Tetrahedron Letters No.27, pp. 2361-2364, 1970. Pergamon Press. Printed in Great Britain.

SYNTHESIS AND REACTIONS OF 1,2,2-TRIMETHYLBICYCLO[1.1.0]BUTANE

Lars Skattebøl

Union Carbide Research Institute, Tarrytown, New York

(Received in USA 5 March 1970; received in UK for publication 15 May 1970)

We have previously reported[1] the reaction of 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (1) with methyllithium to give 1-isopropenyl-1-methylcyclopropane (2) as the major product. The primary product from the reaction was proposed as 1,2,2-trimethylbicyclo-[1.1.0]butane (3) which subsequently rearranged to 2. At the time we were not able to obtain pure 3 either by distillation or by preparative glc. The present paper describes the isolation, characterization and some reactions of this bicyclobutane derivative.[*]

Reaction of the <u>gem</u>-dibromocyclopropane derivative 1 with methyllithium was carried out as previously described;[1] however, care was taken that at all time during isolation basic environment was maintained. This was achieved by purging the distillation column with ammonia and addition of some anhydrous sodium carbonate to the pot. Under these conditions a liquid was obtained, bp 84°, n^{20}D 1.4214, in 90-95% yield which consisted essentially of 3, but with variable amounts (1-5%) of 2. The structure 3[2] was assigned on the basis of spectroscopic as well as chemical evidence.[‡]

Hydrogenation of a methanol solution of 3 over Pd/C catalyst gave 1,1,2-trimethylcyclobutane (4) (78%) and 2,3-dimethylpentane 5 (22%) identified by comparison with authentic samples. The use of platinum as catalyst and dimethoxyethane as solvent resulted in 4 (10%) and 5 (73%) besides two additional unidentified compounds.

The bicyclobutane is extremely sensitive to acids. When distilled in the pre-

---

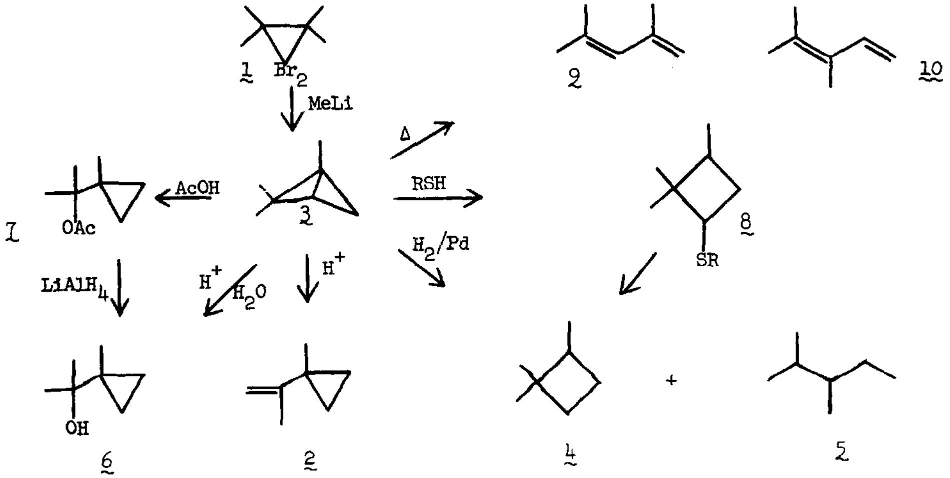
[*] The compound has also been obtained by W. R. Moore and co-workers; see <u>Tetrahedron Lett.</u>, 4353 (1969).

[‡] Mwt. 96 (mass spec.); uv: end absorption; ir: 3070 cm^{-1}, 1.66 μ (ε 0.70); nmr (60 MHz, CCl_4, δ) 0.77 s and 1.06 s (CH_3) 1.48 t J < Hz (angular CH_3) 1.19 s and 1.38 m (CH_2) and a broad singlet at ~ 0.80 (CH) partially hidden under the 0.77 ppm resonance.

sence of a trace of strong acid it was converted in high yield to the vinyl cyclopropane 2. Reaction of 3 with 10^{-4} N HCl at 25° gave quantitatively dimethyl 1-methylcyclopropyl carbinol (6),[3] mp 39°, and the reaction with glacial acetic acid at 0° gave a 68% yield of 7, the acetate of the above carbinol, bp 68-69° (25 mm) $n^{23}D$ 1.4275, besides some of 2; the structures were assigned on the basis of spectroscopic evidence and the conversion of 7 into 6 by lithium aluminum hydride.

Addition of benzenethiol to an ether solution of 3 resulted in practically quantitative formation of 1-phenylthio-2,2,3-trimethylcyclobutane (8, R=φ); the reaction proceeded rapidly at 0° after a short induction period. The structure was proven by spectroscopic data as well as its reduction to 4 by lithium in dimethylamine.[4] Compound 8 appeared homogeneous by glc, but the 220 MHz nmr spectrum showed the presence of two stereoisomers in a ratio of 4:1; the major component probably has the cis-configuration.[5] Likewise the sulfide 8, R=o-$C_6H_4CO_2CH_3$, was obtained in excellent yield as a mixture of stereoisomers from the corresponding mercaptan and 3.

When passed through a tube kept at 300° 3 was partially converted to a mixture of 2,4- (9) and 3,4-dimethyl-1,3-pentadiene (10), in 47% and 53%, respectively; the compounds were identified by comparison with authentic samples. These are the expected products from a concerted ring-opening.[6] The results described are summarized below:



Tetramethylallene rather than 3 was actually the expected product from the reaction of 1 with methyllithium. The bicyclobutane is most probably formed by insertion of a carbene (or carbenoid) intermediate, into one of the C-H bonds. Several cases of insertion into CH bonds have previously been observed in similar reactions.[7,8,9] In all these cases, however, the corresponding allenes would be extremely strained, which is not true of tetramethylallene. If one assumes that the preferred reaction path is formation of allenes from the lithium derivative by ring-opening and loss of lithium bromide,* it is only when the barrier to such a process is increased that α-elimination to a free carbene or carbenoid becomes important. Since 1,1-dibromo-2,2,3-trimethylcyclopropane gives exclusively the corresponding allene under the same conditions,[1] one is left with the task of explaining the drastic change in the reaction path caused by a methyl group. This remains unanswered, but molecular models indicate that the steric effect introduced by the additional methyl group would retard a concerted ring opening and probably enhance α-elimination.

The product selectivity of the electrophilic reactions leading to compounds **2**, **6**, and **7** is expected as a result of a cyclopropylcarbinyl ion intermediate.[10,11] The addition of thiols[12] presumably by a radical chain mechanism has not previously been demonstrated with alkyl-substituted bicyclobutanes.

By this two-step procedure compound **3** is available in better than 70% overall yield from a commercial olefin; moreover, the treatment of 1,1-dibromo-2-ethyl-2,3,3-trimethylcyclopropane with methyllithium gave a mixture of bicyclobutane derivatives, thus suggesting that the reaction may be quite general for dibromocarbene adducts of tetraalkyl-substituted olefins.

---

*Allenes are also derived from ring opening of the carbene, e.g. cyclopropylidene[13]

REFERENCES

1) L. Skattebøl, Acta. Chem. Scand., **17**, 1683 (1963).

2) All new compounds gave correct elemental analyses.

3) N. L. Goldman, Chem. & Ind., 1036 (1963).

4) W. E. Truce, D. P. Tate and D. N. Berge, J. Am. Chem. Soc., **82**, 2872 (1960).

5) E. B. Whipple and G. R. Evanega, Org. Magnetic Resonance, in press.

6) K. B. Wiberg, Tetrahedron, **24**, 1083 (1968).

7) W. R. Moore and H. R. Ward, J. Am. Chem. Soc., **83**, 2019 (1961).

8) E. T. Marquis and P. D. Gardner, Tetrahedron Lett.,2793 (1966).

9) R. Vaidyanathaswamy and D. Devaprabhakara, Chem. & Ind., 515 (1968).

10) K. B. Wiberg and G. Szeimies, J. Am. Chem. Soc., **92**, 571 (1970) and references therein.

11) C. U. Pittman and G. A. Olah, ibid, **87**, 5123 (1965).

12) E. P. Blanchard and A. Cairncross, ibid, **88**, 487 (1966).

13) W. M. Jones, ibid, **82**, 6200 (1960) ; P. S. Skell, and R. R. Engel, ibid, **89**, 2192 (1967).