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%).

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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).

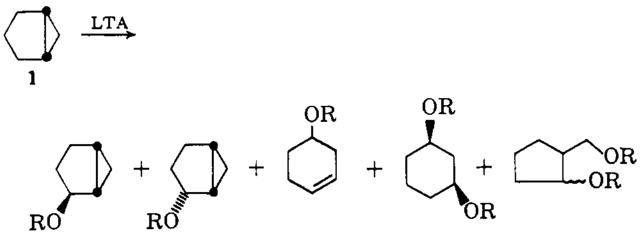
[3] R. J. Ouellette and D. L. Shaw, *J. Am. Chem. Soc.*, **86**, 165 (1964).

reported the cleavage of a phenyl-substituted cyclopropane ring by lead tetraacetate.

Bicyclo[3.1.0]hexane (**1**), on treatment with lead tetraacetate in refluxing acetic acid for 2 hr., gave a mixture of monoacetates and diacetates in addition to the starting alcohol, **1**.

The monoacetate fraction could not be separated on three different gas chromatography columns. However, reduction of the monoacetate fraction with lithium aluminum hydride gave three alcohols: *exo*- (**2a**, 12%) and *endo*-bicyclo[3.1.0]hexan-2-ol (**3a**, 10%) and 3-cyclohexen-1-ol (**4a**, 10%), identified by comparison with authentic samples.[4] Comparison of the infrared spectrum of the initial monoacetate fraction with the spectrum of 2-cyclohexen-1-yl acetate indicated that little or no 2-cyclohexen-1-yl acetate was present.

The diacetate fraction was shown by gas chromatography to be a mixture of two compounds, *cis*-1,3-cyclohexanediol diacetate[5] (**5b**, 43%) and 2-acetoxymethylcyclopentyl acetate (**6b**, 25%). The stereochemistry of the acetate **6b** was not determined. Although the retention time of *trans*-1,3-cyclohexanediol diacetate was similar to that of the acetate **6b**, comparison of their infrared spectra showed that there was little, if any, *trans* isomer present.

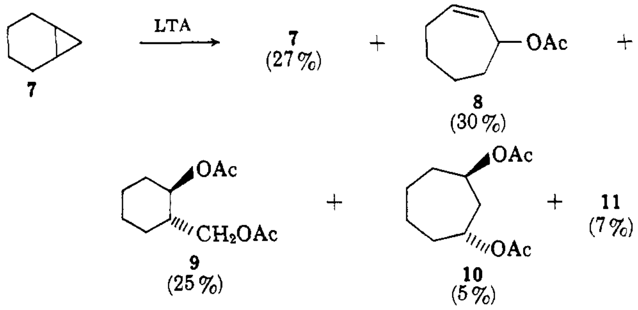


2a, R = H	3a, R = H	4a, R = H	5a, R = H	6a, R = H
b, R = Ac	b, R = Ac	b, R = Ac	b, R = Ac	b, R = Ac
(12%)	(10%)	(10%)	(43%)	(25%)

In a qualitative sense, bicyclo[4.1.0]heptane was much less reactive than cyclohexene toward lead tetraacetate. Treatment of bicyclo[4.1.0]heptane with lead tetraacetate in refluxing acetic acid for 2 hr. yielded a mixture consisting of recovered bicyclo[4.1.0]heptane (**7**, 27%), 2-cyclohepten-1-yl acetate (**8**, 30%), *trans*-2-acetoxymethylcyclohexyl acetate[3] (**9**, 25%), *trans*-1,3-cycloheptanediol diacetate[6] (**10**, 5%), and an unidentified acetate (**11**, 7%).[7] (See Scheme I.)

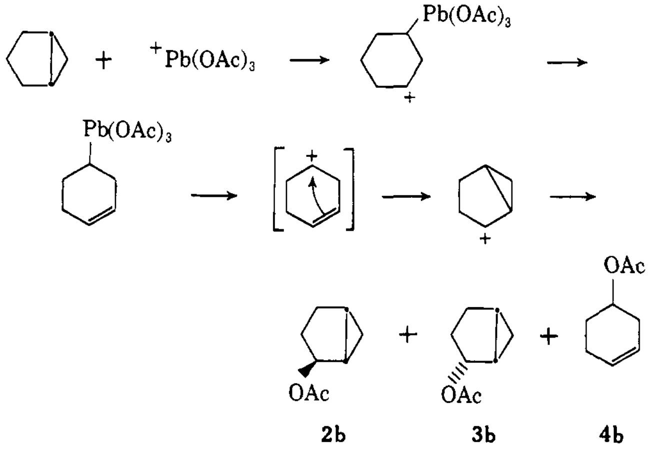
In order to show that these were primary products resulting from the reaction with lead tetraacetate and not merely from a reaction with acetic acid, bicyclo[4.1.0]heptane was subjected to refluxing acetic acid for 3 hr.[8] It was recovered unchanged.

SCHEME I

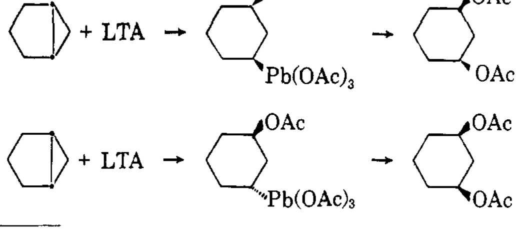


The formation of acetates **2b** and **3b** is of special interest. It is very unlikely that the position adjacent to the cyclopropane ring is activated sufficiently to lead to substituted products. The mechanism in Scheme II is offered as a possible path to these acetates. In support of this, it may be pointed out that Moore and Thornton[4] obtained the acetates **2b**, **3b**, and **4b** in similar distribution from the solvolysis of bicyclo[3.1.0]hex-2-yl derivatives. Also, the formation of bicyclic acetates containing a cyclopropane ring from solvolysis of 3-cyclohepten-1-yl[9] and 3-cycloocten-1-yl[10] derivatives has been reported.

SCHEME II



Stereospecificity of the addition reaction of lead tetraacetate to the cyclopropane ring is suggested by isolation of only the *cis* isomer of 1,3-cyclohexanediol diacetate. Therefore, any mechanism to explain the products must not include formation of a free ionic intermediate, since this would lead to a mixture of *cis* and *trans* isomers. Two possible mechanisms may be written for the formation of *cis*-1,3-cyclohexanediol diacetate. Addition of lead tetraacetate at the carbon–carbon bridge may occur in a *cis* and concerted manner, and the lead ester may subsequently be converted to an acetate with retention of configuration to



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[4] W. R. Moore and R. Thornton, unpublished work. The author is grateful to Dr. Moore for supplying him with the infrared spectra of these authentic samples.

[5] (a) W. Rigby, *J. Chem. Soc.*, 1586 (1949); (b) B. Franzus and B. E. Hudson, Jr., *J. Org. Chem.*, **28**, 2238 (1963).

[6] (a) A. C. Cope, J. K. Heeren, and V. Seeman, *ibid.*, **28**, 516 (1963); (b) A. C. Cope, M. Gordon, S. Moon, and C. H. Park, to be published.

[7] Comparison of the retention time of authentic *cis*-1,3-cycloheptanediol diacetate with those of the products excluded its presence in the mixture.

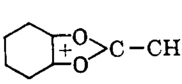
[8] LaLonde had shown earlier [*J. Org. Chem.*, **27**, 2275 (1962)] that bicyclo[4.1.0]heptane was recovered unchanged after treatment with acetic acid at 46.5° for 1 week.

[9] A. C. Cope, C. H. Park, and P. Scheiner, *J. Am. Chem. Soc.*, **84**, 4862 (1962).

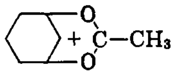
[10] A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

give *cis*-1,3-cyclohexanediol diacetate. Alternatively, the addition may occur in a *trans* and concerted manner, the lead ester subsequently being converted to an acetate with the inversion of the configuration to *cis*-1,3-cyclohexanediol diacetate.

In view of the fact that only the *trans* isomer of 1,3-cycloheptanediol diacetate was formed, the above mechanisms do not apply to the bicycloheptane system. Winstein[11] reported that the configuration of the 1,2-cyclohexanediol diacetate obtained from cyclohexene on treatment with thallic acetate depends on the concentration of water in the reaction mixture. Presumably, the process involves the acetoxium ion **12**, which would yield the *cis* isomer of the diacetate by attack of water, or the *trans* isomer by nucleophilic attack of an acetate ion. However, it does not seem to be reasonable to apply such an explanation to the present case, since 1,3-position is too far apart to postulate the acetoxinium ion **13** as an intermediate for the formation of the diacetates.



12



13

It is noteworthy that, as the ring size is increased from bicyclo[2.1.0]pentane to bicyclo[3.1.0]hexane to bicyclo[4.1.0]heptane, cleavage of the bond between the bridgehead and the methylene increases at the expense of cleavage of the bond between the two bridgeheads. This is probably due to strain on the carbon–carbon bridge, which increases as the size of the ring fused to the cyclopropane decreases. The cleavage of both bicyclo[4.1.0]heptane and bicyclo[3.1.0]hexane by either acid[12] or mercuric acetate[13] has been reported to occur predominantly between the bridgehead and the methylene.

Experimental[14]

Bicyclo[3.1.0]hexane and Bicyclo[4.1.0]heptane.—The starting hydrocarbons were prepared by the method of Simmons and Smith[15] and were purified by distillation through a 0.8 × 40 cm. spinning-band column followed by collection by gas chromatography (silicone oil, 70°).

Reaction of Bicyclo[3.1.0]hexane with Lead Tetraacetate.—A mixture of 1.7 g. of bicyclo[3.1.0]hexane, 8 g. of lead tetraacetate, and 40 ml. of glacial acetic acid was refluxed for 2 hr. After the reaction mixture was cooled to room temperature, the excess lead tetraacetate was decomposed by adding 5 ml. of ethylene glycol and stirring for 15 min. at room temperature. The mixture was diluted with 120 ml. of water and extracted with ether. The ether solution was washed with water, 10% sodium carbonate solution, 10% potassium iodide solution, 10% sodium thiosulfate solution, 10% sodium carbonate solution, and water, and then dried over magnesium sulfate and concentrated. It was separated into a monoacetate fraction and diacetate fraction by gas chromatography.

Although the monoacetate fraction was homogeneous on gas chromatography, the corresponding alcohols, obtained by treatment with lithium aluminum hydride, were well separated (TCEP at 115°) and identified as *exo*-bicyclo[3.1.0]hexan-2-ol (**2a**, 12%, $\nu_{\max}^{CS_2}$ 3400, 3050, 3015, 2980, 2930, 2850, 1100, 1045, 1025, 985, and 940 cm.$^{-1}$), *endo*-bicyclo[3.1.0]hexan-2-ol (**3a**, 10%, $\nu_{\max}^{CS_2}$ 3400, 3050, 3020, 2980, 2950, 2920, 1050, 1020, 970, and 825 cm.$^{-1}$), and 3-cyclohexen-1-ol (**4a**, 10%, $\nu_{\max}^{CS_2}$ 3400, 3020, 2910, 1070, 960, and 660 cm.$^{-1}$) by comparison of their infrared spectra with those of authentic samples.[4] Although 2-cyclohexen-1-ol had a retention time similar to that of the alcohol **2a**, comparison of their infrared spectra showed that little or none of the former was present.

The diacetate fraction was shown to be a mixture of *cis*-1,3-cyclohexanediol diacetate (**5b**, 43%) and 2-acetoxymethylcyclopentyl acetate (**6b**, 25%) by comparison of their retention times and infrared spectra with those of authentic samples.

***cis*- and *trans*-1,3-Cyclohexanediol Diacetate.**—A sample of *cis*-1,3-cyclohexanediol was obtained from a mixture of *cis*- and *trans*-1,3-cyclohexanediol (available from K and K Laboratories, Inc.) by recrystallization from benzene in a manner similar to that described by Rigby.[5a] The 1,3-cyclohexanediol (5 g.) was added to 100 ml. of benzene and heated to effect solution. The mixture was allowed to stand at 5° overnight. The semisolid material which formed was separated from the benzene and recrystallized from acetone, yielding 1.7 g. of *cis*-1,3-cyclohexanediol, m.p. 82–84° (lit.[5a] m.p. 83.0–83.5°). Gas chromatography of the diacetate, prepared from this diol by treatment with acetic anhydride in pyridine, showed that the *cis* isomer thus obtained was not contaminated by the *trans* isomer. The *cis* diacetate had a longer retention time than the *trans* diacetate on gas chromatography (Carbowax 1540 at 170°).

2-Acetoxymethylcyclopentyl Acetate.—A sample of the diacetate **6b** was obtained from 2-carboethoxycyclopentanone by reduction[16] with lithium aluminum hydride, followed by treatment with acetic anhydride in pyridine. Its stereochemistry was not determined.

Reaction of Lead Tetraacetate with Bicyclo[4.1.0]heptane.—A mixture of 1.7 g. of bicyclo[4.1.0]heptane, 40 ml. of acetic acid, and 8.0 g. of lead tetraacetate was heated to reflux for 2 hr. The products, isolated as described for bicyclo[3.1.0]hexane, were identified as bicyclo[4.1.0]heptane (**7**, 27%), 2-cyclohepten-1-yl acetate (**8**, 30%), *trans*-2-acetoxymethyl cyclohexyl acetate (**9**, 25%), and *trans*-1,3-cycloheptanediol diacetate[6] (**10**, 5%, $\nu_{\max}^{CS_2}$ 2920, 2850, 1735, 1250, 1025, and 975 cm.$^{-1}$) by comparison of their retention times and infrared spectra with those of authentic samples. Three minor components, obtained in 2, 3, and 7% yields, were not identified.

An authentic sample of the acetate **10** was obtained from cyclohexene by Prins reaction in the manner described by Dolby.[17] In addition the stereochemistry of the acetate was confirmed in the following way. The reaction mixture, obtained from refluxing bicyclo[4.1.0]heptane (1.3 g.) and lead tetraacetate (8 g.) in acetic acid (40 ml.) for 2 hr., was reduced with 2 g. of lithium aluminum hydride to a mixture of alcohols. The diol fraction (0.408 g., 0.0031 mole), separated by column chromatography on 50 g. of neutral, activity I, Wohlm alumina, was converted to 2-hydroxycyclohexylmethyl tosylate by treatment with tosyl chloride (0.6 g., 0.0031 mole) in pyridine. On treatment with lithium hydride, the tosylate yielded 2-methylcyclohexanol. Gas chromatography on TCEP at 90° showed that the 2-methylcyclohexanol, thus obtained, was 99% *trans* isomer. Therefore the configuration of the acetate **10** is believed to be *trans*, with less than 1%, if any, of the *cis* isomer present.

Acknowledgment.—This work was supported in part by grants provided by Research Corporation and the Petroleum Research Fund of the American Chemical Society (PRF 1773-A4).

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[11] C. B. Anderson and S. Winstein, *J. Org. Chem.*, **28**, 605 (1963).

[12] R. T. LaLonde and L. S. Forney, *ibid.*, **85**, 3767 (1963).

[13] R. Ya. Levina, V. N. Kostin, and T. K. Ustynyuk, *J. Gen. Chem. USSR*, **30**, 383 (1960).

[14] For gas chromatographic analyses, a F and M Model 810 flame ionization gas chromatograph and a "MIT" gas chromatograph with thermal conductivity detectors (ref. 10, footnote 24) were used. The liquid-phase absorbants employed were Dow-Corning silicone oil no. 710 and 1,2,3-tris-(cyanoethoxy)propane (TCEP), and Carbowax 1540. The per cent distribution of the products was determined by gas chromatography of the crude reaction mixture without any attempt to correct for unequal response of the detectors toward different compounds.

[15] (a) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959); (b) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

[16] A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).

[17] L. J. Dolby, *J. Org. Chem.*, **27**, 2971 (1962).