FIRST FORMATION OF 1,1-DIHALO-1,3-BUTADIENES FROM REACTIONS OF DICHLORO- AND DIBROMOCARBENES WITH CYCLOPROPENES VIA NEW ADDITION-REARRANGEMENTS[≠]

Jürgen Weber, Linxiao Xu, and Udo H. Brinker*

Department of Chemistry, State University of New York at Binghamton Binghamton, New York 13902-6000

SUMMARY: New dichloro- and dibromocarbene addition-rearrangements are reported. In the reactions of 1,2-diarylcyclopropenes with difluoro-, dichloro-, dibromo-, and bromofluorocarbene, 2,3-diaryl-1,1-dihalo-1,3-butadienes are formed. In addition, 1,3-diaryl-2,3-dihalocyclo-1-butenes are formed. For the formation of the 1,1-dihalobutadienes, new addition-rearrangement mechanisms are proposed. Furthermore, some reactions of cyclobutenes with dihalocarbenes are described.

Additions to carbon-carbon double bonds are the archetypical reactions of carbones. While thousands of dihalocarbone reactions with open chain and cyclic olefins larger than four-membered rings can be found in the literature,¹ only a few studies with small-ring olefins have been reported.² In the dichloro- and dibromocarbone reactions, however, in no case could the likely intermediate adducts **2** and **5** either be isolated or spectroscopically proven without doubt, and only **3** and **6** were found, probably deriving from cationic cyclopropyl allyl (CCA) rearrangements.³ While 6,6-dibromobicyclo[3.1.0]hexane rearranges to 2,3-dibromocyclohex-2-ene above $155^{\circ}C$,⁴ *Vogel* found that the reaction of dichlorocarbone with cyclobutene afforded **6** (X=Cl) at 0°C.^{2e} Theoretical analyses show that fluorine substituents at C5 of bicyclo[2.1.0]pentane **5** (X=F) reduce the barrier for cleavage of the central bond.⁵ *Mahler*^{2g}, however, reported that perfluoro-1,3-dimethylbicyclo[1.1.0]butane, formed from the gas-phase pyrolysis of (CF₃)₃PF₂ in the presence of perfluorobut-2-yne, at 300°C only slowly rearranged to perfluoro-2,3-dimethylbutadiene in low conversion.



Figure 1

To our knowledge, only reactions of dichlorocarbene with cyclopropenes^{2a-c} and cyclobutenes^{2d,f} have been published. Herein, we report on the reactions of dichloro-, dibromo-, difluoro-, and bromofluorocarbene with 1,2-diarylcyclopropenes and with two cyclobutenes.

In a typical experiment, a mixture of 1,2-diphenylcyclopropene (8) in chloroform, powdered sodium hydroxide, and *ca*. 0.5% of triethylbenzylammonium chloride (TEBA) was ultrasonicated for 20 min in the water bath of an ultrasonic cleaner (35 kHz and 120 W).^{6a} 14a and 11a were isolated by HPLC in a yield of 70% (ratio: 14a:11a=3.8:1; a dichlorocarbene adduct of 11a was also found). The reaction of 8 with dichlorocarbene generated by the Doering-Hoffmann method (HCCl₃, KOBu^t, -45°C)⁷ afforded 14a and 11a in a yield of 21% (ratio: 3.5:1). In the reactions with dibromocarbene, 14b and 11b were formed in total yields of 63% (ultrasonication)^{6b} and 17% (HCBr₃, KOBu^t)⁷, respectively. To our knowledge, the formation of butadienes has never been observed in reactions of dichloro- and dibromocarbene with cyclopropenes.

Cyclobutenes 14 may derive from CCA rearrangements of intermediate 12. Breakage of the central bond in 12 with loss of a halide anion leads to a symmetrical, stabilized cyclobutenyl cation which is trapped by halogen anion to give 14. In contrast, the formation of 11 may proceed *via* the three pathways depicted below.



Both intermediates 10 and 12 result from the reactions of 8 with dihalocarbenes (paths A and B). Like other additions of nucleophiles to strained double bonds,⁸ trihalomethyl anion, the dihalocarbene precursor, may nucleophilicly attack the cyclopropene double bond (path C) leading to cyclopropyl anion 7 which rearranges to 11. In addition, 12 can also be formed from both 10 and 7. The formation of

cyclobutenes 14, besides deriving directly from 12, can also first pass through either 10 or 7 which undergo ring closure to 12.

11c was isolated in low yield (8%) in the reaction of 8 with difluorocarbene (ultrasonication, [Ph₃PCF₂Br]Br, KF).⁹ Although it has been claimed that perfluoro-1,3-dimethylbicyclo[1.1.0]butane is stable up to 300°C^{2e}, 12 (X, X'=F) could not be detected¹⁰. As expected, with two non-nucleofugous fluorine atoms present, 14c, the product deriving from 12, was not found. In contrast, the reaction with bromofluorocarbene generated from HCFBr2 and NaOH under ultrasonication afforded a 21% yield of 11d and 11e (ratio=7:1).11 14d was also isolated (yield: 14%). Due to steric interaction of the two phenyl groups and one bromine atom at the same side, exo 12 (X=Br, X'=F) is expected to be the minor product in the reaction of 8 with bromofluorocarbene, *i.e.*, 11d should be formed in lower amounts than 11e. Thus, although concerted $[_{\sigma}2_{s} + {}_{\sigma}2_{a}]$ rearrangements of bicyclo[1.1.0]butanes to 1,3-butadienes have been suggested,¹² it seems that, with bromofluorocarbene, path B mainly leads to CCA rearrangements of 12 and contributes only little, if at all, to the formation of 11. Furthermore, when carrying out the reaction of 9 with dibromocarbene, the ratio of 13a to 13b (33:67)¹³ also suggests that 11 is not formed from 12, because concerted cleavage of two side bonds in 12 ($\alpha\beta$ or $\alpha'\beta'$ cleavages) should provide 13a and 13b in a ratio close to 1:1. On the other hand, if the reaction proceeds via intermediate 7, 13a should be obtained as the main isomer. In contrast, if zwitterion 10 is an intermediate, 13b should be expected as the major product. Thus, the formation of 1,1-dihalo-1,3-butadienes should proceed predominantly via path A. The results suggest that with more interferences to complete the ring closure of a cyclopropane in a concerted fashion, carbene additions to strained double bonds, like those in 8 and 9, might partially lead to intermediates with zwitterionic character affording novel addition-rearrangement products.

From the reactions of 4 and 16 with dihalocarbenes, 6 $(X=Br)^{2i}$ and 17, probably deriving from CCA rearrangements, could be isolated. 15^{2i} which resulted from a secondary dibromocarbene addition to 6 at 50°C underwent a renewed rearrangement to 1,2,3,6-tetrabromocyclohexene.¹⁴ Under similar conditions, 16 was converted into 17 which contains an *endo* chlorine at C4, as was indicated by NOE experiments.



Figure 3

Acknowledgment: U.H.B. thanks the State University of New York at Binghamton for start-up funds. Professor W. M. Jones, University of Florida, and Professor W. B. Smith, Texas Christian University, are acknowledged for a helpful discussion and NOE experiments, respectively.

REFERENCES AND NOTES

- ≠ Carbene Rearrangements 39. Part 38: Xu, L.; Smith, W. B.; Brinker, U. H., J. Am. Chem. Soc., 1992, 114, 783-4.
- a) Kirmse, W., "Carbene Chemistry", Academic Press, New York, 1971, pp 267-380. b) Moss, R. A., in "Carbenes", Vol. 1, Jones, M., Jr.; Moss, R. A., Eds., Wiley, New York, 1973, pp 153-304. c) Jones, W. M.; Brinker, U. H., in "Pericyclic Reactions", Marchand, A. P., Lehr, R. E., Eds., Academic Press, New York, 1977, pp 110-7. d) Moss, R. A., Acc. Chem. Res., 1989, 22, 15-21. e) Dehmlow, E. V. in Houben-Weyl "Methoden der Organischen Chemie", Vol. E19, Regitz, M., Ed., Thieme, Stuttgart, 1989, pp 1461-627.
- a) Trost, B. M.; Atkins, R. C., J. Chem. Soc., Chem. Commun., 1971, 1254-5. b) Yakushkina, N. I.; Leonova, L. I.; Bolesov, I. G., Proceedings of the 2nd All-Union Conference on the Chemistry of Carbenes and Their Analogues, Izv. Akad. Nauk., Moscow, 1977, 68-70. c) Dehmlow, E. V., Tetrahedron Lett., 1975, 203-6. d) Dehmlow, E. V., Tetrahedron, 1972, 28, 175-9. e) Vogel, E.; Kiefer, H., unpublished results, cited in Vogel, E., Angew. Chem., 1962, 74, 829-39. f) Hart, H.; Nitta, M., Tetrahedron Lett., 1974, 2109-12. g) Mahler, W., J. Am. Chem. Soc., 1962, 84, 4600. i) Jones, W. M.; Sütbeyaz, Y., personal communication, 1986.
- Woodward, R. B.; Hoffmann, R., "The Conservation of Orbital Symmetry", Academic Press, New York, 1977.
- 4. Sonnenberg, J.; Winstein, S., J. Org. Chem., 1962, 27, 748-51.
- 5. Chesnut, D. B.; Ferguson, S.; Smith, L. D.; Porter, N. A., Tetrahedron Lett., 1972, 3713-6.
- a) Xu, L.; Tao, F.; Yu, T., Acta Chim. Sinica, Engl. Ed., 1987, 294-8. b) Xu, L.; Tao, F.; Yu, T., Acta Chim. Sinica, Chin. Ed., 1988, 46, 608-11 (CA: 109, 189862r). c) Xu, L.; Tao, F., Synth. Commun., 1988, 2117-21.
- 7. Doering, W. v. E.; Hoffmann, A. K., J. Am. Chem. Soc., 1954, 76, 6162-5.
- 8. Halton, B.; Banwell, M. G., in "The Chemistry of the Cyclopropyl Group", Part 2, Rappoport, Z., Ed., 1987, pp 1258-61.
- 9. Jefford, C. W.; Roussihe, J.; Papadopoulos, M., Helv. Chim. Acta, 1985, 68, 1157-68.
- 1,3-Diphenylbicyclo[1.1.0]butane is stable at room temperature. Jain, R.; Sponsler, M. B.; Coms, F. D.; Dougherty, D. A., J. Am. Chem. Soc., 1988, 110, 1356-66.
- The ⁵J_{H-F} coupling constants of 11d (2.0 Hz) and 11e (~0 Hz) indicate that 11d should have a planar zig-zag configuration. See: Becker, E. D., "High Resolution NMR, Theory and Chemical Applications", 2nd Ed., Academic Press, New York, 1980, pp 94-105.
- 12. a) Closs, G. L.; Pfeffer, P. E., J. Am. Chem. Soc., 1968, 90, 2452-3. b) Gajewski, J. J., "Hydrocarbon Thermal Isomerizations", Academic Press, New York, 1981, pp 45-6.
- 13. The comparison of both ¹H and ¹³C NMR data of 13a and 13b with those of 11b strongly suggests the main isomer isolated to be 13b. This is further supported by hetero NOE experimental data for 11b.
- 14. Domnin, N. A., J. Gen. Chem. (USSR), 1946, 16, 1729-36.

(Received in USA 24 April 1992)