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Lead Tetraacetate. I. Reactions with 3-Buten-1-ol, 4-Penten-1-ol, and 2-Phenylethanol

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Reactions of lead tetraacetate with 3-buten-1-ol and 2-phenylethanol gave cleavage products. 3-Buten-1-ol gave allyl acetate, and 2-phenylethanol yielded benzyl acetate. The driving force for the cleavage reaction is attributed to the stabilities of the allyl and benzyl intermediates. 4-Penten-1-ol gave tetrahydrofurfuryl acetate and 3-acetoxytetrahydropyran, cyclization products resulting from interaction of the hydroxyl group and the double bond.

The reactions of lead tetraacetate with olefins have been reported to give a glycol diacetate and an allylic acetate. Thus, on treatment with lead tetraacetate, cyclohexene[1] yielded 1,2-cyclohexanediol diacetate and 2-cyclohexen-1-yl acetate. Similar products have been obtained from other olefins.[2]

On the other hand, the reactions of lead tetraacetate with alcohols in some cases yielded cyclic ethers in steroidal systems.[3] More recently, this reaction was extended to an acyclic system and it was found that cyclic ethers were also formed.[4]

It was of interest to investigate the reaction of lead tetraacetate with compounds containing both a double bond and a hydroxyl group, in order to see whether there would be an interaction between the two functional groups. This paper reports the reaction of lead tetraacetate with a homoallylic alcohol and a homobenzylic alcohol. They were selected because of the proximity of the two functional groups.

The results of the reactions of lead tetraacetate with 3-buten-1-ol are summarized in Table I.

Gas chromatographic analysis of the mixture obtained when the solvent was refluxing benzene showed four peaks. Since the corresponding acetate is one of the products expected from the reaction of an alcohol, 3-buten-1-yl acetate (**3**) was looked for and immediately identified.

The infrared spectrum of compound **1** showed bands for an acetoxy group (1740 and 1370 cm.$^{-1}$) and a vinyl group (925 and 980 cm.$^{-1}$). The retention time on a nonpolar gas chromatographic column was shorter than that of compound **3**, indicating that compound **1** must have a lower molecular weight than compound **3**. Finally its mass spectrum had a molecular ion peak at $m/e = 100$. Therefore, it was identified as allyl acetate.

The infrared spectrum of compound **2** showed bands for a vinyl group but none for a hydroxyl group or a carbonyl group. Its mass spectrum had a molecular ion peak at $m/e = 112$. It was identified as 3-buten-1-yl allyl ether.

The infrared spectrum of compound **4** showed no bands for a carbonyl group or a hydroxyl group, but it showed bands for an aromatic system (3020, 3055, 3080, and 700 cm.$^{-1}$) and a vinyl group (915 and 990 cm.$^{-1}$). Its mass spectrum showed a molecular ion peak at $m/e = 118$ and the cleavage pattern indicated an aromatic system. It was identified as allylbenzene.

Change of the solvent from benzene to cyclohexane drastically changed the product distribution. The yield of allyl acetate, a cleavage product, decreased threefold. On the other hand, the yield of 3-buten-1-yl allyl ether, another product resulting from the cleavage reaction, increased almost six times.

The formation of allyl acetate from 3-buten-1-ol is significant. The starting material, the alcohol **5**, was homogeneous on gas chromatography and was shown to be free of allyl alcohol. Formation of the acetate **1** may be pictured as coming from the internal decomposition of the tetravalent lead ester **6**. Alternatively, acetate **1** may come from the cation **7** or the radical **8**

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[1] (a) R. Criegee, *Ann.*, **481**, 263 (1930); (b) C. B. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 605 (1963); (c) H. J. Kabbe, *Ann.*, **656**, 204 (1962).

[2] (a) E. Dane and K. Eder, *ibid.*, **539**, 207 (1939); (b) G. H. Whitham, *J. Chem. Soc.*, 2232 (1961); (c) K. Alder, F. H. Flock, and H. Wirtz, *Chem. Ber.*, **91**, 609 (1958).

[3] (a) G. Gainelli, J. Lj. Mihailovic, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **42**, 1124 (1959); (b) A. Bowers and E. Denot, *J. Am. Chem. Soc.*, **82**, 4956 (1960); (c) J. Kalvoda, G. Anner, D. Arigoni, K. Heusler, H. Immer, O. Jeger, M. Lj. Mihailovic, K. Schaffner, and A. Wettstein, *Helv. Chim. Acta*, **44**, 186 (1961); (d) K. Heusler and J. Kalvoda, *Tetrahedron Letters*, 1001 (1963); (e) G. B. Spero, J. L. Thompson, W. P. Schneider, and F. Kagan, *J. Org. Chem.*, **28**, 2225 (1963); (f) J. Tadanier, *ibid.*, **28**, 1744 (1963); (g) P. B. Sollman, *ibid.*, **28**, 3559 (1963).

[4] V. W. Micovic, R. I. Mamuzic, D. Jeremic, and M. Lj. Mihailovic, *Tetrahedron Letters*, 2091 (1963).

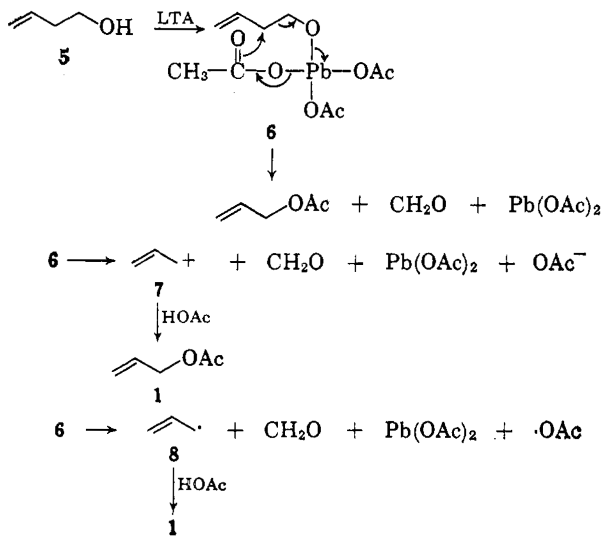
TABLE I

PRODUCTS OF REACTION OF LEAD TETRAACETATE WITH 3-BUTEN-1-OL[a]

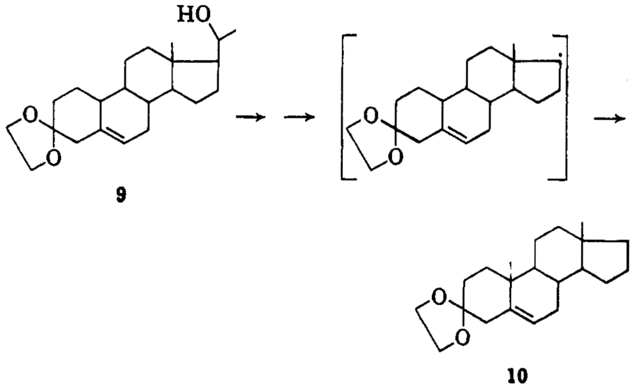
Solvent (time, hr.)	Yield, %				
	Allyl acetate (**1**)	3-Buten-1-yl allyl ether (**2**)	3-Buten-1-yl acetate (**3**)	Allylbenzene (**4**)	Total yield
Refluxing benzene (20)	30	13	20	32	75
Refluxing cyclohexane (20)	10	60	13	0	83

[a] Yields were based on the starting material and estimated by the use of an internal standard.

SCHEME I



SCHEME II



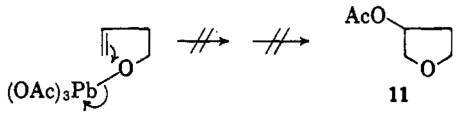
produced by decomposition of lead ester **6** (Scheme I). A free oxy radical has been postulated[5] as an intermediate formed on treatment of an alcohol with lead tetraacetate, but the possibility of an ionic mechanism must also be considered.

Oxidative deformylation in the reaction of alcohols with lead tetraacetate is uncommon, but not unknown. Mosher[6] reported that methyl-*t*-butylcarbinol on treatment with lead tetraacetate produced *t*-butyl acetate among other products. Because of the absence of isobutane and hexamethylethane in the product mixture, the authors favored an ionic mechanism over a free-radical mechanism for the formation of *t*-butyl acetate. On the other hand, Jeger and his co-workers,[7] having obtained 3,3-ethylenedioxy-5-androstene (**10**) on treatment of 3,3-ethylenedioxy-20-hydroxy-5-pregnene (**9**) with lead tetraacetate, pictured this cleavage as most easily proceeding *via* a free-radical intermediate (Scheme II). However, the question of whether a homolytic or heterolytic intermediate is involved on treatment of alcohols with lead tetraacetate has not been settled.[8]

In either case, the driving force for the cleavage reaction seems to be the enhanced stabilities of the intermediates, allyl and *t*-butyl carbonium ion (or less likely the free radical). As discussed below, 4-penten-1-ol under similar conditions does not give a cleavage product, probably because the intermediate is not particularly stabilized.

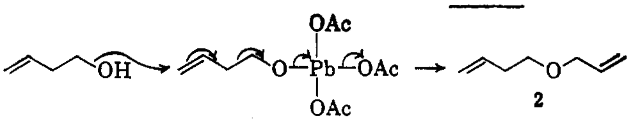
It is worthy of note that neither of two possible products from the reaction of 3-buten-1-ol, the cyclic ether **11** (Scheme III) nor the product of addition to the olefinic double bond, 1,2,4-butanetriol triacetate, were found. Other compounds that were not found, but which would have been detected if present, were 3,4-diacetoxy-1-butene and 1,2,3,4-tetraacetoxybutane. However, our method would not have detected such compounds as carbon dioxide, formaldehyde, or propylene.

SCHEME III



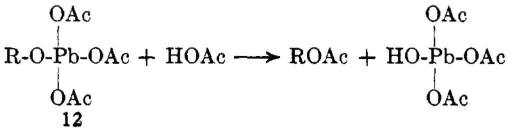
Formation of the ether **2** is of special interest. It may have come from the reaction of the alcohol **5** with the cation **7** or the radical **8**. An interesting alternative would be an attack of the alcohol **5** on the lead ester **6** with the allylic rearrangement depicted in Scheme IV.

SCHEME IV



Allylbenzene must come from the reaction of benzene with the cation **7** (or less likely the radical **8**).

Alcohols generally yield some of the corresponding acetate on treatment with lead tetraacetate. Mosher[6] pictured this as proceeding *via* the decomposition of a tetravalent lead ester **12**. We believe a more plausible



$$\mathrm{R\text{-}O\text{-}\overset{OAc}{\underset{OAc}{Pb}}\text{-}OAc + HOAc \longrightarrow ROAc + HO\text{-}\overset{OAc}{\underset{OAc}{Pb}}\text{-}OAc}$$

12

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(5) J. Kalvoda and K. Heusler, *Chem. Ind.* (London), 1431 (1963).

(6) W. A. Mosher, C. L. Kehr, and L. W. Wright, *J. Org. Chem.*, **26**, 1044 (1961).

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

(8) R. E. Partch, *J. Org. Chem.*, **28**, 276 (1963).

TABLE II

PRODUCTS OF REACTION OF LEAD TETRAACETATE WITH 2-PHENYLETHANOL

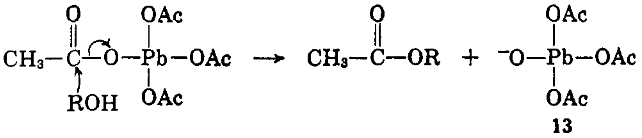
	Yield, %			
Solvent (time)	Benzaldehyde (**14**)	Benzyl acetate (**15**)	2-Phenylethyl acetate (**16**)	2-Phenylethanol (**17**)
Refluxing benzene (overnight)	15	15	63	7
Refluxing benzene (3 hr.)	3	7	61	29
Refluxing cyclohexane (overnight)	8	3	89	0

TABLE III

PRODUCTS OF REACTION OF LEAD TETRAACETATE WITH 4-PENTEN-1-OL

	Yield, %				
Solvent (time)	4-Penten-1-ol (**18**)	4-Penten-1-yl acetate (**19**)	3-Acetoxytetrahydropyran (**20**)	Tetrahydrofurfuryl acetate (**21**)	Unidentified compd. (**22**)
Refluxing benzene (overnight)	19	16	26	14	8

path to be a nucleophilic attack of the alcohol on the acetyl carbon of lead tetraacetate as shown below.



$$CH_3-\underset{\underset{ROH}{\uparrow}}{\overset{\overset{O}{\|}}{C}}-O-\underset{\underset{OAc}{|}}{\overset{\overset{OAc}{|}}{Pb}}-OAc \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OR + {}^{-}O-\underset{\underset{OAc}{|}}{\overset{\overset{OAc}{|}}{Pb}}-OAc$$

13

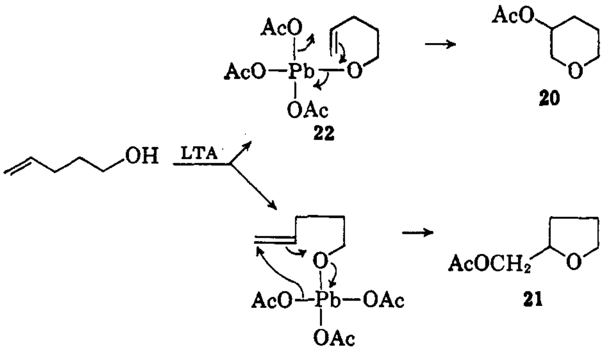
In order to test the generality of the oxidative deformylation reaction, a homobenzylic alcohol, 2-phenylethanol, was treated with lead tetraacetate. As expected, benzyl acetate, a cleavage product, was obtained in 15% yield. The reaction products and their yields are listed in Table II. Change of the solvent from benzene to cyclohexane did not change the product distribution greatly except to lower the yield of benzyl acetate. Here again, the driving force for the cleavage reaction seems to be the stability of the benzyl ion (or free radical). The formation of benzaldehyde is more difficult to explain. It may be, at least in part, an oxidation product of benzyl acetate. Benzyl acetate on treatment with lead tetraacetate in refluxing benzene gave 2% of benzaldehyde in addition to 98% of unchanged benzyl acetate.

4-Penten-1-ol was treated with lead tetraacetate in order to see whether acetoxy ethers would be formed as a result of interaction between the two functional groups. The results are summarized in Table III.

The structure of the acetate **20** followed from its elemental analysis and n.m.r. spectrum which had broad multiplets centered at τ 6.5 (4H, α-protons of oxirane ring[9]) and 5.3 (1H, tertiary proton on carbon bearing an acetoxy group). In addition the mass spectrum showed a large peak at $m/e = 84$, indicative of a tetrahydropyran moiety. The position of the acetoxy group on the tetrahydropyran ring was deduced by a process of elimination. The tertiary proton of 2-acetoxytetrahydropyran would have a much lower chemical shift than the observed τ 5.3. The 4-isomer was eliminated on mechanistic grounds; acetate **20** was therefore 3-acetoxytetrahydropyran.

Formation of the acetates **20** and **21** shows that there is an interaction between the hydroxyl group and the olefinic double bond. Probably the first intermediate formed is the ester **22** which then reacts with the double bond, shown in Scheme V.

SCHEME V



Since no product resulting from the addition of lead tetraacetate to the double bond was obtained, we favor the mechanism in Scheme V over an alternative one[10] in which initial reaction occurs between the double bond and lead tetraacetate.

Experimental[11]

3-Buten-1-yl Allyl Ether.[12]—To a solution of 1.5 g. of 3-buten-1-ol in 25 ml. of benzene was added 0.5 g. of sodium metal, and the mixture was heated to reflux for 2 hr. The mixture was cooled to room temperature and 2.5 g. of allyl bromide was added. After stirring for 5 min., the mixture was heated to reflux for 6 hr. It was then cooled and diluted with water. The benzene layer was separated and washed with water until the washings were neutral, and dried over magnesium sulfate. Gas chromatography on TCEP did not separate 3-buten-1-yl allyl ether and benzene, but they were separated on silicone oil and a sample of 3-buten-1-yl allyl ether[13] was isolated from a silicone oil column at 70°.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.18; H, 10.77.

Reaction of 3-Buten-1-ol with Lead Tetraacetate.—A heterogeneous mixture of 1 g. of 3-buten-1-ol (Columbia Organic Chemicals Co.), 4 g. of lead tetraacetate (with 10% acetic acid, from Arapahoe Chemical, Inc.), and 20 ml. of benzene was heated to reflux overnight with stirring. The mixture was cooled to room temperature. Then 5 ml. of ethylene glycol was added and the mixture was stirred for 15 min. in order to decompose any excess lead tetraacetate. The benzene layer was separated and washed with water, 10% sodium bicarbonate solution, and water, and dried over magnesium sulfate. The benzene was removed by distillation. Gas chromatography on silicone oil at 70° showed four peaks in addition to the solvent

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(9) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p.55.

(10) R. M. Moriarty and K. Kapadia, *Tetrahedron Letters*, 1165 (1964).

(11) For gas chromatographic analyses, an F and M Model 810 flame ionization gas chromatograph and a "MIT" gas chromatograph with thermal conductivity detectors [A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959), footnote 24] were used. The liquid-phase absorbants employed were Dow-Corning silicone oil no. 710 and 1,2,3-tris-(cyanoethoxy)propane (TCEP). We are indebted to Dr. E. P. Burrows for the mass spectra and their interpretation.

(12) The procedure for a Williamson synthesis was similar to that described by M. T. Leffler and A. E. Calkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 544.

(13) J. P. Guermont and I. Marszak, *Compt. rend.*, **235**, 252 (1952).

peak. All four peaks had shorter retention times than that of 1,5-pentanediol diacetate, indicating that none was butanetriol triacetate, one of the expected products. 3-Buten-1-ol and benzene could not be separated by gas chromatography on silicone oil at 70°, but they were separated on TCEP at 80°. It was shown that the reaction mixture did not contain any 3-buten-1-ol. The four components were isolated by gas chromatography and identified as allyl acetate (**1**, 30%),[14] 3-buten-1-yl allyl ether (**2**, 13%), 3-buten-1-yl acetate (**3**, 20%), and allylbenzene (**4**, 32%) by comparison of their infrared spectra with those of authentic samples, and by their retention times on silicone oil at 70°.

The mass spectrum of compound **1** showed a molecular ion peak at $m/e = 100$ (0.1)[15] and small peaks at 85 (0.27), 78 (1.1), 72 (0.6), and 61 (1.8) and very large peaks at 58 (8.1), 57 (6.3), and 43 (100). The base peak at $m/e = 43$ is characteristic of an acetoxy group. The mass spectrum of 3-buten-1-yl allyl ether (**2**) had a molecular ion peak at $m/e = 112$ (0.11) and peaks at 111 (0.7), 91 (9.2), 71 (24), 67 (5.0), 55 (16), 41 (100), and 29 (13). The mass spectrum of allylbenzene (**4**) had very large peaks at $m/e = 117$ (77) and 118 (100), which were larger than any other peaks in the spectrum. Other peaks were at $m/e = 91$ (45.7), 77 (6.7), and 41 (11.5). Such a larger molecular ion peak ($m/e = 118$) combined with a large M-1 peak is often characteristic of an aromatic system.[16]

The reaction was repeated using 1 g. of 3-buten-1-ol in 20 ml. of cyclohexane and 4 g. of lead tetraacetate. The product mixture isolated in 84% yield, was shown to consist of the acetate **1** (10%), the ether **2** (60%), and the acetate **3** (13%).[14]

Reaction of 2-Phenylethanol with Lead Tetraacetate.—A mixture of 1 g. of 2-phenylethanol, 4 g. of lead tetraacetate, and 20 ml. of benzene was heated to reflux overnight with stirring. The product was isolated as described above. Gas chromatography showed a mixture of four compounds, later identified as benzaldehyde (**14**, 15%), benzyl acetate (**15**, 15%), 2-phenylethyl acetate (**16**, 63%), and unchanged 2-phenylethanol (7%) by comparison of their infrared spectra with those of authentic samples, and by their retention times on gas chromatography on TCEP at 160°.

The reaction was repeated on a larger scale. A mixture of 20 g. of 2-phenylethanol, 80 g. of lead tetraacetate, and 500 ml. of benzene was refluxed overnight. The products were isolated as described above, except that benzene was removed by distillation through a 0.8 × 40 cm. spinning-band column. The residue was distilled through the same column and six fractions totaling 12.2 g. (61%) were collected. All fractions contained mixture of products as shown by gas chromatography.

In another run, a mixture of 1 g. of 2-phenylethanol, 4 g. of lead tetraacetate, and 25 ml. of cyclohexane was refluxed overnight. The products were isolated as described previously and were identified as the aldehyde **14** (8%), the acetate **15** (3%), and the acetate **16** (89%).

In still another run, a mixture of 1 g. of 2-phenylethanol, 4 g. of lead tetraacetate, and 25 ml. of benzene was refluxed for 3 hr. The products were isolated as described before, and were identified as the aldehyde **14** (3%), the acetate **15** (7%), the acetate (61%), and the alcohol **17** (29%).

Reaction of 4-Penten-1-ol with Lead Tetraacetate.—A mixture of 1 g. of 4-penten-1-ol, 4 g. of lead tetraacetate, and 20 ml. of benzene was refluxed overnight. The reaction mixture was isolated as described for the reaction of 3-buten-1-ol. Gas chromatography (silicone oil at 150°) showed that there were at least five components, later shown to be 4-penten-1-ol (**18**, 19%), 4-penten-1-yl acetate (**19**, 16%), 3-acetoxytetrahydropyran (**20**, 26%), tetrahydrofurfuryl acetate (**21**, 14%), and an unidentified compound **22** (8%). The alcohol **18** and the acetates **19**, **20**, and **21** were identified by comparison of their retention times and infrared spectra with those of authentic samples. A sample of the acetate **20** was collected by gas chromatography.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.20; H, 8.47.

The n.m.r. spectrum (in CCl_4) of the acetate **20** had a singlet at τ 8.02 (3H), a multiplet at 8.2 (4H), a multiplet at 6.5 (4H), and a multiplet at 5.3 (1H).

The mass spectrum of the acetate **20** showed peaks at $m/e =$ 84 (30.5), 71 (34.2), 55 (8.0), and 43 (100). The mass spectrum of the acetate **21** showed peaks at $m/e = 84$ (7.2), 71 (89), 55 (3.4), and 43 (100).

3-Acetoxytetrahydropyran (20).[17]—Refluxing tetrahydrofurfuryl tosylate in acetic acid in the presence of excess sodium acetate for 2 hr. gave a mixture which consisted of the acetate **20** (40%) and **21** (60%).

Acknowledgment.—This work was supported in part by grants provided by Research Corporation, The Petroleum Research Fund of the American Chemical Society (PRF 1773-A4), and National Aeronautics and Space Administration (NsG 394).

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[14] The yields are based on the starting material and were estimated by gas chromatography using cyclohexyl acetate as an internal standard.

[15] The figures in parentheses are intensities of the peaks relative to the base peak set as 100.

[16] H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p. 453.

[17] D. Gagnaire, *Compt. rend.*, **248**, 420 (1959).

Lead Tetraacetate. II. Reactions with Bicyclo[3.1.0]hexane and Bicyclo[4.1.0]heptane

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The reaction of lead tetraacetate with cyclopropane hydrocarbons was investigated. Bicyclo[3.1.0]hexane on treatment with lead tetraacetate gave *endo*- and *exo*-bicyclo[3.1.0]hex-2-yl acetate, 3-cyclohexen-1-yl acetate, *cis*-1,3-cyclohexanediol diacetate, and 2-acetoxymethylcyclopentyl acetate. Bicyclo[4.1.0]heptane (norcarane) under similar conditions gave 2-cyclohepten-1-yl acetate, *trans*-1,3-cycloheptanediol diacetate, and *trans*-2-acetoxymethylcyclohexyl acetate. The possible mechanisms are discussed.

Although lead tetraacetate has found extensive use in organic chemistry,[1] little is known about its reactions with cyclopropane hydrocarbons. Such an investigation would be of interest since cyclopropane has some characteristics of an olefinic double bond. Prior to our work, Criegee[2] reported that bicyclo[2.1.0]pentane, on treatment with lead tetraacetate, gave *cis*-1,3-cyclopentanediol diacetate. However, owing to its high strain, this compound has been known to exhibit abnormal chemical behavior in other reactions such as its ready addition of hydrogen bromide, indicating that it is not representative of cyclopropane hydrocarbons. After our work was essentially complete, Ouellette and Shaw

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[1] For reviews of the subject, see (a) R. Criegee, in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948; (b) R. Criegee, *Angew. Chem.*, **70**, 173 (1958); (c) A. S. Perkin in "Advances in Carbohydrate Chemistry," Vol. 14, M. L. Wolfrom, Ed., Academic Press, Inc., New York, N. Y., 1959.

[2] R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

[3] R. J. Ouellette and D. L. Shaw, *J. Am. Chem. Soc.*, **86**, 165 (1964).