:5)decane-3-yl p-nitrobenzoate.

[c] Estimated from data in 80 per cent aq. acetone at 100.6°C using a $\Delta H^{\ddagger}$ value of 27.0 kcal/mole and assuming a rate factor of 15 for the solvent difference.

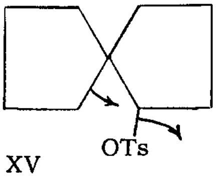
the possible competing reactions of the spirodienyl cationic intermediates IV and VIII. With the 5-ring spirodienyl esters I-OPNB and II-OPNB, no trace of open-chain 4-phenyl-1-butanol or 4-phenyl-1-butene was observed. Neither was an appreciable quantity of either spirodienol detected, even under conditions which were shown to permit their survival. Thus, methylene shift (ring expansion) in the spirobenzenonium cation is considerably faster than either ring opening or solvolysis. Ion pair return[9,10] in the ion pa IV does compete with methylene shift, however. Thus, the instantaneous first-order rate constants for acid production in 90 per cent acetone drift down during a run in the case of the unconjugated spirodienyl ester I-OPNB, solvolysis being accompanied by allylic rearrangement to the less reactive conjugated ester II-OPNB. We can therefore write the following rate sequence for the various phenomena in solvolysis of the 5-ring spirodienyl esters:

ionization > ion pair return (allylic rearrangement) ≈ methylene shift (ring expansion) > solvolysis, ring opening.

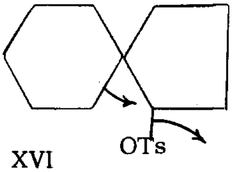
With the 6-ring spirobenzenonium intermediate VIII, solvolysis definitely competes with ring expansion, since only ca. 40 per cent of the solvolysis product from the 6-ring spirodienyl ester VII-OPNB in buffered 90 per cent acetone is benzosuberan (X). The remainder is a mixture of the isomeric 6-ring spirodienols. Thus, in this case, the latter part of the rate sequence for competing phenomena must be:

methylene shift (ring expansion) ≈ solvolysis ≫ ring opening.

The greater tendency for the 5→6 ring expansion in the spirobenzenonium cation IV compared to the 6→7 ring enlargement in cation VIII is quite reasonable since the former is expected to be more advantageous than the latter. An interesting parallel to the present observations is the recent



XV



XVI

[10a] W.G. Young, S. Winstein and H.L. Goering, J. Amer. Chem. Soc. 73, 1958 (1951); [b] S. Winstein, Experientia Supplementum II 137 (1955); [c] S. Winstein and G.C. Robinson, J. Amer. Chem. Soc. 80, 169 (1958).

report[11] that anchimerically accelerated acetolysis of the 5-ring spirotoluenesulfonate XV is more rapid than that of the 6-ring analog XVI by a factor of 64 at 25°C.

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[11] A.P. Krapcho and M. Benson, J. Amer. Chem. Soc. 84, 1036 (1962).