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THE OXIDATION OF CYCLIC OLEFINES AND UNSATURATED TERPENES WITH THALLIUM III SALTS

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ALTHOUGH the action of mercury II salts and lead IV salts upon olefines has been well studied,[1] it is only recently that the action[2] upon olefines of the salts of the very similar thallium III state has been examined.

The action of thallium III acetate upon ethylene and *n*-hexene involved attack upon the double bond, and in the case of *n*-hexene, attack also upon the allylic position.[2a] We have examined[2b] the action of thallium III salts upon a range of olefines, including alicyclic olefines and unsaturated terpenes Generally attack upon the allylic position, leading to *αβ*-unsaturated alcohols, their esters, and *αβ*-unsaturated carbonyl compounds, was observed. However, some attack upon

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[1] For a review of metal-olefine complexes see R.N. Keller, Chem.Revs. 28, 229 (1941). Also Chatt, ibid. 48, 7 (1951).

the double bond directly occurred. In the case of terpenes rearranged products and polymeric material were sometimes obtained, but allylic attack again predominated.

Typically, *cyclo*hexene, oxidised in acetic acid solution under a variety of conditions, gave *cyclo*hex-2-enyl acetate[3] (b. 67-70°/15mm., identical upon gas-liquid chromatography and in infra-red spectrum, (bands at 3025,1738,1640,1240, 1030,1010,961,947,920,908,855,840,and 800 cm.$^{-1}$) with authentic material, converted by potassium bisulphate to *cyclo*hexadiene, adduct with maleic anhydride[4] m. 143-145°C.), *cyclo*hex-2-en-one (infra-red bands at 3020 and 1675 cm.$^{-1}$ 2,4-dinitrophenylhydrazone m. 132-4° C. Found:C,51.3;H,4.8;N,20.3. $C_{12}H_{12}O_4N_4$ requires C,52.2;H,4.3;N,20.3%), *cyclo*hexan-1,2-diol monoacetate (identical upon gas-liquid chromatography and in infra-red spectrum with authentic material) and *cyclo*hex-2-en-1,4-diol diacetate (identical on gas-liquid chromatography and in infra-red spectrum with authentic material, b. 114-122°/ 11 mm.).[4]

α-Pinene, oxidised under similar conditions, gave in most cases,

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[2a] R.G. Grinstead, *J.Org.Chem.* **26**, 239 (1961).

[b] M.J. Price, Thesis, Loughborough College of Technology (1960). J.B. Lee and M.J. Price, *in preparation*.

[3] Cf. R. Criegee, *Ann.* **481**, 265 (1930). N. Arbuzov, A. Zelinskii, and R. Shuiken, *Bull.Acad.Sci.U.R.S.S.* 163 (1945).

two major and four minor components. One (major) component was myrtenal (identified by gas-liquid chromatography, separated as the 2,4-dinitrophenylhydrazone, m. 217-220° not depressed on admixture with authentic material). A second (minor) component was β-pinene glycol, separated as white leaflets, m. 76-77°C.,[5] infra-red bands at 820,905,950,990,1020,1065, 1115,1125,1166,1215,1302,and 3200-3400 (bd.) cm.$^{-1}$. Sobrerol and myrtenol were likewise obtained and identified by comparison with authentic samples. An unidentified hydroxy-ketone, which gave a 2,4-dinitrophenylhydrazone, m. 180-3°C., analysing for a derivative of $C_{10}H_{16}O_3$ (Found: C,52.99;H,5.48. $C_{16}H_{20}O_6N_4$ requires C,52.75;H,5.49%), was also obtained.

In the course of this work, and in connection with some irradiation studies on terpenes, we had reason to re-examine the oxidation of _a_-pinene with several reagents. The products obtained were initially examined by gas-liquid chromatography, and some typical results are given in the Table (retention times quoted relative to sobrerol = 1.0), including the estimated percentage composition (average of several oxidations). In each case under the conditions we used myrtenal was a major product. For comparison, the compounds recorded in the literature as being formed in

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[4] N. Arbuzov, A. Zelinskii, and R. Shuikin, _loc.cit._.

[5] O. Wallach, _Annalen_ **363**, 11 (1908).

Gas-liquid chromatographic analysis of products from the oxidation of α-Pinene.

Reagent:	Thallium III acetate		Selenium IV oxide		Mercury II acetate		Lead IV acetate		Chromium VII oxide		Irradiated* U.V.	
	R_S	%	R_S	%	R_S	%	R_S	%	R_S	%	R_S	%
					0.24	4						
	0.30	4	0.30	4	0.30	4	0.30	18	0.30	10		
	0.37	14	0.36	66	0.37	83	0.37	6	0.37	13		
	0.47	2										
			0.53	5					0.53	9	0.54	45
	0.61	39	0.61	25								
	0.68	2			0.67	9	0.76	37	0.67	68	0.69	55
							0.88	18				
	1.0	39					1.0	17				
							1.12	4				

*Liquid pinene irradiated (ultra-violet); irradiation in solvents produces a different pattern of behaviour.

Column (6ft.) packed with silicone 301-Celite, t = 172°, Flow rate (N_2) 1.25 l./h..

Lit. product	——	myrtenal, myrtenol.	sobrerol, hydroxycarvotanacetone	sobrerol	verbenone, verbenol.	——
Reference		6	7	8	9	cf.10

these reactions are also quoted.

Examination of the Table shows that in each case a complex mixture results; the relative proportions of the various components naturally vary with the conditions of reaction. A detailed discussion of these results is in preparation.

We wish to thank Dr. R.F. Phillips for his interest in this work.

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[6] G. Dupont, *Bull.soc.chim.* **53**,(iv) 599 (1933). *Compt.rend.* **198**, 1699 (1934).**200**, 759 (1935). *Chem.Zentr.* II, 2384 (1936).

[7] L. Balbiano,*Ber.* **35**, 2994 (1902).**36**, 3575 (1903).**48**, 395 (1915). G.G. Henderson, *J.Chem.Soc.* **95**, 289,1465 (1909).

[8] P. Ward, *J.Amer.Chem.Soc.* **60**, 325 (1938).

[9] W. Treibs and H. Schmidt, *Ber.* **61**, 459 (1928).

[10] H. Weinhaus and P. Schumm, *Annalen.* **439**, 31 (1924).