CHEMISTRY LETTERS, pp. 997-1000, 1981.

VINYL MIGRATION IN THE OXYTHALLATION OF SOME 1,3-DIENES

Masashi MURAKAMI* and Shinya NISHIDA
Department of Chemistry, Faculty of Science, Hokkaido University
Sapporo, Hokkaido 060

The oxythallation of certain 1,3-dienes with thallium(III) nitrate trihydrate in MeOH-CH_2Cl_2 at 0-20 °C gave products after vinyl migration. Methyl 1-methylcyclopropyl ketone, obtained in the reaction of 2,3-dimethyl-1,3-butadiene, was presumably derived from a cyclopropylmethyl cation, an intermediate in the vinyl migration.

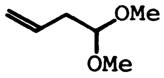
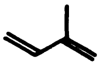
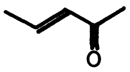
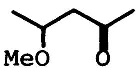
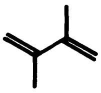
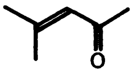
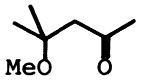
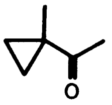
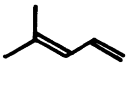
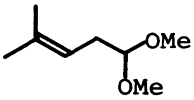
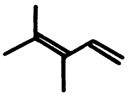
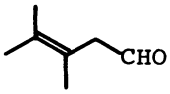
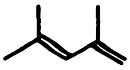
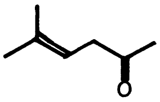
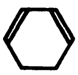
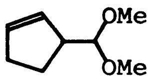
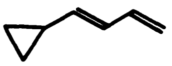
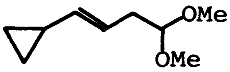
Among oxymetalation reactions, the oxythallation of an olefin,[1,2] particularly the reaction with thallium(III) nitrate trihydrate (TTN),[3] is of great interest because rearranged oxidation products are often produced. Thus, many workers have devoted to apply the reaction to alkenes for preparing certain specific compounds.[1-3] In the reaction of alkadienes and polyenes, however, there has been no report describing the preferential carbon-skeleton rearrangement under the oxythallation conditions, to the best of our knowledge. Several workers[4] have shown that the reaction of non-conjugated alkadienes and polyenes produces a cyclic product, indicating that the intramolecular participation of a double bond is important, whereas Uemura et al.[5] and Emmer and Zbiral[6] have demonstrated that mere 1,2- and 1,4-oxidation is the major pathway in the reaction of conjugated dienes. Lack of the rearrangement, in particular, in the reaction of conjugated alkadienes seems curious for us, since the vinyl migration is well known to occur in cationic intermediates.[7] This, however, may well be due to the nature of the counter anion in the thallium(III) salts used;[3] the previous works have been carried out with thallium(III) acetate[5] or trifluoroacetate.[6] Accordingly, we examined the reaction of some representative 1,3-alkadienes with TTN,[3] and found that the vinyl migration took place in such reactions. Especially, it was the major pathway in the reaction of relatively simple 1,3-dienes.

The oxythallation reaction was carried out by adding a stoichiometric amount of

TTN in methanol to a dichloromethane solution of 1,3-dienes[8] at an ice-bath temperature within a period of 15 min. The resultant mixture was then stirred at a room temperature for an additional hour. After removal of precipitated thallium(I) nitrate (quantitative recovery) by filtration, the products were purified by means of distillation followed by preparative GLPC. The each product was characterized by ^{1}H NMR and IR examinations.[9]

As summarized in Table 1, the major product obtained in the reaction of 1,3-butadiene, 2-methyl-1,3-butadiene, and 2,3-dimethyl-1,3-butadiene was the one after vinyl migration. Usually, a terminal carbonyl compound was isolated as an acetal,

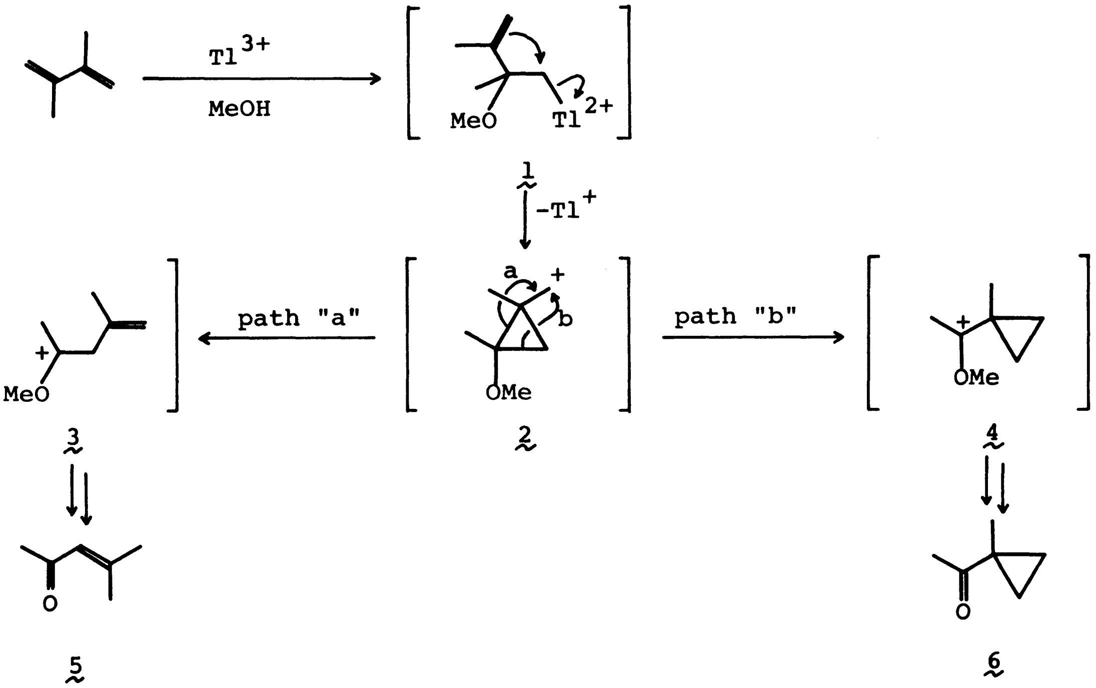
Table 1. Oxythallation of 1,3-Dienes with TTN in Methanol-Dichloromethane [a]

Entry	1,3-Diene	Product after Vinyl Migration	Others[b]
1		 (43)	1,2 (trace)
2		 (7)  (51)	None
3		 (35)  (14)  (9)	None
4		 (32)	1,2 (31)[c] 1,4 (7)
5		 (5)	1,2 (35)[c] 1,4 (22)
6		 (12)	1,2 (36)[c,d] 1,4 (28)[d]
7		 (31)	1,2 (10) 1,4 (12)
8	 e)	 (28)	1,2 (44)[c]

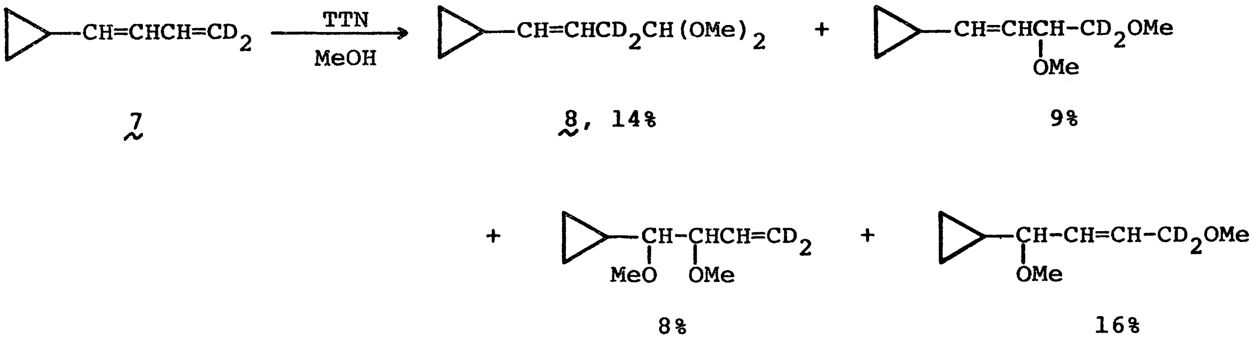
a) Figures given in the parenthesis are the yield of the product calculated from the weight of the distillates and the ratio observed in the GLPC analysis.
b) 1,2 refers to <u>vic</u>-dimethoxy compounds and 1,4 to 1,4-dimethoxybutene derivatives. Details will be reported elsewhere.
c) A mixture of 1,2- and 3,4-dimethoxy derivatives.
d) A mixture of a dimethoxy derivative and a methoxyalkenyl nitrate.
e) A mixture of trans and cis isomers in 87:13 ratio.

whereas an internal oxidation product was obtained as a ketone. In progress of the reaction, nitric acid was inevitably produced, which resulted in some complexities in the reaction. Namely, a double bond in the product was shifted to a conjugated position in some cases and the Michael addition of methanol to the resultant conjugated enone took place (entry 2 and 3).10)

In the reaction of 2,3-dimethyl-1,3-butadiene, methyl 1-methylcyclopropyl ketone (6)11) was obtained in 9% yield (entry 3). The formation of 6 will most reasonably be rationalized in the following way. Namely, in the first intermediate 1, the π bonding electron pair of the vinyl group will participate in the C-Tl bond heterolysis to form a cyclopropylmethyl cation 2. The cyclopropylmethyl-3-butenyl type ring opening7) (path "a") of 2 produces 3, from which 4-methyl-3-penten-2-one (5) is formed after the double bond shift, whereas the cyclopropylmethyl-cyclopropylmethyl rearrangement7) (path "b") will lead to the formation of the second cyclopropylmethyl cation 4. 4 then gives the observed product 6. Thus, the formation of 6 is a good evidence that the present transformation producing the carbonyl compounds, or their alternatives, involves the vinyl migration.



An additional evidence indicating that the acetal formation was a result of the vinyl migration, not of the methoxyl migration,12) was obtained in the reaction of a deuterium labeled substrate. Namely, the acetal 8 isolated from the product mixture obtained in the reaction of 1-cyclopropyl-4,4-dideuterio-1,3-butadiene (7) was substituted by deuteron only at the 3-position. The result is compatible with the vinyl migration. No deuterium transposition was observed in the 1,2- and 1,4-oxidation products.[13)]



The present work was supported by the Grant-in-Aid for Scientific Research (No. 547017) provided by the Ministry of Education, Science and Culture.

REFERENCES AND NOTES

1) R. Criegee, Angew. Chem., 70, 173 (1958); H. J. Kabbe, Justus Liebigs Ann. Chem., 656, 204 (1962); C. B. Anderson and S. Winstein, J. Org. Chem., 28, 605 (1963); J. B. Lee and J. M. Price, Tetrahedron, 20, 1017 (1964); P. M. Henry, J. Am. Chem. Soc., 88, 1597 (1966).

2) Review articles: A. McKillop and E. C. Taylor, Adv. Organomet. Chem., 11, 147 (1973); K. Iguchi and Y. Yamada, Yuki Gosei Kagaku Kyokai Shi, 36, 259 (1978); S. Uemura, Kagaku, 34, 786 (1979).

3) A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, Tetrahedron Lett., 1970, 5275; A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, J. Am. Chem. Soc., 95, 3635 (1973).

4) M. Anteunis and A. De Smet, Synth., 1974, 868; F. J. McQuillin and D. G. Parker, J. Chem. Soc. Perkin Trans. I, 1975, 2092; Y. Yamada, H. Sanjoh, and K. Iguchi, J. Chem. Soc. Chem. Commun., 1976, 997; Y. Yamada, A. Shibata, K. Iguchi, and H. Sanjoh, Tetrahedron Lett., 1977, 2407.

5) S. Uemura, A. Tabata, M. Okano, and K. Ichikawa, J. Chem. Soc. Chem. Commun., 1970, 1630; S. Uemura, H. Miyoshi, A. Tabata, and M. Okano, Tetrahedron, 37, 291 (1981).

6) G. Emmer and E. Zbiral, Tetrahedron, 33, 1415 (1977).

7) P. R. Story and B. C. Clark, Jr., "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Eds., Vol. 3, Wiley, New York, 1972, Chapter 23; K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, ibid., Chapter 26; H. G. Richey, Jr., ibid., Chapter 25.

8) Ca. 0.5 M solution of TTN and 1 M solution of the diene were used in the reaction.

9) All new compounds gave satisfactory elemental analyses.

10) In a control experiment, it was observed that 4-methyl-3-penten-2-one gave 4-methoxy-4-methyl-2-pentanone in acidic methanol at a room temperature.

11) 6 was confirmed by comparisons with an authentic sample prepared from α-acetyl-α-methyl-γ-butyrolactone; bp 124-126 °C (lit. 125-127 °C): N. L. Goldman, Chem. Ind., 1963, 1036.

12) P. M. Henry, J. Am. Chem. Soc., 87, 4423 (1965).

13) Because of a limited amount of 7, the yields of the products were relatively low.

(Received May 16, 1981)