423. *The Reaction of α-Pinene with Lead Tetra-acetate.*

By G. H. Whitham.

The primary product from the reaction of α-pinene with lead tetra-acetate in benzene has been shown to be *cis*-2-acetoxypin-3-ene (III; R = Ac). This unsaturated acetate undergoes rapid allylic rearrangement to *trans*-verbenyl acetate (II) in acetic acid.

In an investigation of the reaction of α-pinene (I) * with lead tetra-acetate in acetic acid Matsubaara [1] obtained a complex mixture containing alcohol monoacetates, glycol diacetates, and hydrocarbons. However, under the conditions used, allylic acetates might be expected to undergo further reactions so that information as to the primary product of the reaction is lost. Criegee,[3] on the other hand, has reported that when benzene is used as solvent *trans*-verbenyl acetate (II) is formed. In his hands the use of acetic acid as solvent led to two additional products, sobrerol diacetate and verbenene, along with *trans*-verbenyl acetate.

Since verbenol was required in connection with other studies [4] we re-investigated the reaction of α-pinene with lead tetra-acetate in benzene and find that it follows a hitherto unsuspected course.

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* The formulæ used in this paper correspond to the absolute configuration of (+)-α-pinene.[2] α-Pinene used in the experiments to be described was optically impure but contained a preponderance of the (+)-isomer.

[1] Matsubaara, *J. Chem. Soc. Japan*, 1957, **78**, 907, 909; cf. *Chem. Abs.*, 1959, 22056.

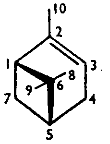
[2] Birch, *Ann. Reports*, 1950, **47**, 191.

[3] Criegee, *Angew. Chem.*, 1958, **70**, 173.

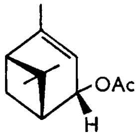
[4] Hurst and Whitham, *J.*, 1960, 2864.

On addition of dry lead tetra-acetate to α-pinene in benzene at 65° a smooth reaction occurred and lead diacetate was precipitated. Criegee [3] describes a working-up procedure which involves filtration of the precipitate and subsequent evaporation and distillation. However, this is complicated by the further precipitation of lead salts during the evaporation so that we employed an alternative method, *viz.*, addition of water to the filtrate followed by removal of precipitated lead dioxide by a second filtration. In this way an unsaturated acetate, $C_{12}H_{18}O_2$, was isolated which was not *trans*-verbenyl acetate since it did not give *trans*-verbenol on alkaline hydrolysis. That the unsaturated alcohol thus obtained was *cis*-pin-3-en-2-ol (III; R = H) (*i.e.* a derivative of *cis*-pinane) was shown in the following way. It exhibited a strong infrared band at 733 cm.$^{-1}$, attributable to a *cis*-disubstituted double bond, and on hydrogenation in ethanol over palladium–carbon one mol. of hydrogen was absorbed, giving a saturated alcohol which had no infrared band at 733 cm.$^{-1}$. Identity of the latter alcohol with *cis*-pinan-2-ol [5] (IV) was shown by comparison with an authentic sample obtained by reduction of β-pinene epoxide with lithium aluminium hydride; it was characteristically different from *trans*-pinan-2-ol.

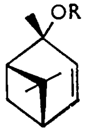
The primary product from the reaction of lead tetra-acetate with α-pinene in benzene is thus *cis*-2-acetoxypin-3-ene (III; R = Ac). In agreement, the infrared spectrum showed a strong band at 745 cm.$^{-1}$ (*cis*-disubstituted double bond).



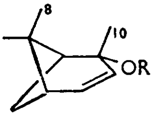
(I)



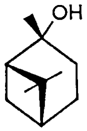
(II)



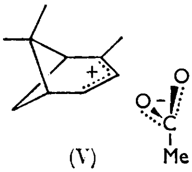
(IIIa)



(IIIb)



(IV)



(V)

It was found that the unsaturated acetate (III; R = Ac) undergoes very ready allylic rearrangement in acetic acid at 20° with the formation, in high yield, of *trans*-verbenyl acetate (II). The latter was identified by alkaline hydrolysis to the known *trans*-verbenol. The rearrangement could be followed by the large change in rotation. In glacial acetic acid the reaction was complete after 5 min. at 20°. It was rather slower in 80% acetic acid in dioxan and a rough kinetic run showed first-order behaviour with a rate constant of *ca.* $2{\cdot}5 \times 10^{-3}$ sec.$^{-1}$ at 20°. Since this very ready rearrangement requires a good ionising solvent and does not occur, for example, on distillation, it is considered to proceed *via* the ion-pair (V) in accordance with the observed stereochemistry of the reaction. The rate-determining ionisation would be facilitated by the release of strain associated with the non-bonded 1,3-diaxial interaction between the 8- and the 10-methyl group (cf. IIIb). Quantitative conversion into *trans*-verbenyl acetate reflects the superior thermodynamic stability of the latter relative to the acetate (III; R = Ac).

It is of interest that although the ion (V) bears a partial positive charge at $C_{(2)}$, skeletal rearrangement to the bornylene system does not occur under these conditions. This contrasts with the rearrangement accompanying solvolysis of the 3,5-dinitrobenzoate of *cis*-pinan-2-ol (IV) which furnishes the 3,5-dinitrobenzoate of borneol.[6] In the present instance the fact that skeletal rearrangement does not intrude is probably due to the high energy content of the bicyclo[2,2,1]hept-2-ene system.[7]

Criegee's observations on the α-pinene–lead tetra-acetate reaction in benzene are readily accommodated by the present results since working up of the reaction mixture under his conditions involves distillation in the presence of the acetic acid produced in the reaction.

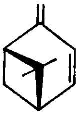
[5] Vilkas, Dupont, and Dulou, *Compt. rend.*, 1956, **242**, 1329; Vilkas, *Bull. Soc. chim. France*, 1959, 1401; Burrows and Eastman, *J. Amer. Chem. Soc.*, 1959, **81**, 245.

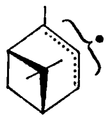
[6] Abraham and Vilkas, *Bull. Soc. chim. France*, 1960, 1450; Abraham, *Ann. Chim. (France)*, 1960, 961.

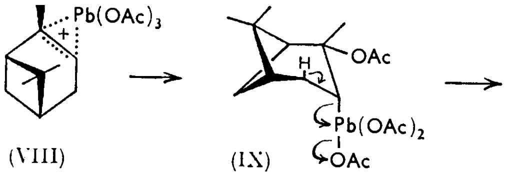
[7] Wheeler, Cetina, and Zabicky, *J. Org. Chem.*, 1957, **22**, 1153; Schleyer, *J. Amer. Chem. Soc.*, 1958, **80**, 1700.

Allylic rearrangement apparently occurred at this stage. In confirmation, a repetition of the reaction with strict adherance to the Criegee procedure gave *trans*-verbenyl acetate identical with that obtained above. From the preparative point of view it is preferable to isolate the intermediate acetate (III; R = Ac) and carry out the rearrangement under controlled conditions. On one occasion use of Criegee's method on a larger scale led to a substantial quantity of verbenene (VI), derived by elimination of acetic acid, along with a reduced yield of *trans*-verbenyl acetate.

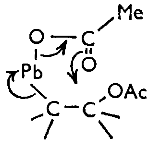
The exclusive formation of *cis*-2-acetoxypin-3-ene (III; R = Ac) in the lead tetra-acetate reaction is of interest in connection with the mechanism of lead tetra-acetate–olefin reactions in general. A free-radical route involving the intermediate radical (VII) seems unlikely since, on this basis, the formation of at least a significant proportion of verbenyl acetate, resulting from attack at C$_{(4)}$, would be expected. On the other hand, electrophilic attack of lead tetra-acetate on α-pinene, from the side remote from the gem-dimethyl bridge, to give the bridged intermediate (VIII) * could be followed by *cis*-Markownikow opening to form the intermediate addition product (IX). Oxidative decomposition of the latter by elimination as shown would give the observed product, acetic acid and lead diacetate. Precedence for the *cis*-opening of a bridged ion of type (VIII) may be claimed in the reaction of norbornene with mercuric acetate, which proceeds as shown (X ⟶ XI).[8] In the case of the ion (VIII) the stereoelectronically more probable process of *trans*-diaxial opening would involve severe steric interaction between the incoming acetate moiety and the 8-methyl group.


(VI)

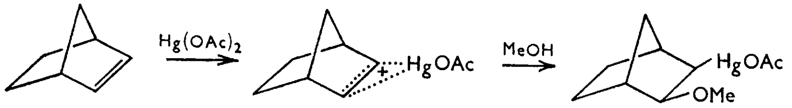

(VII)



(VIII) (IX)

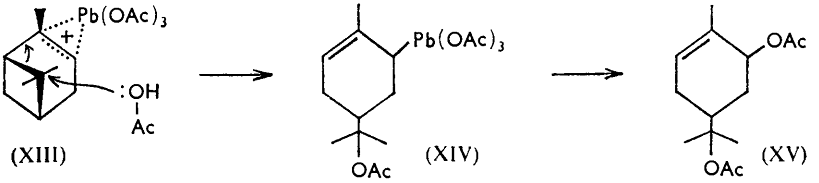


(XII)



(X) (XI)

Criegee [3] has postulated intermediates of type (IX) to rationalise the addition of two acetate residues across the double bond in the reaction of lead tetra-acetate with certain olefins. In such cases the intermediate is considered to decompose as in (XII). The decomposition route proposed for intermediate (IX) is a *trans*-diaxial elimination and represents an alternative mode of breakdown of a Criegee intermediate. In the present case it may be preferred because it releases strain associated with the boat " flagpole " substituents at positions 3 and 7.



(XIII) (XIV) (XV)

It seems likely that decomposition of a Criegee intermediate by elimination may be significant in other cases where the reaction of lead tetra-acetate with an olefin leads to

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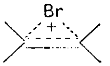
* This intermediate ion is the analogue of a bromonium ion, *viz.*: 

[8] Traylor and Baker, *Tetrahedron Letters*, 1959, No. 19, 14.

apparent allylic substitution by an acetoxyl group, *e.g.*, the formation of cyclohex-2-enyl acetate from cyclohexene.[3]

Our scheme also explains Criegee's isolation of sobrerol diacetate (XV): this may be derived from the intermediate ion (VIII) by the route (XIII ⟶ XIV ⟶ XV).

EXPERIMENTAL

Infrared spectra and rotations were taken for carbon disulphide and chloroform solutions respectively. Light petroleum refers to the fraction of b. p. 40—60°.

cis-2-*Acetoxypin*-3-*ene*.—α-Pinene [27 g., freshly redistilled, $[\alpha]_D$ +28° (*c* 2·0)] in dry benzene (500 c.c.) was warmed to 65° and lead tetra-acetate (84 g., dried over phosphorus pentoxide) was added during 20 min. to the stirred solution, the temperature being maintained at 60—65°. After an initial bright yellow coloration, gradual precipitation of lead diacetate occurred. On completion of the addition the suspension was stirred at 60—65° for a further 30 min. After cooling and filtration the filtrate was added to water, and precipitated lead dioxide was removed. Evaporation of the dried benzene layer followed by distillation gave cis-2-*acetoxypin*-3-*ene* (21·2 g., 55%), b. p. 96—97°/9 mm., n_D^{21} 1·4735, $[\alpha]_D$ −78° (*c* 1·9) (Found: C, 74·5; H, 9·5. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·35%). Strong bands in the infrared spectrum at 1109, 920, 840, and 748 cm.$^{-1}$ served to distinguish it from *trans*-verbenyl acetate which is transparent in these regions. The absence of bands at 970 and 773 cm.$^{-1}$ indicated that verbenyl acetate was not present.

cis-*Pin*-3-*en*-2-*ol*.—*cis*-2-Acetoxypin-3-ene (18·7 g.) in aqueous-methanolic 10% potassium hydroxide (100 c.c.) was set aside at 20° for 16 hr. After removal of most of the methanol by distillation, water was added and the product was isolated with ether. Distillation gave cis-*pin*-3-*en*-2-*ol* (11·2 g., 76%), b. p. 84—88°/10 mm., n_D^{23} 1·4852 (Found: C, 78·95; H, 11·0. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The highly characteristic infrared spectrum was quite different from that of *trans*-verbenol and had strong bands at, *inter alia*, 900 and 733 cm.$^{-1}$.

cis-*Pinan*-2-*ol*.—*cis*-Pin-3-en-2-ol (2 g.) was stirred with pre-reduced Adams platinum catalyst (50 mg.) in ethanol (50 c.c.) under hydrogen (absorption 300 c.c., 0·94 mol.). After filtration the solution was evaporated and the residue was filtered in light petroleum through a short column of alumina. Evaporation of the eluate gave *cis*-pinan-2-ol (1·98 g.), m. p. (after sublimation) 74—77° undepressed on admixture with a sample (m. p. 76—77°) prepared by reduction of β-pinene epoxide with lithium aluminium hydride.[5] The infrared spectra of the two samples were rich in detail and virtually identical. *trans*-Pinan-2-ol prepared from methylmagnesium iodide and nopinone had a very different infrared spectrum.

Rearrangement of cis-2-*Acetoxypin*-3-*ene*.—(i) *cis*-2-Acetoxypin-3-ene (5 g.) in glacial acetic acid (25 c.c.) was set aside at 20° for 30 min. After addition of water and ether-extraction the extract was washed with aqueous sodium carbonate. Evaporation of the dried solution followed by distillation gave *trans*-verbenyl acetate (4·25 g.), b. p. 97—98°/9 mm., n_D^{20} 1·4731, $[\alpha]_D$ +77° (*c* 2·1). The infrared spectrum was characteristically different from that of starting material: two diagnostic bands occur at 970 and 773 cm.$^{-1}$ in regions of only low absorption for *cis*-2-acetoxypin-3-ene.

The *trans*-verbenyl acetate was identified by alkaline hydrolysis to trans-verbenol, b. p. 91—92°/6 mm., $[\alpha]_D$ +66° (*c* 2·0); the highly characteristic infrared spectrum of the latter was identical with that of an authentic sample. This value for the specific rotation of the *trans*-verbenol corresponds to 40% optical purity on the basis of +168° for (+)-*trans*-verbenol.[9] The α-pinene used in the lead tetra-acetate reaction had an optical purity of 55% based on the value +51° for (+)-α-pinene.[10] Since optical fractionation should not have occurred during the isolation procedure the reason for this discrepancy is not clear, however, in view of the various errors involved it is not considered to be serious.

(ii) A solution of *cis*-2-acetoxypin-3-ene (2·08 g./100 c.c.) in 80% acetic acid–dioxan (8 vol. of glacial acetic acid made up to 10 vol. with dioxan) was made and rapidly transferred to a polarimeter tube; readings were taken at intervals during 15 min. and are tabulated. The zero reading was calculated from the known specific rotation of *cis*-2-acetoxypin-3-ene in chloroform. The infinity reading +0·76° was in good agreement with the specific rotation of *trans*-verbenyl

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[9] Elsevier's "Encyclopedia of Organic Chemistry," Vol. 12A, Elsevier, Amsterdam 1948, p. 505.

[10] Ref. 9, p. 456.

acetate. First-order rate constants were calculated in the usual way and are tabulated. The average value for the rate constant for the reaction, obtained graphically, is 2·48 × 10^{-3} sec.$^{-1}$ at 20°.

t (sec.)	0	180	270	330	390	450	510
[α]	−0·76°	−0·16°	−0·02°	+0·11°	+0·18°	+0·27°	+0·35°
10^3k (sec.$^{-1}$)	—	2·77	2·48	2·57	2·46	2·51	2·57
t (sec.)	570	630	690	750	810	870	∞
[α]	+0·38°	+0·42°	+0·48°	+0·52°	+0·57°	+0·59°	+0·76°
10^3k (sec.$^{-1}$)	2·43	2·38	2·45	2·45	2·57	2·52	—

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