Anal. Calcd for $C_6H_{11}F_3N_2O_4S$: C, 27.28; H, 4.20. Found: C, 27.34; H, 4.10.

General Procedure for the Formation of Acylhydrazones. The reaction times and temperatures are found in Table I. A solution of 1 equiv each of the alkyl halide and the trifyl hydrazide was stirred in dry CH_3CN with 2 equiv of anhydrous K_2CO_3. The reaction was monitored by TLC. A typical work-up involved filtration of the reaction mixture and evaporation of the solvent in vacuo followed by trituration of the residue with several portions of hot CH_2Cl_2. The acylhydrazones were obtained on evaporation of the CH_2Cl_2 in vacuo and were recrystallized from ethanol or CH_2Cl_2–hexane.

Registry No.—Benzaldehyde benzoylhydrazone, 956-07-0; acetaldehyde benzoylhydrazone, 1483-22-3; acetophenone benzoylhydrazone, 1219-41-6; benzenepropanal benzoxylhydrazone, 56572-26-0; 2-propenal benzoylhydrazone, 6631-27-2; benzaldehyde *tert*-butoxycarbonylhydrazone, 24469-50-9; acetophenone *tert*-butoxycarbonylhydrazone, 56572-27-1; acetaldehyde *tert*-butoxycarbonylhydrazone, 56572-28-2; benzenepropanal *tert*-butoxycarbonylhydrazone, 56572-29-3; benzoylhydrazine, 613-94-5; triflic anhydride, 358-23-6; *tert*-butyl carbazate, 870-46-2.

References and Notes

(1) B. Ganem and R. K. Boeckman, Jr., *Tetrahedron Lett.*, 917 (1974); N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959); D. M. Lemal and A. J. Fry, *J. Org. Chem.*, **29**, 1673 (1964); I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Wiley-Interscience, New York, N.Y., 1971.

(2) J. F. W. McOmie, "Protective Groups in Organic Chemistry", Plenum Press, New York, N.Y., 1973, pp 340–342, and references cited therein.

(3) L. Horner and H. Ferenkess, *Chem. Ber.*, **94**, 712 (1961).

(4) (a) A survey of the main reactions of *N*-trifyl compounds is found in J. B. Hendrickson, R. Bergeron, A. Giga, and D. Sternbach, *J. Am. Chem. Soc.*, **95**, 3412 (1973). (b) A similar reaction has been reported with *N*-benzoyl-*N*'-toluenesulfonylhydrazine under harsher conditions: M. S. Newman and I. Ungar, *J. Org. Chem.*, **27**, 1238 (1962).

(5) D. D. Sternbach, unpublished data from these laboratories.

(6) S. Schwartzman, unpublished data from these laboratories.

(7) K. V. Auwers and P. Heimke, *Justus Liebigs Ann Chem.*, **458**, 186 (1927).

(8) The data for $C_6H_5CONHN{=}CHCH{=}CH_2$ are as follows: NMR (CD_3CN,$CDCl_3$) δ 10.0 (broad s, 1 H), 7.98–7.30 (m, 6 H), 6.90–6.25 (m, 1 H), 5.76–5.66 (m, 1 H), 5.58–5.40 (m, 1 H); ir 3260, 3100, 1650, 1550 cm^{-1}; MS parent molecular ion *m/e* 174. Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.96; H, 5.93; N, 16.07.

(9) J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2574 (1957).

Regio- and Stereospecificity in the Addition of Hydrogen Bromide to Some Cyclic Allenes

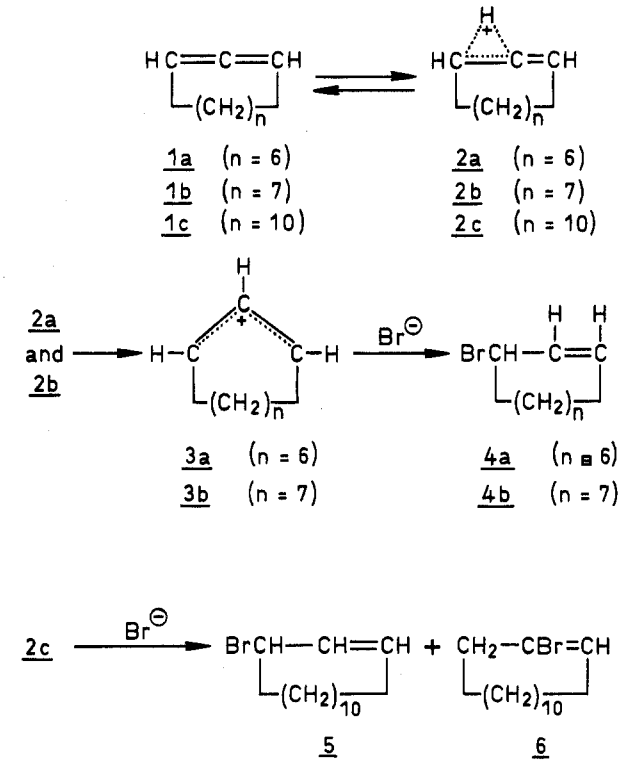
S. N. Moorthy, A. Singh, and D. Devaprabhakara*[1]

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

Received March 20, 1975

Addition of an unsymmetrical electrophilic reagent to an allenic bond is attractive as the system has more than one center for electrophilic attack. Many unsymmetrical electrophilic reagents such as hydrogen halides, water, mercuric acetate, 2,4-dinitrobenzenesulfenyl chloride, and organoboranes have been added to cyclic allenes.[2] However, the addition of hydrogen halides to cyclic allenes has not been systematically examined. Gardner et al.[3] have shown that hydrogen chloride gas adds to 1,2-cyclononadiene (**1a**) at −70° to form 3-chlorocyclononene. A similar regiospecificity has been observed in the addition of hydrogen bromide to **1a**.[4] Therefore, we thought that it would be interesting to examine the addition of hydrogen bromide to different cyclic allenes to know the effect of ring size on the regio- and stereospecificity of addition. We report here our work on the addition of hydrogen bromide to 1,2-cyclononadiene (**1a**), 1,2-cyclodecadiene (**1b**), and 1,2-cyclotridecadiene (**1c**) (Scheme I).

Scheme I



The addition of hydrogen bromide in acetic acid to 1,2-cyclononadiene (**1a**) in 1:1 mole ratio at ca. 20° gave only *cis*-3-bromocyclononene (**4a**) in 86% yield. Careful GLC analysis on a silicone rubber column indicated it to be pure. Its ir spectrum had absorptions at 2018, 1635, and 710 cm^{-1}. There was no ir absorption in the region 960 cm^{-1}, suggesting the cis configuration for the double bond. The NMR spectrum of **4a** showed two olefinic protons at δ 5.60, one methine proton at 5.00, and 12 methylene protons from 1.00 to 2.40 as multiplets. The identity was further confirmed by comparison of GLC retention times, ir, and NMR spectra with those of an authentic sample prepared from *cis*-cyclononene and *N*-bromosuccinimide.[5] Furthermore, the addition of deuterium bromide to **1a** gave *cis*-3-bromocyclononene-2-*d*. Its NMR spectrum exhibited one olefinic proton at δ 5.60, one methine proton at 5.00, and 12 methylene protons from 1.00 to 2.40. The mass spectrum showed characteristic molecular ion peaks of almost equal intensity at *m/e* 203 and 205. These results rule out the possibility of initial isomerization of **1a** to 1,3-cyclononadiene prior to addition to hydrogen bromide, and also suggest that the possible isomerization of the initially formed *trans*-3-bromocyclononene to the observed product, **4a**, is less likely. Finally, the addition of hydrogen bromide to **1a** was unaffected in the presence of a free radical inhibitor which excludes free radical addition.

In a similar manner, the addition of hydrogen bromide to 1,2-cyclodecadiene (**1b**) occurred to yield *cis*-3-bromocyclodecene (**4b**, 75%) as the sole product whose identity was established using an authentic sample prepared from *cis*-cyclodecene.[5] Hydrobromination of 1,2-cyclotridecadiene (**1c**), on the other hand, provided a mixture of 1-bromocyclotridecene (**5**) and 3-bromocyclotridecene (**6**), in a ratio 45:55. The regioisomers were separated by preparative GLC, and their structures secured by elemental analysis and comparison of GLC retention times and spectral properties with those of authentic samples.[5,6] Our attempts to separate the possible stereoisomers of **5** or **6** by GLC were not successful.

Our results demonstrate that hydrogen bromide addition to **1a** and **1b** is regiospecific as well as stereospecific, whereas the addition of **1c** is nonregiospecific. The most convincing rationale of our results is depicted in Scheme I. We suggest that **1a** or **1b** reacts with hydrogen bromide in a reversible process to form the corresponding unstable π-proton complex (**2a** or **2b**), which readily breaks up to form a planar resonance stabilized π-allylic cation (**3a** or **3b**). The addition of bromide anion to **3a** or **3b** can give rise to the observed allylic bromide (**4a** or **4b**) in each case. The stereospecificity observed can be explained as the cis configuration of **3a** or **3b** is much more stable than its trans configuration in a nine- or ten-membered ring. In the case of **1c** we argue that the π-proton complex (**2c**) is stable, and it is attacked by the nucleophile (Br^-) both at central and terminal centers to form 1-bromocyclotridecene (**5**) and 3-bromocyclotridecene (**6**), respectively. However, the possibility of the formation of the observed products (**5** and **6**) via nonplanar allylic and vinylic cations cannot be ruled out completely.

In conclusion, the reactions reported here represent the first example of change of orientation of hydrogen bromide addition with change in the ring size. The mode of addition of hydrogen bromide to strain-free 1,2-cyclotridecadiene (**1c**) resembles that of simple 1,3-disubstituted acyclic allenes.[7] We propose that the strain factor could be responsible for the observed difference in behavior of C-9 or C-10 as compared to C-13 allene in hydrogen bromide addition.

Experimental Section

All boiling points are uncorrected. Ir spectra were recorded on a Perkin-Elmer IR-137 using neat liquids. NMR spectra were recorded on a Varian Model A-60 NMR spectrometer relative to internal standard Me_4Si. The mass spectral measurements were performed by the Mass Spectrometry Laboratory, National Chemical Laboratory, Poona, India. The gas–liquid chromatography utilized a Varian Model 90-P gas chromatograph with a thermal conductivity detector. Elemental analyses were performed by the Microanalysis Laboratory, Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India.

General Procedure for the Addition of Hydrogen Bromide to Cyclic Allenes. The cyclic allene (0.05 mol) was taken in a three-necked round-bottomed flask and cooled to around 15–20° in a nitrogen atmosphere. Hydrogen bromide solution in acetic acid (40% w/v, 12.0 ml, 0.055 mol) was added dropwise with magnetic stirring over a period of 30 min. After the addition was over, it was allowed to stir for another 2 hr. The reaction mixture was poured into 200 ml of water, neutralized carefully with sodium bicarbonate, and extracted with petroleum ether (bp 40–60°). The combined extract was washed thoroughly with water and dried over anhydrous $MgSO_4$. Removal of solvent and distillation under vacuum gave the monobromo adduct.

Addition of Hydrogen Bromide to 1,2-Cyclononadiene. From 1,2-cyclononadiene (6.1 g, 0.05 mol) and hydrogen bromide (0.055 mol), there was obtained 8.8 g (86%) of *cis*-3-bromocyclononene: bp 87–88° (5 mm) [lit.[5] bp 34–35° (0.05 mm)]; ir (neat) 2018, 1635, and 710 cm^{-1}; NMR ($CDCl_3$) δ 5.60 (m, 2 H), 5.00 (br m, 1 H), and 1.00–2.40 (m, 12 H).

Anal. Calcd for $C_9H_{15}Br$: C, 53.20; H, 7.39. Found: C, 53.41; H, 7.21.

Addition of Deuterium Bromide to 1,2-Cyclononadiene. Following the general procedure, the treatment of 1,2-cyclononadiene (1.22 g, 0.01 mol) with deuterium bromide (0.012 mol) in acetic acid-*d* provided 1.5 g (74%) of 3-bromocyclononene-2-*d*: bp 90° (5 mm); ir (neat) 2020, 1636, and 712 cm^{-1}; NMR ($CDCl_3$) δ 5.60 (m, 1 H), 5.00 (br m, 1 H), and 1.00–2.40 (m, 12 H); mass spectrum *m/e* 203 and 205 (M^+) of almost equal intensity.

Addition of Hydrogen Bromide to 1,2-Cyclodecadiene. Treatment of 1,2-cyclodecadiene (6.8 g, 0.05 mol) with hydrogen bromide (0.055 mol) in acetic acid gave 8.0 g (75%) of *cis*-3-bromocyclodecene: bp 91–92° (5 mm) [lit.[5] bp 86–87° (3 mm)]; ir (neat) 2018, 1634, and 712 cm^{-1}; NMR ($CDCl_3$) δ 5.58 (m, 2 H), 5.00 (br m, 1 H), and 1.00–2.42 (m, 14 H).

Anal. Calcd for $C_{10}H_{17}Br$: C, 55.30; H, 7.83. Found: C, 55.13; H, 7.71.

Addition of Hydrogen Bromide to 1,2-Cyclotridecadiene. 1,2-Cyclotridecadiene (9.0 g, 0.05 mol) was treated with hydrogen bromide (0.055 mol) to yield 9.0 g (70%) of a mixture of 3-bromocyclotridecene and 1-bromocyclotridecene, bp 93–101° (1 mm). Careful GLC analysis (10% silicone rubber SE-30, 5 ft × 0.25 in., 100°, 30 ml/min N_2) of the reaction product showed two closely situated peaks having 1-bromocyclotridecene (shorter retention time) and 3-bromocyclotridecene in the ratio 45:55. The two components were separated by GLC and compared with authentic samples.[5,6]

An authentic sample of 3-bromocyclotridecene was prepared from cyclotridecene (cis and trans mixture) and *N*-bromosuccinimide:[5] ir (neat) 2014, 1636, 970, and 710 cm^{-1}; NMR ($CDCl_3$) δ 5.56 (m, 2 H), 4.96 (br m, 1 H), and 0.96–2.45 (m, 20 H). An authentic sample of 1-bromocyclotridecene was made by lithium aluminum hydride reduction of 2,3-dibromocyclotridecene:[6] ir (neat) 2016, 1636, 850, and 820 cm^{-1}; NMR ($CDCl_3$) δ 5.50 (t, J = 7.0 Hz, 1 H) and 0.98–2.54 (m, 22 H).

Anal. Calcd for $C_{13}H_{23}Br$: C, 60.23; H, 8.88. Found: C, 59.98; H, 8.50.

Registry No.—**1a,** 1123-11-1; **1b,** 4415-98-9; **1c,** 5601-67-2; **4a,** 33332-75-1; **4b,** 56412-17-0; **5,** 56412-18-1; **6,** 38916-95-9; hydrogen bromide, 10035-10-6; deuterium bromide, 13536-59-9; 3-bromocyclononene-2-*d*, 56412-19-2; *cis*-cyclotridecene, 2484-66-4; *trans*-cyclotridecene, 2484-65-3; 2,3-dibromocyclotridecene, 34833-29-9; *N*-bromosuccinimide, 128-08-5.

References and Notes

(1) Visiting Professor, Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India, 1974–1975. Address correspondence to author at the Indian Institute of Science.
(2) (a) M. C. Caserio in "Selective Organic Transformations", Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N.Y., 1970; (b) W. R. Moore, H. W. Anderson, and S. D. Clark, *J. Am. Chem. Soc.*, **95,** 835 (1973); (c) T. L. Jacobs and R. C. Kammerer, *ibid.*, **96,** 6213 (1974); (d) R. D. Bach and H. W. Holubka, *ibid.*, **96,** 7814 (1974).
(3) R. K. Sharma, B. A. Shoulder, and P. D. Gardner, *J. Org. Chem.*, **32,** 241 (1967).
(4) G. Nagendrappa, P. Mohanakrishnan, G. Mehta, and D. Devaprabhakara, *Chem. Ind. (London)*, 850 (1971).
(5) R. W. Fawcett and J. O. Harris, *J. Chem. Soc.*, 2673 (1954).
(6) J. Casanova and B. Wagell, *Bull. Soc. Chim. Fr.*, 2669 (1972).
(7) A. V. Fedorova, *J. Gen. Chem. USSR (Engl. Transl.)*, **33,** 3508 (1963).

Sodium Borohydride–Carboxylic Acid Systems. Useful Reagents for the Alkylation of Amines

Paolo Marchini, Gaetano Liso, and Antonia Reho

Istituto di Chimica Organica, Facoltà di Farmacia, Università di Bari, Bari, Italy

Felice Liberatore* and Franco Micheletti Moracci

Cattedra di Chimica Farmaceutica Applicata, Università di Roma, Roma, Italy

Received March 25, 1975

The recent paper by Gribble et al.[1] concerning the alkylation of aromatic amines with liquid carboxylic acids and sodium tetrahydroborate has prompted us to publish our own data on the same reaction, since they not only support the findings of the authors cited, but extend the scope of the reaction to the N-alkylation of amines with *solid* carboxylic acids, and provide further insight on the possible reaction pathway.

In the course of an investigation aimed at determining the reactivity of some 1,4-benzothiazines of structure **1**[2] we observed that their treatment with $NaBH_4$, in neat acetic acid as solvent, gave rise to the expected dihydro-1,4-benzothiazines **2** or to the corresponding *N*-ethyl derivatives **3** (R = CH_3) (Scheme I) depending on the amount of $NaBH_4$ added. The unexpected formation of *N*-alkyl derivatives prompted us to extend the reaction to a number of primary and secondary amines, both aliphatic and aromatic, and to