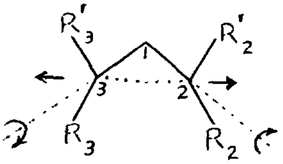
Tetrahedron Letters No.52, pp. 4553-4556, 1970. Pergamon Press. Printed in Great Britain.

COMPETITIVE BICYCLOBUTANE AND ALLENE FORMATION FROM PHENYL-SUBSTITUTED GEM-DIBROMOCYCLOPROPANES[1a]

William R. Moore and John B. Hill[1b]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

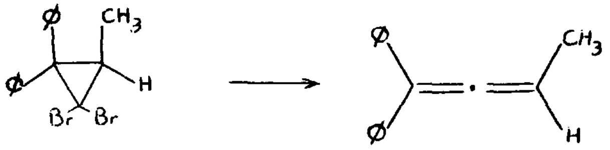
(Received in USA 6 October 1970; received in UK for publication 12 October 1970)

Tetraalkylsubstituted gem-dibromocyclopropanes react with methyllithium to afford bicyclobutanes rather than allenes.[2] The intermediate cyclopropylidenes, free or complexed, must suffer sufficient steric hindrance to opening that insertion into an alpha CH bond takes precedence.[2c] Any factor which will lead to an increase in the C_2-C_3 stretching in the transition state 1 for ring opening should tend to accelerate allene formation. A possible example of such an effect follows.



1

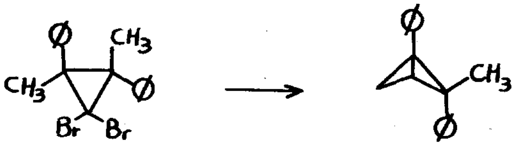
Treatment of 2, the dibromocarbene adduct of 1,1-diphenylpropene, with methyllithium in ether at 0° gives only 1,1-diphenylbutadiene-1,2 (3) in essentially quantitative yield.[3] Thus the course of reaction is the same as with the dibromocarbene adduct of trimethylethylene, only allene formation occurs; no CH insertion is observed.



2 3

Under the same conditions, dibromide 4, the dibromocarbene adduct of 2,3-

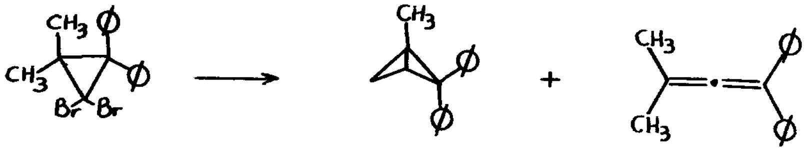
diphenyl-*trans*-butene-2, reacts with methyllithium to give a single product, 5, 1,2-diphenyl-*exo*-2-methylbicyclobutane.[4] No allene could be detected, indicating that as with tetraalkyl-substituted systems, CH insertion occurs instead of ring



4 5

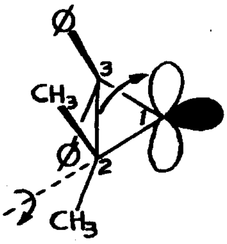
opening. The *endo*-configuration for the 2-phenyl group of 5 is required by the method of synthesis and supported by the nmr spectrum.

In striking contrast to the behavior of 4, the isomeric dibromide 6, the dibromocarbene adduct of 1,1-diphenyl-2-methylpropene, reacts with methyllithium[5] to afford a mixture (98-99% yield) of 73% 2,2-diphenyl-1-methylbicyclobutane (7)[6] and 27% 1,1-diphenyl-3-methylbutadiene-1,2 (8).[7]



6 7 8

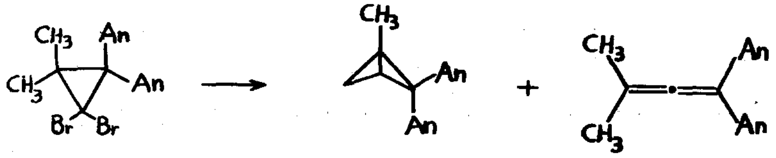
Why does 6 lead to a significant amount of ring opening and why do 4 and 6, which are isomers, behave differently? In light of our previous observations with tetrasubstituted systems, one might expect that the greater bulk of phenyl compared to methyl would tend to further the inhibition of allene formation. However, it seemed possible that putting phenyl groups on the carbon atoms involved in bond breaking might provide a stabilizing effect which would increase the extent of C_2-C_3 bond breaking at the transition state (refer to 1) and thus facilitate ring opening. That is, if the C_2-C_3 bond is stretched far enough, rotational barriers should be diminished. Still, why does 6 open but not 4?[8] The answer must lie in the "unsymmetrical" substitution pattern of 6. If the ring opening were to follow a monorotatory path, 9, the $C(CH_3)_2$group is the one which should rotate. Consider the following simple model for this



9

process. The electrons in the C_2-C_3 bond must be supplied to C_1 by what amounts to overlap of a p orbital developing at C_2 with the vacant p orbital at C_1. In a sense, the electrons in the C_2-C_3 bond must "rotate" with C_2. As a consequence, a vacant, or at least partially vacant, orbital must develop at C_3 (this orbital will interact with the filled orbital at C_1). To the extent that C_3 does suffer a deficiency of electrons, phenyl substitution at C_3 should provide stabilization which could be sufficient to cause greater stretching of the C_2-C_3 bond.

We find some, if not compelling, support for this picture in the observation that putting p-methoxy substituents on the phenyl groups <u>increases</u> the amount of allene formation. Thus <u>10</u> reacts with methyllithium to give a mixture



An = p-$CH_3OC_6H_4$

10

11

12

(98%) of 56% bicyclobutane <u>11</u> and 44% allene <u>12</u>.[9]

REFERENCES

1. (a) Acknowledgment is made to the donors of the Petroleum Research fund, administered by the American Chemical Society (1549-A4) and to the National Science Foundation (GP8181) for support of this research. (b) National Institutes of Health Predoctoral Fellow 1965-1968.

2. (a) W. R. Moore, K. G. Taylor, P. Muller, S. S. Hall, and Z. L. F. Gaibel, *Tetrahedron Lett.*, 2365 (1970). (b) L. Skattebøl, *ibid.*, 2361 (1970). (c) W. R. Moore and J. B. Hill, *ibid.*, 0000 (1970).

3. 3, mass spectrum m/e 206 (M^+); ir 1945 cm^{-1} (C=C=C); nmr (CCl_4) δ 1.80 (3H, d, C=CHCH_3), 5.61 (1H, q, C=CHCH$_3$); 7.30 (10H, broad s, phenyl).

4. 5, mass spectrum m/e 220 (M^+); nmr (CCl_4) δ 1.10 (1H, broad s, *endo*-3-H), 1.35 (3H, s, CH_3), 1.98 (2H, broad s, 3-H and *exo*-4-H), 7.0-7.4 (10H, m, phenyl).

5. The methyllithium contained lithium iodide; the ratio of 7 to 8 varies somewhat with the temperature and the nature of the lithium halide present.

6. 7, mass spectrum m/e 220 (M^+); ir 1370 cm^{-1} nmr (CCl_4) δ 0.72 (1H, broad s, *endo*-4-H), 1.40 (1H, d, *exo*-4-H), 1.55 (3H, s, CH_3), 2.08 (1H, d, 3-H), 7.0-7.3 (10H, m, phenyl).

7. (a) 8, mass spectrum m/e 220 (M^+); δ 1.80 (6H, s, CH_3), 7.0-7.4 (10H, m, phenyl). (b) G. Wittig and A. Haag, *Chem. Ber.*, 96, 1535 (1963).

8. Note that even if a disrotatory opening occurred via organometallic intermediates, the steric interactions in 4 and 6 must be the same.

9. Spectral data for 11 and 12 are similar to those for 7 and 8.