Tetrahedron Letters No.19, pp. 1503-1506, 1971. Pergamon Press. Printed in Great Britain.

THE ADDITION OF THE PRENYL CATION TO PRENYL THIOL ACETATE

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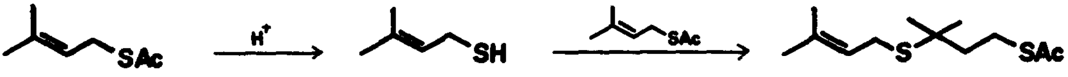
(Received in Japan 31 March 1971; received in UK for publication 5 April 1971)

It has been known that prenyl halides (3-methyl-2-butenyl halides)$^{1)}$ and prenyl acetate$^{2)}$ were dimerized to the lavandulyl compounds, the 4,3-coupling monoterpenes, selectively by the action of the acids.

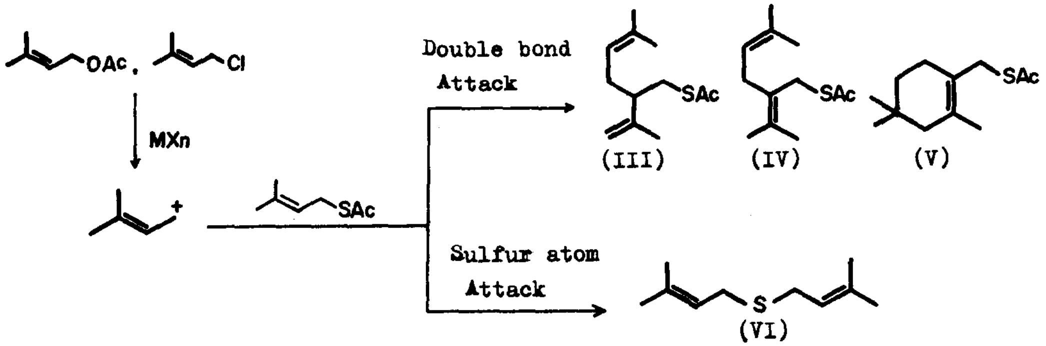
In the case of prenyl thiol acetate (I), S-lavandulyl compounds could be obtained hardly and the sulfide thiol acetate (II) was a main product (cf. Table 2) (Reaction A). The reaction of prenyl acetate with (I) by aluminium chloride, however, gave lavandulyl thiol acetate (III), isolavandulyl thiol acetate (IV), β-cyclolavandulyl thiol acetate (V) and diprenyl sulfide (VI) (Reaction B). The similar products were obtained when prenyl chloride was used in place of prenyl acetate.

The schemes of these reactions seem to be as follows: In the reaction A, (I) undergoes the acyl-sulfur cleavage$^{3)}$ to give the methyl oxocarbonium ion and the corresponding mercaptane by the action of the acid catalyst, and the addition reaction of this mercaptan to (I) gives the sulfide thiol acetate (II).



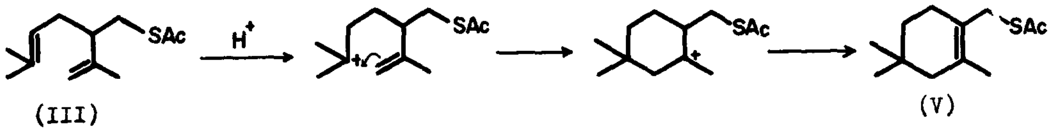
(I) (II)

In the reaction B, at first, the more reactive prenyl compound^{*1} is converted into the prenyl cation by the action of aluminium chloride, and this prenyl cation attacks on either the double bond or the sulfur atom of (I).



It is evident from the $\nu_{C=O}$ shift (II: 1690 cm^{-1}, II-AlCl$_3$: 1565 cm^{-1}) that the mixture of prenyl thiol acetate with aluminium chloride forms the complex (A)*2. (Figure 1). The distribution of the electron in the complex (A) seems to be different from that of (I), that is, the electron density on the sulfur atom is poorer than that of (I). Therefore, prenyl cation attacks more readily on the double bond of the complex (A), and the S-lavandulyl compounds (III), (IV) and(V) are increased. But in the case of free prenyl thiol acetate (I)*3, the prenyl cation attacks more readily on the sulfur atom than the double bond of (I) and diprenyl sulfide (VI) is obtained mainly.

In addition, the cyclization route of lavandulyl thiol acetate by the acid catalysts is presumed to be as follows:



Sulfide thiol acetate (II); mass(m/e): 203(M^+-43), 101($C_5H_9S^+$), 69($C_5H_9{}^+$). ir (cm^{-1}): 3030, 840($R^1R^2C=CR^3H$), 1690, 1135, 950(R-SAc). pmr(τ)*4: 8.72(6H, s), 8.29(2H, t, J=5.8Hz), 8.33(6H, br s), 7.75(3H, s), 7.20(2H, t, J=5.8Hz), 6.97 (2H, d, J=7.2Hz), 4.83(1H, t, J=7.2Hz).

Lavandulyl thiol acetate (III); mass(m/e): 169(M^+-43). ir(cm^{-1}): 3075, 1648, 892($CH_2=CR^1R^2$), 1690, 1135, 950(R-SAc), 830($R^1R^2C=CR^3H$). pmr(τ): 8.33(6H, s),

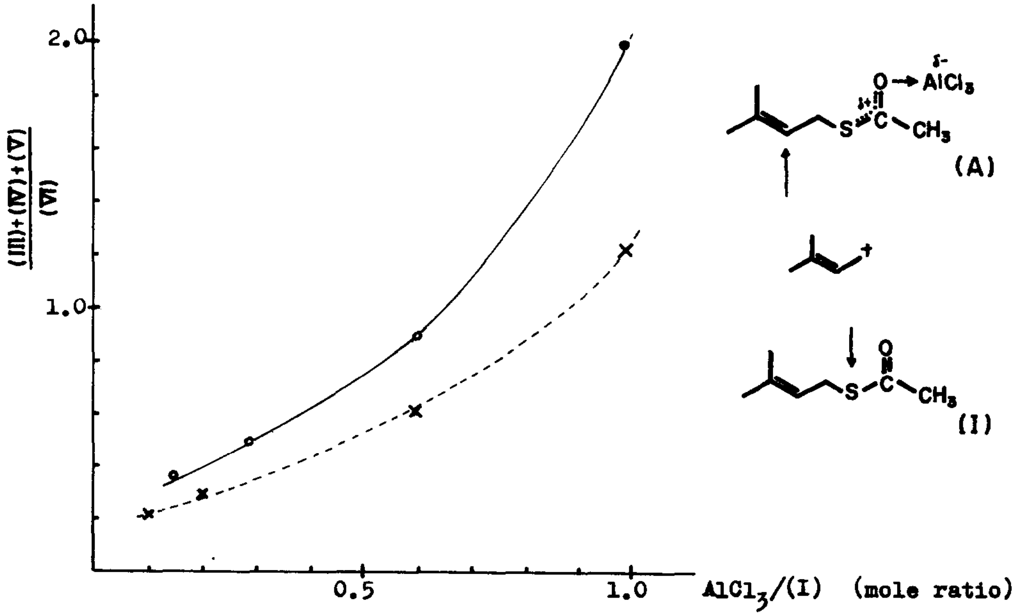


Figure 1. The Product Ratio.

(The Difference of Attacking Positions)

(I): 5.0g, (I)/Prenyl-OAc(mole ratio)=2.0, EtOAc: 10g,

Reaction Temp. (—•— : 25°C, --×-- : 50°C), 3 hours.

8.40(3H, s), 7.76(3H, s), 7.75-8.04(3H, m), 7.13(2H, d, J=6.0Hz), 5.30(2H, br s), 5.00(1H, t, J=6.9Hz).

Isolavandulyl thiol acetate (IV); mass(m/e): 169(M^+-43). ir(cm^{-1}): 830($R^1R^2C=CR^3H$), 1685, 1130, 952(R-SAc). pmr(τ): 8.32(12H, br s), 7.76(3H, s), 7.36(2H, d, J=7.2Hz), 6.53(2H, s), 5.04(1H, t, J=7.2Hz).

β-Cyclolavandulyl thiol acetate (V); mass(m/e): 212(M^+), 169(M^+-43). ir(cm^{-1}): 1685, 1130, 950(R-SAc). pmr(τ): 9.14(6H, s), 8.33(3H, s), 6.50(2H, s), 7.74(3H, s), 7.90-8.80(6H, m).

Diprenyl sulfide (VI); mass(m/e): 170(M^+), 101($C_5H_9S^+$), 69($C_5H_9^+$). ir(cm^{-1}): 3030, 1660, 845($R^1R^2C=CR^3H$). pmr(τ): 8.26(6H, s), 8.16(6H, s), 7.03(4H, d, J=7.2Hz), 4.83(2H, t, J=7.2Hz).

Table 1. The Reactions of (I) with The Prenyl Compounds.
(I)/Reactant (molar ratio)=2, (I); 5.0g, Solvent; 10g, 50°C, 3 hr.

Prenyl-X	Catalyst (g)	Solvent	Product (g)	Products(% by glc analyses)				
				II	III	IV	V	VI
-OAc	$AlCl_3$ (1.0)	CCl_4	3.0	t	19	6	t	60
-OAc	$ZnCl_2$ (1.7)	EtOAc	2.5	t	13	5	t	74
-Cl	$ZnCl_2$ (2.0)	EtOAc	3.2	t	7	5	3	75

t: trace

References and Footnotes

1) J. Tanaka, T. Katagiri, K. Takabe, Nippon Kagaku Zasshi, 89, 872 (1968), ibid., 90, 943 (1969).

2) Haarmann and Reimer G. m. b. H., Berg. P. 615,962 (1962).(C.A. 58, 11223.)

3) G. A. Olah, T. T. Ku, A. M. White, J. Org. Chem., 34, 1827 (1969).

*1 The order of reactivity to the Lewis acids among these prenyl compounds was Pre-Cl > Pre-OAc > Pre-SAc from Table 2.

Table 2. The Cationic Polymerization of Prenyl Compounds

Prenyl-X (g)	Catalyst (g)	Solvent (g)	Temp.(°C)	Time (hr)	Product (g)
-SAc (5.0)	$AlCl_3$ (1.0)	EtOAc (10)	50	10	1.3^{*a}
-OAc (6.4)	$BF_3 \cdot Et_2O$(0.9)	EtOAc (6)	20	1	2.0
-Cl (10.3)	$ZnCl_2$ (0.15)	C_6H_6 (40)	40	1	8.0

*a Products ratio(glc %); II:87, III:--, IV:--, V: t, VI: t.

*2 It has been reported that the compounds containing the carbonyl group form the complexes with the Lewis acids due to the donation of the lone pair of electron by oxygen. (G. A. Olah,"Friedel Crafts and Related Reactions", Interscience Publishers, London, 1963, I, p 623.)

*3 When the molar ratio of $AlCl_3$/(I) was extraporated to the point of intersection in Figure 1, the products ratio(III+IV+V/VI) was estimated to be approximately 0.2.

*4 The pmr spectra were taken with a Hitachi-Perkin Elmer R-20(60 MHz) in CCl_4 solutions at an ordinary temperature.