Tetrahedron Letters,Vol.23,No.32,pp 3281-3282,1982 0040-4039/82/323281-02$03.00/0
Printed in Great Britain

FORMATION OF 1,3-DIOXOLENIUM SALTS BY THE Ad_E-REACTION OF NITRONIUM TETRAFLUOROBORATE WITH ALLYL ESTERS

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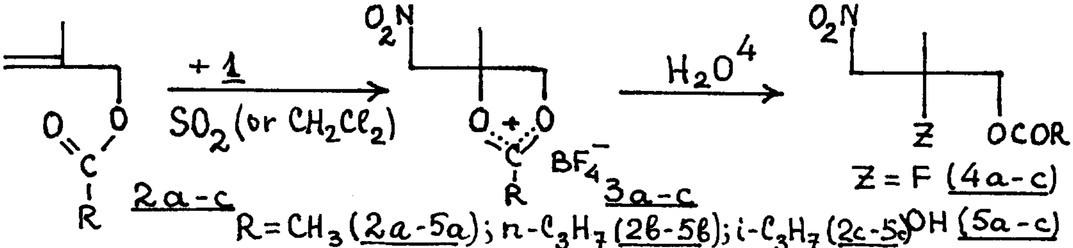
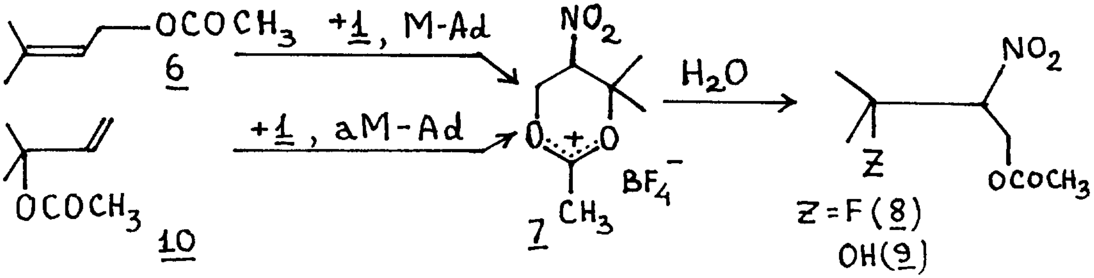
Abstract: Nitration of allyl esters with NO_2BF_4 proceeds with nucleophilic participation of carbonyl and yields nitro-substituted oxonium salts.

Nitration of alkenes with NO_2BF_4 1 may yield nitroalkenes[1a], 1,2-fluoronitroderivatives[1b] or solvoadducts[1c]. Here we report results showing that the interaction of 1 with allyl esters proceeds by electrophilic attack of NO_2^+ at the double bond with nucleophilic participation of the neighbouring carbonyl group leading to formation of nitrosubstituted oxonium salts.

Thus the nitration of methallyl esters 2a-c with 1 in liquid SO_2 at -40°C produces 2-alkyl-4-methyl-4-nitromethyl-1,3-dioxolenium tetrafluoroborates 3a-c formed as the only products (PMR-data). These salts could be isolated as stable solids, their structure being ascertained by PMR data[3] (see Table).



Under similar conditions the reaction of 1 with prenylacetate 6 proceeds via formation of unstable 3,3-dimethyl-4-nitro-1,3-dioxenium tetrafluoroborate 7[5]. Quenching of the latter with water yields the mixture of 8 and 9 in the ratio 3:1 (total yield 67%). Rather unexpectedly the same intermediate salt 7[5] (PMR-data) and quenching adduct 8 (yield 43%) were formed in the reaction of 1 with dimethylvinylcarbinol acetate 10. Evidently in the latter case the addition of NO_2^+ proceeds mainly in an anti-Markovnikov direction.



Table

Preparation and properties of 1,3-dioxolenium tetrafluoroborates 3a-c

Compound (R)	Yield (%)	m.p. (°C)	PMR-spectra (Tesla BS 487, 80 MHz, liquid SO_2, 30°C, HMDS, δ)				
			CH_AH_B;	J_{AB}	CH_2NO_2	C-CH_3	R - C$\lessdot^{+}$
3a (CH_3)	65	54-55	5.41;	11Hz	5.19 s	1.99 s	2.95 s
3b (n-C_3H_7)	60	44-45	5.47;	11Hz	5.25 s	2.09 s	1.21 t; 2.00 sext 3.26 t
3c (i-C_3H_7)	45	64-65	5.43;	10Hz	5.19 s	2.00 s	1.53 d; 3.50 sept

1,3-Dioxolenium salts are well-known as stable and synthetically useful oxonium salts[6a]. The usual methods of their preparation include intramolecular cyclisation of ß-substituted ethyl esters[6b] and ionization of the appropriate 2-halogeno- or 2-hydroxydioxolanes[6c]. The salts of the same structure could also be made by Ad_E-reaction of allyl ester with strong acids[6d]. The examples described in this paper clearly indicate that nitration of allyl esters with 1 could serve as the method for the preparation of 1,3-dioxolenium salts bearing the synthetically useful nitro-group in the side chain. One might expect that a similar reaction using other cationic electrophiles would open the entry to other functionally substituted oxonium salts. The study of these possibilities is now under way.

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2.By quenching of the reaction mixture with abs.ether, followed by SO_2 removal, additional washing with ether, filtration under argon and drying in vacuo at 20°C. Salts 3a-c are extremely moisture sensitive compounds; no reproducible analytical date could be obtained.

3.The observed pattern of PMR spectra is similar to that reported earlier[6d] for various 1,3-dioxolenium salts. The ascribed structure of the cyclic oxonium salts has also been confirmed by CMR spectrum of 3a (Brucker WP 60, 15.08 MHz, CH_2Cl_2, 30°, TMS, δ): 195.4 (C$\lessdot$+), 95.6 (O-C$\overline{\ }$-), 81.1 (O-CH_2), 75.9 (CH_2NO_2), 22.34 (2-CH_3), 15.66 (4-CH_3).

4.Quenching of the salts 3a-c with water-ether affords the mixture of 4a-c and 5a-c; total yield 80-90%, the ratio 4:5 varies from 17:1 for 3a to 3:1 for 3c. No attempts were made to optimize the yields of both 4a-c and 5a-c. Their separation is easily achieved by distillation. Analytical and spectral data for 4a-c, 5a-c, 8 and 9 are in a full accord with the ascribed structures.

5.The attempts to isolate salt 7 failed. However PMR spectrum of the reaction mixture indicates the presence of 7 as the main product /(δ,TMS): 1.73, 1.89 and 2.8 (3H-singlets) and 5.2-5.6 (3H-multiplet)/.

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(Received in UK 8 June 1982)