Experimental Section

Organometallic reagents were manipulated using standard procedures.[15] GLC analyses were carried out using an F & M Model 810 instrument and flame ionization detection, by unexceptional internal standard techniques. Butane and butene analyses utilized a 3-ft 3% Apiezon on alumina column; other analyses utilized an 8-ft 20% UC-W98 silicone rubber on Chromosorb P column. *n*-Hexane was purified by distillation under nitrogen from a suspension of sodium benzophenone ketyl. THF was distilled from $LiAlH_4$, and DME from disodium benzophenone dianion. TEMPO· was prepared by oxidation of TEMP with hydrogen peroxide catalyzed by sodium phosphotungstate;[6] it had mp 34–35° (lit.[6] mp 39°). Reagent dimethyl sulfate was purified by washing with cold saturated sodium bicarbonate solution and drying over potassium carbonate.[16] The dry solution was transferred to a Schlenk tube and traces of methanol were removed by a vacuum of 0.05 Torr. The dimethyl sulfate was stored in the Schlenk tube under prepurified nitrogen. It was reevacuated before use. Organolithium reagents were supplied by Foote Mineral Co., and were analyzed by the Gilman double titration method.[17]

***N*-Methoxy-2,2,6,6-tetramethylpiperidine (TEMPOCH$_3$).** DME (50 ml), 0.147 g (6.4 mg-atoms) of sodium metal, and 0.885 g (5.67 mmol) of freshly sublimed 2,2,6,6-tetramethylpiperidine nitroxyl were added to a flame-dried round-bottomed flask equipped with a condenser and a magnetic stirring bar and stoppered with a serum cap. The mixture was stirred under nitrogen at ambient temperature for 8 hr. Iodomethane (0.805 g, 5.67 mmol) was added to the resulting pale yellow solution of TEMPO$^-$Na$^+$, and the solution was stirred for an additional 4 hr under nitrogen. The reaction solution was saturated with sodium chloride, extracted with 50 ml of ether, and washed with distilled water and saturated sodium chloride solution. The ether was dried ($MgSO_4$) and concentrated to give a crude oil which was purified by column chromatography. The product was eluted from 6 g of silica gel G with 40 ml of cyclohexane followed by 40 ml of benzene, to give 0.4 g (41%) of *N*-methoxy-2,2,6,6-tetramethylpiperidine, having ir (CCl_4) 2980, 2930, 2810, 1475, 1385, 1355, 1060 cm^{-1}; NMR (CCl_4) δ 3.6 (s, 3 H, OCH_3), 1.0–1.5, multiplet (18 H); mass spectrum (70 eV) *m/e* (rel intensity) 171 (10.5), 156 (100), 88 (17), 69 (16), 55 (15), 41 (17).

***N*-Butoxy-2,2,6,6-tetramethylpiperidine (TEMPOBu).** The procedure for synthesizing TEMPOCH$_3$ was repeated using 1-iodobutane instead of 1-iodomethane, yielding 0.196 g (19%) of *N*-butoxy-2,2,6,6-tetramethylpiperidine, a colorless liquid, having ir (CCl_4) 2990, 2980, 2970, 2810, 1450, 1380, 1365, 1260, 1250, 1210, 1190, 1140, 1070, 1050 cm^{-1}. This ir spectrum was indistinguishable from that of TEMPOBu collected by GLC from a typical reaction of 2,2,6,6-tetramethylpiperidine and *n*-butyllithium. TEMPOBu had NMR (CCl_4) δ 3.6 (t, 2 H, J = 7 Hz, OCH_2–), 1.0–1.8 (m, 25 H).

Anal. Calcd for $C_{13}H_{27}NO$: C, 73.20; H, 12.74; N, 6.57. Found: C, 73.06; H, 12.62; N, 6.44.

Lithium 2,2,6,6-Tetramethylpiperidine Nitroxide. A solution of 0.03 g (0.192 mmol) of TEMPO· in 3 ml of DME was titrated to a colorless end point with 0.47 *M* lithium naphthalenide in DME, giving lithium 2,2,6,6-tetramethylpiperidine nitroxide and naphthalene. Hydrolysis of this solution afforded *N*-hydroxy-2,2,6,6-tetramethylpiperidine. Treatment with dimethyl sulfate yielded TEMPOCH$_3$ in quantitative yield.

Reaction between *n*-Butyllithium and 2,2,6,6-Tetramethylpiperidine Nitroxyl. Typical Procedure. Freshly sublimed TEMPO· (0.278 g, 1.8 mmol) and ca. 10 ml of *n*-hexane were added under nitrogen to a dry, stoppered, 40-ml centrifuge tube. *n*-Dodecane (104 mg) and *n*-pentane (28 mg) were added as internal GLC standards, and the solution was cooled to −78° in a Dry Ice–isopropyl alcohol bath. One milliliter of 1.60 *M* *n*-butyllithium was added to the mixture by syringe. When the reaction was complete, excess *n*-butyllithium was quenched with ca. 100 mg (0.535 mmol, 0.05 ml) of 1,2-dibromoethane. Five milliliters of the resulting solution was transferred to another dry centrifuge tube and hydrolyzed with 0.5 ml of distilled water. The remaining solution was treated with 0.2 ml (excess) of dimethyl sulfate, and shaken vigorously for 1 min. The products were analyzed by GLC. The hydrolyzed sample was used for butane, butene, and 2,2,6,6-tetramethylpiperidine analyses, the alkylated sample for all others. The results of this and similar reactions are summarized in Table I.

Registry No.—TEMPOCH$_3$, 34672-84-9; 2,2,6,6-tetramethylpiperidine nitroxyl (TEMPO), 2564-83-2; iodomethane, 74-88-4; TEMPOBu, 56514-19-3; 1-iodobutane, 542-69-8; *n*-butyllithium, 109-72-8.

References and Notes

(1) Supported by the National Science Foundation.
(2) E. G. Rozantsev, "Free Nitroxyl Radicals", Plenum Press, New York, N.Y., 1970; A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals", Academic Press, New York, N.Y., 1968.
(3) E. G. Rozantsev and V. D. Sholle, *Synthesis*, 190 (1971).
(4) E. G. Rozantsev and V. D. Sholle, *Synthesis*, 401 (1971).
(5) R. P. Mason, C. F. Polnaszek, and J. H. Freed, *J. Phys. Chem.*, **78**, 1324 (1974); R. P. Mason and J. H. Freed, *ibid.*, **78**, 1321 (1974); L. J. Berliner, *Prog. Bioorg. Chem.*, **3**, 1 (1974); P. Jost, A. S. Waggoner, and O. H. Griffith in "Structure and Function of Biological Membranes", L. J. Rothfield, Ed., Academic Press, New York, N.Y., 1971, p 83; H. M. McConnell and B. G. McFarland, *Q. Rev. Biophys.*, **3**, 91 (1970).
(6) R. Briere, H. Lemaire, and A. Russat, *Bull. Soc. Chim. Fr.*, **11**, 3273 (1965).
(7) K. Marugama, *Bull. Chem. Soc., Jpn.*, **37**, 1013 (1964); A. Rieker, *Angew. Chem., Int. Ed. Engl.*, **3**, 654 (1964); A. Rieker, E. Müller, and W. Beckert, *Z. Naturforsch. B*, **17**, 718 (1962); K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions", Wiley, New York, N.Y., 1971; G. M. Whitesides and J. San Filippo, Jr., *J. Am. Chem. Soc.*, **92**, 6611 (1970); J. F. Garst in "Free Radicals", Vol. I, J. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 9; A. G. Davies and B. P. Roberts, *ibid.*, Chapter 10.
(8) G. M. Whitesides, D. E. Bergbreiter, and P. E. Kendall, *J. Am. Chem. Soc.*, **96**, 2806 (1974).
(9) The extent of aggregation of neophyllithium influences the products of its reaction with molecular oxygen: E. J. Panek and G. M. Whitesides, *J. Am. Chem. Soc.*, **94**, 8768 (1972).
(10) C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, **77**, 6032 (1955); G. A. Razuvaev, V. A. Shushunov, V. A. Dodonov, and T. G. Brilkina in "Organic Peroxides", Vol. 3, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1972; T. G. Brilkina and V. A. Shushunov, "Reactions of Organometallic Compounds with Oxygen and Peroxides", Iliffe Books, London, 1969.
(11) W. A. Nugent, F. Bertini, and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 4945 (1974), and references cited therein.
(12) The photolysis of azoethane in *n*-heptane yields ethane, ethylene, and butane in relative yields 4:1:6 [S. Kodama, S. Fujita, J. Takeshita, and O. Toryama, *Bull. Chem. Soc. Jpn.*, **39**, 1009 (1966)]. See also W. E. Morganroth and J. G. Calvert, *J. Am. Chem. Soc.*, **88**, 5387 (1966); P. S. Dixon, A. P. Stefani, and M. Szwarc, *ibid.*, **85**, 2551 (1963); A. P. Stefani, *ibid.*, **90**, 1694 (1968); R. A. Sheldon and J. K. Kochi, *ibid.*, **92**, 4395 (1970); M. J. Giban and R. C. Corley, *Chem. Rev.*, **73**, 441 (1973).
(13) K. S. Chen, F. Bertini, and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 1340 (1973).
(14) Other methods of destroying nitroxyl radicals have been reported: cf. ref 4, and H. Alper, *J. Org. Chem.*, **38**, 1417 (1973); C. M. Paleos, N. M. Karayannis, and M. M. Labes, *Chem. Commun.*, 195 (1970); N. Kornblum and H. W. Pinnick, *J. Org. Chem.*, **37**, 2050 (1972); J. F. W. Keana, R. J. Dinerstein, and F. Baitis, *ibid.*, **36**, 209 (1971).
(15) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969, Chapter 7.
(16) A. I. Vogel, "Practical Organic Chemistry", Longmans, Green and Co., New York, N.Y., 1962, p 804.
(17) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Am. Chem. Soc.*, **93**, 1379 (1971); H. Gilman, F. K. Cartledge, and S.-Y. Sim, *J. Organomet. Chem.*, **1**, 8 (1963).

A Mild Oxidation of Alkyl Halides to Aldehyde Derivatives

James B. Hendrickson* and Daniel D. Sternbach

Edison Chemical Laboratories, Brandeis University, Waltham, Massachusetts 02154

Received May 29, 1975

There have been several reports of the oxidation of alkyl halides to ketones or aldehydes.[1] None of these methods offer the direct conversion of an alkyl halide to a protected aldehyde (ketone). This type of transformation has synthetic utility especially in the case of labile aldehydes.

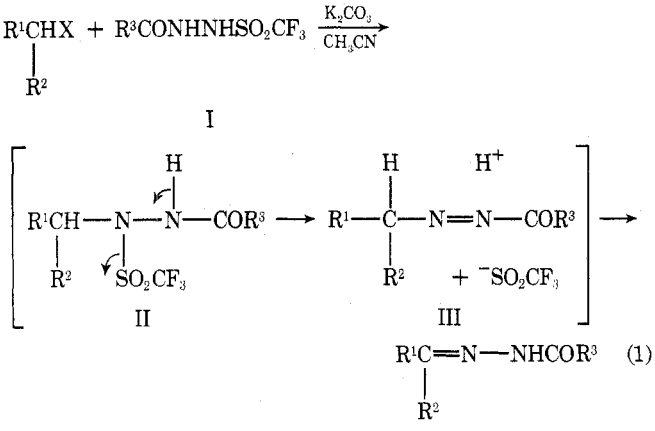
Hydrazones have not been widely used for protection of aldehydes or ketones,[2] probably owing to the widespread belief that they are difficult to cleave. Recently, however, several methods of mild hydrolytic cleavage for hydrazones and substituted hydrazones have been developed,[2,3] making the use of this group a viable means of carbonyl protection.

In this communication we wish to report a high-yield synthesis of acyl hydrazones from alkyl halides. This reac-

Table I
Acylhydrazone Synthesis

Alkyl halide	Registry no.	Temp, time	Yield of hydrazone derivative of		Mp, °C	Authentic sample mp,[a] °C
		A. From $C_6H_5CONHNHSO_2CF_3$[d]				
$C_6H_5CH_2Br$	100-39-0	Room temp, overnight	90%	C_6H_5CHO	210–212	207–208
C_2H_5I	75-03-6	Reflux, overnight	96%	CH_3CHO	159–162	162
$C_6H_5CHBrCH_3$	585-71-7	Reflux, 48 hr	70%	$C_6H_5COCH_3$	152–153	153
$C_6H_5(CH_2)_3ONs$	56572-24-8	Room temp, 48 hr	87%	$C_6H_5(CH_2)_2CHO$	119–121	119–120
$CH_2=CHCH_2Br$	106-95-6	Room temp, overnight	86%	$CH_2=CHCHO$	146–148	175–177[b]
c-$C_6H_{11}OTs$	953-91-3	No reaction				
		B. From $(CH_3)_3COCONHNHSO_2CF_3$[e]				
$C_6H_5CH_2Br$		Room temp, 48 hr	85%	C_6H_5CHO	184–185	185–186
$C_6H_5CHBrCH_3$		Room temp, 48 hr	43%	$C_6H_5COCH_3$	168–169	169–170
C_2H_5I		Room temp, 48 hr	96%	CH_3CHO	Oil	Oil
$C_6H_5(CH_2)_3Br$	637-59-2	60°, 42 hr[c]	80%	$C_6H_5(CH_2)_2CHO$	135–137	139–140

[a] Authentic samples were prepared from the corresponding aldehyde (ketone) and $C_6H_5CONHNH_2$ or $(CH_3)_3COCONHNH_2$. [b] There is some doubt as to whether this value is correct. On repeating the literature procedure[7] with $C_6H_5CONHNH_2$ and freshly distilled acrolein a compound that melted at 165–168° was isolated. The NMR spectrum of this compound showed no absorptions in the olefin region whereas the compound we prepared from I and allyl bromide exhibited satisfactory elemental analysis (C, H, N) and spectral data (NMR, ir, MS).[8] [c] A catalytic amount of KI was added. [d] Registry no., 41804-90-4. [e] Registry no., 56572-25-9.



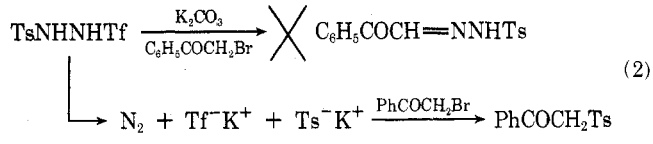
(1)

tion involves the alkylation of an *N*-acyl-*N'*-trifylhydrazine, subsequent elimination of triflinate ($SO_2CF_3^-$), and tautomerization to an acylhydrazone (eq 1).[4] The alkylation appears to be the rate-limiting step, for neither the alkylated trifyl hydrazide (II) nor the alkyl acyl azo compound (III) could be isolated. The hydrazone formation is postulated to occur by elimination of triflinate via removal of the amide N–H followed by tautomerization, rather than by the direct cleavage of the C–H bond, since alkylated triflamides without relatively acidic β hydrogen fail to undergo triflinate elimination even under more vigorous conditions [e.g., PhN(Tf)-*n*-Bu is unreactive even on treatment with *tert*-butyllithium in refluxing benzene[5]].

The reaction proceeds at room temperature for activated primary halides or unactivated nosylates, but requires refluxing and KI catalysis for unactivated primary halides or activated secondary halides. The reaction does not occur with unactivated secondary halides. Examples demonstrating the scope of the reaction are collected in Table I.

Tertiary-butoxycarbonyl (*t*-BOC) protected hydrazones are also available in good yield by this route (Table I). These compounds are potentially useful in forming specific alkyl hydrazones (N-alkylation followed by *t*-BOC removal[6]), mixed azines (*t*-BOC removal in the presence of another carbonyl compound), or other hydrazone derivatives.

Analogous attempts to form tosylhydrazones by alkylating TsNHNHTf were unsuccessful (eq 2). Apparently elimination of toluenesulfinate occurred faster than alkylation



(2)

of the triflamide, for only toluene sulfones were isolated (formed by alkylation of Ts^-); however, tosylhydrazones are potentially available from the *t*-BOC protected hydrazones.

Our examination of two representative acyl substituents [i.e., C_6H_5CO–, $(CH_3)_3COCO$–] indicates that the reaction is probably amenable to the synthesis of a wide variety of acylhydrazones under mild conditions.

Experimental Section

All melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian Model A-60A spectrometer. Ir spectra were recorded on a Perkin-Elmer Infracord, Model 137 spectrophotometer. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. The CH_3CN was distilled from CaH_2 and stored over 3 Å molecular sieves. Anhydrous K_2CO_3 was activated before each use by heating over a Fisher burner for 0.5 hr.

***N*-Benzoyl-*N'*-trifylhydrazine.** Benzoylhydrazine (Aldrich) (5.44 g, 0.04 mol) was added portionwise to a solution of triflic anhydride[9] (5.64 g, 0.02 mol) in methylene chloride (150 ml) at −78°, with stirring. The reaction mixture was allowed to warm to room temperature and stirred for an additional 1 hr, then evaporated in vacuo, taken up in ether, and filtered and the ether was evaporated in vacuo to yield 5.00 g (93%) of a white solid which melted at 156–158°. An analytically pure sample (sublimed at 140°, 60 μ) melted at 159–160°: ir (KBr) 2.95 m, 3.30 m, 6.00 s, 8.13–8.29 μ s (three absorptions); NMR (CD_3CN) δ 9.22 (s, 1 H), 7.94–7.49 (m, 6 H).

Anal. Calcd for $C_8H_7F_3N_2O_3S$: C, 35.83; H, 2.63. Found: C, 35.91; H, 2.70.

***N*-*tert*-Butoxycarbonyl-*N'*-trifylhydrazine.** Triflic anhydride (5.64 g, 20.0 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a solution of *tert*-butyl carbazate (Aldrich) (2.64 g, 20.0 mmol) and triethylamine (2.22 g, 22.0 mmol) in CH_2Cl_2 (100 ml) at −78° with stirring. The reaction mixture was allowed to warm to room temperature and stirred for a total of 2 hr, then washed twice with H_2O, once with 5% HCl, and once with H_2O and dried (Na_2SO_4) and the solvent was evaporated in vacuo. This residue crystallized on cooling (0°) overnight. Two recrystallizations from CH_2Cl_2–hexane afforded 2.67 g (50%) of colorless crystals: mp 92–94°; ir (KBr) 2.84 m, 3.03 m, 5.74 s, 7.20 s, 8.12 s, 8.28 s, 8.63 μ s; NMR ($CDCl_3$) δ 7.99 (broad s, 1 H), 6.94 (broad s, 1 H), 1.47 (s, 9 H).

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

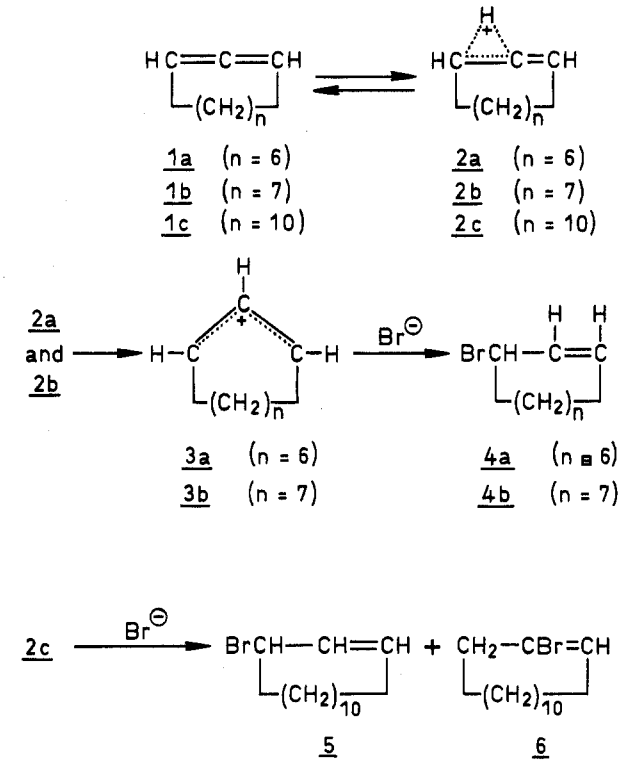
S. N. Moorthy, A. Singh, and D. Devaprabhakara*[1]

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.