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BASIC ELIMINATION OF SULFONIUM SALTS.
NEIGHBOURING GROUP INFLUENCE ON REGIOSELECTIVITY.

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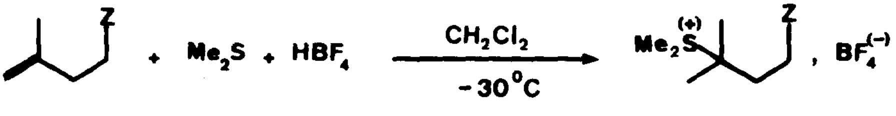
Abstract : *A simple preparation of sulfonium salts functionalized by oxygenated groups is reported. The nature and the position of the latter control the regiochemistry of elimination of the sulfonium moiety leading to selective formation of Saytsev or Hofmann olefins.*

Since the discovery of the Saytsev and Hofmann rules, many factors have been shown to influence the direction of elimination [1].

During an investigation of the regioselectivity of geranyl pyrophosphate biosynthesis [2], we studied the effect, if any, of various oxygen functions in the base promoted elimination of t-amyl dimethyl sulfonium salts 1.

The required sulfonium salts 1 bearing alkyl, acetoxy or ether groups in γ-position were readily obtained from the corresponding isopentenyl derivatives by treatment with dimethyl sulfide (1.2 eq.) and tetrafluoroboric acid diethyl ether complex (1.0 eq.) in dichloromethane at - 30°C [3]. This general procedure, however, failed to give pure hydroxyl sulfonium salt (1, Z=OH) which was best prepared by methanolysis of the acetoxy compound (1, Z=OAc).



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When submitted to two sets of basic elimination conditions, the preceding sulfonium salts 1 gave the results reported below.

1 2 3

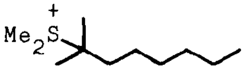
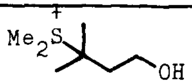
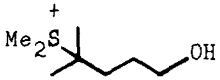
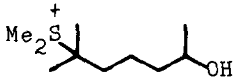
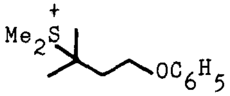
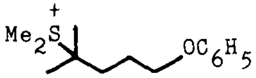
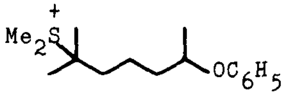
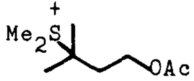
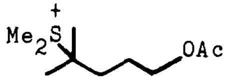
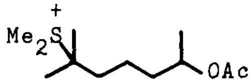
Z	Reaction conditions			
	A:0.1M sol. of 1 in DMSO, tBuOK(1eq.) R.T., 24 hours		B:0.1M sol. of 1 in CH_2Cl_2/MeOH (4/1), NaOH 10N(1eq.), R.T., 24 hours	
	2 + 3 % yield	ratio 2/3	2 + 3 % yield	ratio 2/3
nBu	82	7/93	86	10/90
OH	45	0/100	37	1/99
OnBu	58	43/57	87	63/37
OC_6H_5	94	52/48	99	82/18
OAc	20[a]	70/30	43	1/99 [b]
OCF_2CFClH	24	71/29	99	98/2

[a] after 2 hours. [b] saponification precedes elimination leading to the same result as the hydroxyl group.

Table I : Direction of basic elimination of sulfoniums salts 1 bearing various oxygenated groups in γ-position.

The reference compound (1,Z=nBu) devoid of any other function gave a typical Hofmann elimination pattern [4] and the alcohol sulfonium salt (1,Z=OH) yielded 100% terminal olefin suggesting an intramolecular assistance of the hydroxyl group [5] (Scheme III,a). The other derivatives, however, gave a large percentage of internal alkenes. This proportion increased markedly with the electron withdrawing properties of the Z group, the effect being especially pronounced under the milder basic conditions.

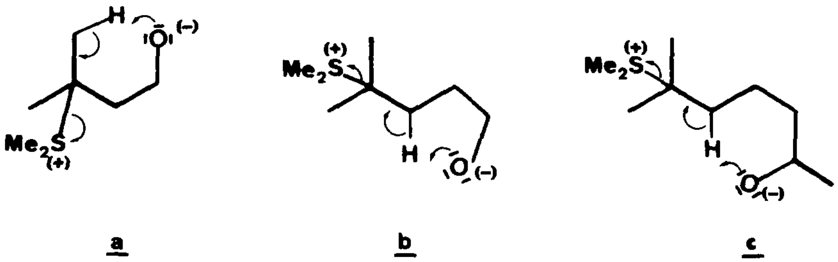
In a second series of experiments, the distance between the hydroxyl, phenoxy and acetoxy group [6] and the leaving group was increased providing the results shown in Table II.

Substrates (tetrafluoroborate salts)	Total % yield	Ratio internal/terminal
	82	7/93
	45	0/100
	35	11/89
	35	41/59
	94	52/48
	91	25/75
	93	18/82
	20[a]	70/30
	50	33/67
	60	17/83

[a] after 2 hours

Table II : Basic elimination of sulfonium salts bearing remote oxygenated functions under t-BuOK , DMSO conditions

With phenoxy and acetoxy derivatives, the orienting effect decreased rapidly as the chain lengthened. With alcohols, the opposite behavior was observed and was ascribed again to intramolecular base relay (Scheme III, b and c).
Under conditions B, which gave good results previously, no participation of the alkoxide group was observed as the concentration of the latter is probably very low due to the relatively large amount of methanol present.



Scheme III

Thus, the nature and the position of an oxygenated group do provide two convenient ways of favouring Saytsev or Hofmann olefin formation in sulfonium salts basic eliminations. The discussion of these results and some synthetic applications will be presented in the full paper.

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Notes and References

1. W.H. Saunders, A.F. Cockerill, "Mechanisms of Elimination Reactions", Wiley-Interscience, New-York, 1973. Chapter IV, R.A. Bartsch, J. Zavada, Chem. Rev. (1980), 80, 453.
2. Preceding communication.
3. Preparation of sulfonium salts 1 (Z, yield, melting point) : nBu, 90%, 124°C ; OAc, 81%, oil ; OnBu, 80%, 68°C; OC_6H_5, 81%, 99°C ; OCF_2CFClH, 84%, 41°C ; OH, 95%, 190°C (dec.).
   All these compounds gave satisfactory spectroscopic data (^1H and ^{13}C NMR).
4. E.D. Hughes, C.K. Ingold, L.I. Woolf, J. Chem. Soc. (1948), 2084.
5. B. Capon, S.P. McManus, "Neighbouring Group Participation", Plenum Press, New York 1976 ; Chapter IV.
6. The corresponding sulfonium salts were prepared as before in similar yields.

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