The Lead Tetraacetate Oxidation of Isoborneol

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Received July 9, 1962

A requirement for large quantities of π-camphether (III)[2-4] prompted a study of the oxidation of isoborneol (I) utilizing a method recently investigated by Jeger.[5]

Isoborneol (I), on treatment with lead tetraacetate under vigorous reaction conditions (80°), affords the cleavage products α-campholenicaldehyde (IV) and iso-α-campholenic aldehyde (V) in good yield (Table I). Mild conditions (25°) lead only to camphor (VI) and camphene (VII) (Table II).

TABLE I

GAS-LIQUID PARTITION CHROMATOGRAPHY DATA[a]—SOME PRODUCTS OF VIGOROUS OXIDATION

Compound	Retention time, min.	Relative amount
VII	6.4	1
Acetic acid	11.7	3
π-Camphether (III)[b]	13.6	..?
IV	20.0	12
V	22.1	8
VI	24.5	1

[a] See ref. 9. [b] See ref. 4.

TABLE II

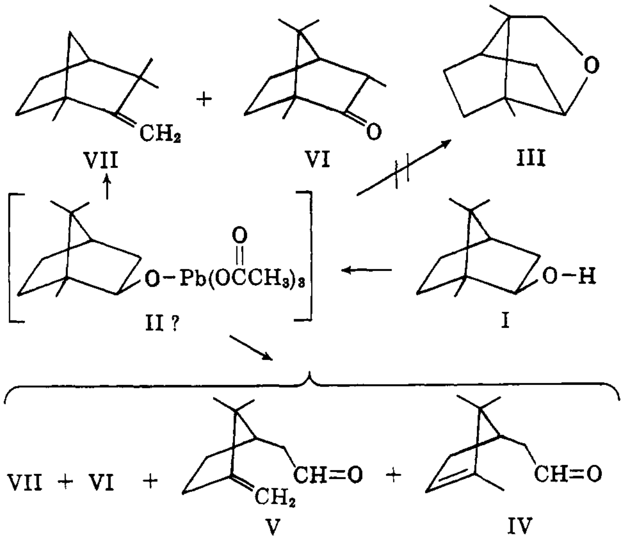
GAS-LIQUID PARTITION CHROMATOGRAPHY DATA[a]—SOME PRODUCTS OF MILD OXIDATION

Compound	Retention time, min.	Relative amount
VII	6.5	1
Acetic acid	11.7	2
VI	25.2	4
I	35.0	8

[a] See ref. 9.

α-Campholenicaldehyde (IV), the major product of the vigorous reaction, was identified by n.m.r. and infrared spectroscopy and by elemental analysis as well as by comparison of derivatives. Srinivasan[6,7] obtained this substance by photolyzing camphor in a variety of solvents. Mosher[8] reported that isoborneol, on treatment with chromic acid, yields only 4% of the related compounds 3-hydroxy-2,2,3-trimethylcyclopentaneacetic acid and α-campholenic acid.

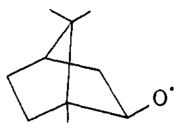
The previously unreported iso-α-campholenicaldehyde (V) was isolated by gas chromatography. Its structure was assigned on the basis of its n.m.r. and infrared spectra and its elemental analysis.



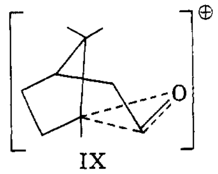
When chromatographed at 145°, iso-α-campholenicaldehyde (V) undergoes some isomerization to α-campholenicaldehyde (IV).[9] The per cent conversion is low (5% increases in IV), however, and little change in concentration appears to occur during isolation. Similar isomerizations are numerous.[10-12]

Small amounts of camphor and camphene from both the vigorous and mild oxidations of isoborneol were identified by comparison of retention times with authentic samples, and, in the case of camphor, by formation of the 2,4-dinitrophenylhydrazone derivative. Camphene (VII) presumably arises from the facile Wagner-Meerwein rearrangement of isoborneol. Camphor and camphene are unaffected by oxidation; isoborneol, under the conditions of vigorous oxidation but without lead tetraacetate, affords only minute amounts of camphene.

On the basis of previous studies of lead tetraacetate oxidations,[13,14] the assumed lead ester intermediate (II) may decompose through structures VIII and/or IX.



VIII



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[2] 1,7-Dimethyl-9-oxatricyclo[2.2.1.2^{2,7}]nonane.

[3] Previously prepared by F. Semmler and K. Bartelt, *Chem. Ber.*, 4465 (1907).

[4] Recently prepared by Mr. Roger Napier, Department of Chemistry, University of Rochester, Rochester, N. Y.

[5] G. Cainelli, M. Lj. Mihailovic, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **42**, 1124 (1959); B. Kamber, G. Cainelli, D. Arigoni, and O. Jeger, *ibid.*, **43**, 347 (1960).

[6] R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 2604 (1959).

[7] Photolysis experiments by the author have shown that irradiation of isoborneol in cyclohexane (under nitrogen) affords low yields of camphor. The experiments were conducted in a quartz cell at 50° with both a Hanovia lamp (mercury, medium pressure, 100 w.) and a hydrogen lamp. The hydrogen lamp experiment gave rise to several other unidentified products.

[8] W. A. Mosher and E. O. Langerak, *J. Am. Chem. Soc.*, **73**, 1302 (1951).

[9] Use was made of a 15-ft. reoplex on Chromosorb column at 145° and a helium flow rate of 110 cc. per minute. A Wilkens "Aerograph" gas chromatograph with a Brown recorder was the instrument employed for separations.

[10] R. Paul and S. Tchelitcheff, *Bull. soc. chim. France*, 520 (1950).

[11] A. C. Cope and E. E. Schweizer, *J. Am. Chem. Soc.*, **81**, 4577 (1959).

[12] A. C. Cope, P. T. Moore, and W. R. Moore, *ibid.*, **81**, 3153 (1959).

[13] G. Cainelli, B. Kamber, J. Keller, M. Lj. Mihailovic, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **44**, 518 (1961).

[14] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 536.

It is not possible to decide unequivocally whether homolytic or heterolytic processes are involved.[15] Camphor is *not* an intermediate as it was unchanged in a control experiment.

Finally, camphor (VI) and iso-α-campholenicaldehyde (V), but not α-campholenicaldehyde (VI) may be formed by an intramolecular concerted decomposition of the lead ester II. Peterson models (using tetrahedral carbon for the lead atom) indicate that little strain is present in transition states leading to such products.

Experimental

Oxidation under Vigorous Conditions.—A mixture of 9.0 g. (0.09 mole) anhydrous calcium carbonate in 200 ml. of dry benzene was placed in a three-necked flask equipped with a condenser, stirrer, and drying tube. After heating the stirred mixture to 40°, 20.0 g. (0.045 mole) of freshly prepared, dry lead tetraacetate was added. The heterogeneous mixture was brought to reflux and a solution of 4.31 g. (0.028 mole) isoborneol in 50 ml. of benzene was added in one batch. Stirring and refluxing was continued for 2 hr. After cooling, filtration gave a pale yellow solution which was washed with 15% potassium iodide, 10% sodium thiosulfate, and water. Excess lead tetraacetate was detected. The organic layer was dried over anhydrous magnesium sulfate and reduced in volume under vacuum to yield 4.2 g. of a pale yellow oil.

Chromatography on neutral alumina (Woelm, activity I) achieved only partial separation of the products.

An attempt to distil part of the crude oil through a 3- in. Vigreux column under nitrogen ended in considerable polymer formation. Only one fraction was obtained; a pale yellow liquid b.p. 80–83° at 14 mm. Infrared analysis of the distillate indicated the presence of aldehyde–olefin functional groups. Gas chromatography showed this fraction to be composed of more than one component.

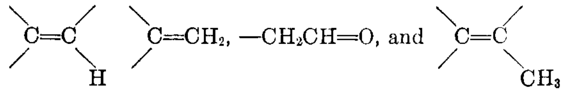
Gas chromatography[9] on the crude oil indicated the presence of not less than ten components. Only five appeared to be in high enough concentration to allow immediate identification.

The high concentrations of α-campholenicaldehyde (IV), iso-α-campholenicaldehyde (V) and acetic acid allowed collection and identification. Component IV (50% yield based on relative gas chromatographic peak areas) showed distinct aldehyde (2670 and 1718 cm.$^{-1}$) and trisubstituted alkene (1649 and 795 cm.$^{-1}$) functional group absorptions in the infrared. The semicarbazone of IV, m.p. 141–142.5° (CH_3OH), was comparable with an authentic sample (m.p. 142–142.5°)[6]; m.m.p. 141–143°.

Component V (30% yield) showed the same aldehyde absorption as IV, however, the alkene absorption had shifted to 875 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}O$ (V): C, 78.89; H, 10.59. Found: C, 78.91; H, 10.67.

Further proof of the structures IV and V was obtained by n.m.r. analysis. The spectrum was taken on a mixture of IV and V in carbon tetrachloride. The proton magnetic resonance signals at 0.35, 4.85, 5.31, 7.66, and 8.40 τ indicate the presence of the functional groups —CH=O,



respectively.

Oxidation under Mild Conditions.—The procedure in this experiment was identical to that described for the vigorous oxidation except the mixture was stirred at room temperature (instead of reflux) for 20 hr. Work-up of the product gave a yellow oil which showed signs of partial crystallization. Benzene was added until the solid dissolved (1 ml.) and the resulting solution was submitted to gas chromatographic analysis. Camphor (VI), camphene (VII), and isoborneol were the only products. The amount of camphene formed was about the same as in the vigorous oxidation. Camphor, however, had become a major product (Table II).

Acknowledgment.—The author is grateful to Drs. R. L. Autrey and M. Gates for helpful comments. Acknowledgment is also given to Mr. Roger Napier for his assistance.

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[15] Compare, P. T. Lansbury, V. A. Pattison, and J. W. Diehl, *Chem. Ind.* (London), **14**, 653 (1962).