Synthesis and Nuclear Magnetic Resonance Spectra of Some 1-Halo-1-iodoalkanes

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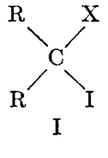
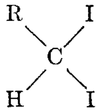
The previously unknown symmetrical dihalides 1,1-diiodopropane and 1,1-diiodo-2-methylpropane, have been synthesized by treatment of the corresponding diazoalkane with iodine. The new asymmetrical dihalides, 1-chloro-1-iodopropane and 1-bromo-1-iodopropane, have been obtained by halodecarboxylation of α-chlorobutyric and α-bromobutyric acid, respectively, with lead tetraacetate in the presence of iodine. Nmr spectral data for these and other geminal dihalides are presented and discussed.

An examination of the literature will reveal the paucity of simple geminal dihaloalkanes of the general formula I.


I

The dihalides, CH_2IX, CH_3CHIX, and $(CH_3)_2CIX$, in which X = Cl, Br, or I, have long been known, but the homologous propylidene compounds, CH_3CH_2CHIX and higher 1,1-dihaloalkanes containing iodine, have been notably absent. Recently we became aware of this situation when we wished to prepare 1,1-diiodopropane ($CH_3CH_2CHI_2$) and 1,1-diiodo-2-methylpropane [$(CH_3)_2CHCHI_2$] for another study. Subsequently, we decided that it would also be desirable to obtain the mixed 1,1-dihalogenated members of the propylidene series: 1-chloro-1-iodopropane and 1-bromo-1-iodopropane. These compounds have been prepared and the synthetic methods which appear to have general applicability for compounds of this type are reported here.

1,1-Diiodoalkanes.—We have synthesized the geminal diiodoalkanes II, in which R = CH_3–, CH_3CH_2–,


II

and $(CH_3)_2CH$–, by treating the corresponding diazoalkane with iodine as shown in reaction 1.[1] Presumably, the diazoalkanes could have been generated by any of a number of methods, but we found it convenient to utilize the alkyl nitrosourea method commonly used to obtain diazomethane.[2,3] Yields of the diiodides ranged from 27 to 37% based on the nitrosourea.[4] Although the yields were low, the desired dihaloalkanes were essentially the only products obtained after solvent evaporation. The major side reactions probably involved decomposition of the diazoalkanes to give volatile hydrocarbon products.

$$RCHN_2 + I_2 \longrightarrow RCHI_2 + N_2 \qquad (1)$$

The compounds, 1,1-diiodopropane and 1,1-diiodo-2-methylpropane, have been characterized by microanalytical data, spectral data, and physical properties. The identity of the known 1,1-diiodoethane[5] has been confirmed chiefly by spectral data.

1-Halo-1-iodoalkanes.—Treatment of α-bromo- or α-chlorobutyric acid with lead tetraacetate and iodine under strong illumination gave 1-bromo-1-iodopropane and 1-chloro-1-iodopropane, respectively.[6] The major side reaction in these syntheses appeared to be ester formation. The side products were removed by column chromatography on silica gel and the pure dihalopropanes were subsequently obtained by preparative vapor phase chromatography (vpc) in 18 and 12% yield based on starting α-halo acid. It was estimated by vpc analysis of the crude reaction mixture that 1-chloro-1-iodopropane had been originally formed in about 50% yield.

In addition to these mixed dihalopropanes, we synthesized the known compound, 1-chloro-1-iodoethane, and characterized it by comparison with an authentic sample prepared by addition of hydrogen iodide to vinyl chloride.[7] The unknown mixed dihalopropanes have been characterized by microanalytical data, spectral data, and physical properties.[8]

We have also prepared 1,1-diiodopropane, but only in trace amounts, by reaction of α-iodobutyric acid with iodine and lead tetraacetate in carbon tetrachloride.[9,10]

Nmr Spectral Correlations.—The nmr spectral data for these and some related compounds have been collected in Table I. The spectra were recorded using neat samples containing tetramethylsilane as the internal standard. An examination of the data for the three dihalopropanes and two dihaloethanes containing at least one iodine atom shows that the expected[11] upfield shift in the –CHIY proton resonance occurs as the second halogen (Y) is varied in the series Cl, Br, and I. Similarly, a comparison of the resonance signals for the $-CHI_2$ and $-CHCl_2$ protons in the dihalopropane and dihaloethane series shows the same expected upfield

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[1] (a) See R. C. Neuman, Jr., *Tetrahedron Letters*, 2541 (1964); (b) see H. V. Pechmann and P. Mank, *Ber.*, **28**, 2374 (1895).

[2] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp 165, 461.

[3] After our preliminary report appeared,[1] an identical synthesis of diazopropane was reported: J. R. Dyer, R. B. Randall, and H. M. Deutsch, *J. Org. Chem.*, **29**, 3423 (1964).

[4] It has been reported that diazopropane is formed in 52% yield from N-propyl-N-nitrosourea.[3] This suggests that the yields of the diiodides in the last step of the synthesis could be on the order of 50–70%.

[5] M. Berthelot, *Ann. Chem.*, **132**, 122 (1864).

[6] See D. H. R. Barton, H. P. Faro, E. P. Serebryakov, and N. F. Woolsey, *J. Chem. Soc.*, 2438 (1965).

[7] M. S. Kharasch and C. W. Hannum, *J. Am. Chem. Soc.*, **56**, 712 (1934).

[8] (a) The compound 1-bromo-1-iodopropane has been reported;[8b] however, no experimental details relating to identification except the constants, $n^{20}D$ 1.583 and bp 61.3° (20 mm), were provided. (b) M. S. Kharasch, J. A. Norton, and F. R. Mayo, *ibid.*, **62**, 81 (1940).

[9] (a) We also attempted to halodecarboxylate α-iodobutyric acid with lead tetraacetate in the presence of calcium chloride;[9b] however, no 1-chloro-1-iodopropane was isolated. (b) J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 2500 (1965); *J. Org. Chem.*, **30**, 3265 (1965).

[10] Preliminary experiments have indicated that reaction of diazopropane and iodine monochloride yields 1-chloro-1-iodopropane and 1,1-diiodopropane. This reaction is being further investigated.

[11] L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," The Macmillan Co., New York, N. Y., 1959, pp 59–60.

TABLE I

NMR SPECTRAL DATA FOR SOME 1,1-DIHALOALKANES[a]

		Chemical shift, cps[b,c]			J, cps	
			CH_3CH_2CHXY			
X	Y	-CH-	-CH$_2$-	-CH$_3$	(CH, CH$_2$)	(CH, CH$_3$)
I	I	312.5	145.0	59.5	6.0	7.0
I	Br	336.0	144.5	63.0	6.0	7.0
I	Cl	347.5	137.0	63.5	6.0	7.0
Cl	Cl	342.5	131.0	66.0	6.0	7.0
			$(CH_3)_2CH\beta CH\alpha XY$			
		-CHα-	-CHβ-	-CH$_3$-	(α, β)	(β, CH$_3$)
I	I	318.0	95.5	59.5	3.0	6.0
			CH_3CHXY			
		-CH-	-CH$_3$		(CH, CH$_3$)	
I	I	314.5	177.5		7.0	
I	Cl	354.0	147.5		6.5	
Cl	Cl	353.5	121.0		6.0	

[a] No solvent; ambient temperature; Varian A-60 spectrometer. [b] Shifts are downfield from internal tetramethylsilane. [c] Integrated peak areas agreed with the assignments.

shift in going from chlorine to iodine. However, the relative shifts of the –CHICl and –CHCl$_2$ resonance signals in both the propane and ethane series seem anomalous. These results may be explained by a "swamping" effect of the strongly deshielding chlorine atom. Electron withdrawal by a second halogen atom would be expected to become increasingly more difficult as the first halogen is varied in the series I, Br, Cl, and F. Thus, when one halogen is the relatively strong electron-withdrawing chlorine atom, the nature of the second halogen may make little difference in the shift of the α-proton signal,[11,12] and this seems to occur here.

Experimental Section

1,1-Diiodopropane.—A solution of 20 g of potassium hydroxide in 30 ml of water, and 150 ml of reagent grade benzene were placed in a 500-ml erlenmeyer flask (carefully fire polished) clamped securely in an ice bath. *All subsequent operations were cautiously carried out behind a safety shield.*[13] The heterogeneous solution was stirred magnetically using a Teflon-covered stirring bar while small portions of a 13-g (0.1-mole) sample of N-propyl-N-nitrosourea[2,3] were added at a rate such that unreacted solid nitrosourea in the reaction mixture was held to a minimum. After addition was completed, the dark orange benzene layer was slowly decanted into another fire-polished 500-ml erlenmeyer flask (immersed in an ice bath) containing a layer of potassium hydroxide pellets under cold benzene. Transfer of the aqueous layer and also a small amount of suspended solid present in the reaction vessel was avoided. The residual diazopropane solution in the reaction flask was quenched with acetic acid. The main solution of diazopropane was decanted from the potassium hydroxide pellets after about 3 min into another 500-ml erlenmeyer flask (immersed in an ice bath) containing a Teflon-covered stirring bar under cold benzene. Again the residual diazopropane solution was quenched with acetic acid. To the stirred diazopropane solution was then added rapidly a previously prepared solution of 20 g of iodine in 300 ml of benzene until the iodine color persisted in the reaction vessel. Stirring was continued until gas evolution ceased. The benzene solution was washed with two portions of aqueous soldium bisulfite solution and two portions of water, dried (magnesium sulfate), and evaporated, yielding 11.6 g (37%) of 1,1-diiodopropane contaminated by a trace of benzene (nmr). A sample was distilled in a microdistillation apparatus: apparent bp 78–80° (10 mm), $n^{25.6}D$ 1.6412, $d^{23}{}_4$ 2.52, nmr data in text.

Anal. Calcd for $C_3H_6I_2$ (295.90): C, 12.18; H, 2.04; I, 85.78. Found: C, 12.33, 12.31; H, 2.06, 1.97; I, 86.0, 86.4.

1,1-Diiodo-2-methylpropane.—This compound was synthesized analogously beginning with N-(2-methylpropyl)-N-nitrosourea:[14] yield 30%, apparent bp 85–88° (8 mm), $n^{25.1}D$ 1.6188, $d^{23}{}_4$ 2.34, nmr data in text.

Anal. Calcd for $C_4H_8I_2$ (309.92): C, 15.50; H, 2.60; I, 81.90. Found: C, 15.72, 15.75; H, 2.57, 2.59; I, 83.3, 83.7.

1,1-Diiodoethane.—This compound was synthesized analogously beginning with N-ethyl-N-nitrosourea:[14] yield 30%, apparent bp 79° (20 mm), $n^{26.3}D$ 1.6684, $d^{23}{}_4$ 2.80 (lit.[15] bp 60–61° (12 mm), $n^{20}D$ 1.673; lit.[16] $d^{23}{}_4$ 2.84), nmr data in text.

1-Chloro-1-iodopropane.—A 6.1-g (0.05-mole) sample of α-chlorobutyric acid, 23 g (0.05 mole) of lead tetraacetate,[17] and 100 ml of carbon tetrachloride were placed in a 250-ml flask fitted with a nitrogen inlet tube and a small Soxhlet extractor (80 × 25 mm thimble). A 10-g sample of iodine was placed in the extractor shell and the extractor–condenser outlet was fitted with a Bunsen valve. The reaction mixture was purged with nitrogen for 5 min with stirring. The nitrogen flow was decreased and the solution was heated to reflux with simultaneous illumination from a 300-w tungsten lamp. The reflux rate was adjusted so that a portion of the carbon tetrachloride–iodine solution was added every 4 min. Within this period, all of the iodine added was consumed. The reflux rate was decreased as the reaction proceeded and heating was stopped when added iodine was no longer decolorized. The required reaction time was 0.5 to 1 hr. The cooled carbon tetrachloride layer was decanted from the resultant insoluble lead diacetate, washed with sodium bicarbonate solution and water, dried (magnesium sulfate), and concentrated on a rotary evaporator at room temperature. An infrared spectrum of the resultant solution showed a strong ester carbonyl band at 5.7 μ. Elution on silica gel allowed several fractions to be collected which were free of the impurity. After concentration of these fractions using a rotary evaporator and purification by preparative vpc using a 2.5 ft × 0.25 in. column (1% SE-30 on 60–80 glass beads) at 75°, a 1.2-g (12%) sample of 1-chloro-1-iodopropane was obtained: $n^{25.8}D$ 1.534, $d^{23}{}_4$ 1.90, nmr data in text.

Anal. Calcd for C_3H_6ClI (204.45): C, 17.62; H, 2.96; Cl, 17.34; I, 62.07. Found: C, 17.42, 17.33; H, 2.97, 2.95; Cl, 16.5, 18.1;[18] I, 62.78.

1-Bromo-1-iodopropane.—This compound was synthesized analogously beginning with α-bromobutyric acid: yield (analytically pure material) 18%, $n^{26.0}D$ 1.573, $d^{23}{}_4$ 2.28, nmr data in text.

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(12) Plots of the nmr data given in Table 4.11 of ref 11 for the three series: CH_2IY (Y = I, Cl), CH_2Y_2 (Y = I, Br, Cl), and CH_2ClY (Y = I, Br, Cl), show the same trends.

(13) No preparation of a diazoalkane has exploded during these syntheses. However, we have not allowed this fact to make us overconfident. These preparations have never been scaled up. The photoinstability of diazoalkanes prompted us to work in a darkened room. The highly toxic nature of diazoalkanes and the potential toxicity of nitrosureas should also be realized.

(14) Syntheses of all N-alkyl-N-nitrosoureas were accomplished as reported for the propyl compound. The intermediate N-2-methylpropylurea precipitated during the synthesis of the nitrosourea.

(15) L. Kahovec and J. Wagner, *Z. Phys. Chem.*, [B] **47**, 53 (1940).

(16) Gustavson, *Ber.*, **7**, 731 (1874).

(17) L. Fieser and M. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., pp 325–326.

Anal. Calcd for C_3H_6BrI (248.90): C, 14.48; H, 2.43; Br, 32.11; I, 50.99. Found: C, 14.55, 14.94, 14.74; H, 2.45, 2.53, 2.47; Br, 33.4;[18] I, 50.61, 50.65.

1-Chloro-1-iodoethane.—This compound was synthesized analogously beginning with α-chloropropionic acid: yield 21%, nmr data in text. Identified by spectral comparison with an authentic sample prepared by the addition of hydrogen iodide to vinyl chloride.[7]

Acknowledgment.—Support by the National Science Foundation is gratefully acknowledged.

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[18] These data were obtained from the difference of a total halide determination and the specific iodine analysis assuming the identity of the second halogen atom.

Direct Fluorination.[1] Addition of Fluorine to Indenes and Acenaphthylenes

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Direct addition of F_2 to olefins at −78° has been shown to produce vicinal difluorides in good yields. Vicinal F-F coupling constants exhibit an angular dependence similar to H-H and H-F coupling constants.

The addition of molecular fluorine to simple unsubstituted olefins as a preparative procedure for vicinal difluorides has received little attention. Additions to perhalo olefins,[2a] vinyl acetate,[2b] and diethyl fumarate[2c] have been successful. It seemed possible that the large heat of reaction could be removed by working at low temperature and thereby eliminating the usual problems of charring, substitution, etc., usually associated with elemental fluorine.

In view of our interest in the synthetic utilization of reactive reagents such as OF_2,[3] which could be completely controlled at −78°, a similar procedure was adopted for pure undiluted fluorine. It was found that direct addition of fluorine will occur in good yield at −78° and that the process is of synthetic utility for the preparation of certain vicinal difluorides.

Experimental Section

Materials.—The fluorine was obtained from Allied Chemical Corp. and passed through a sodium fluoride HF scrubber prior to use. The 2-methylindene[4a] and 1-methylacenaphthylene[4b] were prepared according to established procedures. The physical properties and spectral characteristics were in agreement with those of the original authors. Freon 11 (CCl_3F) and 4A Molecular Sieve[5] were carefully dried before use. The indene was carefully fractionated and stored under nitrogen. The acenaphthylene was used as received from Aldrich Chemical Co.

Apparatus.—The fluorination reactor and auxilliary equipment were constructed entirely of Pyrex with the exception of stirring vanes, which were of Teflon. The reactor was a cylindrical vessel (30 × 300 mm) fitted with a side arm and a topmounted magnetically driven stirrer. The inner magnet was sealed with Pyrex to avoid exposure to fluorine. The stirrer was driven with standard magnetic driving assembly used for spinning-band columns. The reactor was separated from the fluorine reservoir (usually 1 l.) by a single stopcock which was used to meter the flow of fluorine. Manometers were placed on both the reactor and reservoir side of the stopcock to monitor the course of the addition. Kel-F 40 grease[6] was used as stopcock lubricant and Kel-F[10] oil[6] was used to protect the mercury manometers. The fluorine reservoir was loaded just prior to use from a standard remote fluorine-handling facility.

Procedure.—The olefin was diluted tenfold with Freon 11 (CCl_3F), and slurried with an equal weight (to olefin) of finely ground anhydrous 4A Molecular Sieve.[5] The mixture was vigorously stirred, cooled to −78°, and thoroughly degassed. The fluorine was slowly metered into the reactor above the stirred solution in such a manner as to keep the pressure of fluorine below 50 mm. The exact stoichiometric amount of fluorine could be controlled by varying the volume or pressure of the reservoir bulb. The uptake of fluorine was usually complete to within the vapor pressure of Freon 11 at −78° (~3 mm).

1,2-Difluoro-2-methylindan.—2-Methylindene (2.60 g, 20 mmoles) was fluorinated at −78° in the manner described above with 20 mmoles of fluorine. The uptake of fluorine was smooth and complete within 2 hr. The fluorine partial pressure never exceeded 50 mm at any time. The solvent was distilled away leaving a colorless oil which rapidly darkened upon exposure to air. Rapid low temperature[7] elution on anhydrous silica gel at 15° produced 0.94 g of *trans*-1,2-difluoro-3-methylindan. Continued elution with 3:1 pentane-methylene chloride afforded 0.51 g of *cis*-1,2-difluoro-2-methylindan. Both isomers decomposed when vacuum distilled. The complete spectral properties are listed in the discussion along with assignment of structure.

Anal. Calcd for $C_{10}H_{10}F_2$: C, 71.41; H, 5.99. Found for *cis:* C, 71.33; H, 6.20. Found for *trans:* C, 70.81; H, 6.36.

1,2-Difluorindan.—Indene (5.1 g, 44 mmoles) was fluorinated at −78° with 45 mmoles of fluorine within 1 hr. The partial pressure of fluorine in the reactor was maintained below 50 mm. Removal of solvent produced the adduct as a colorless oil which was immediately chromatographed on silica gel. The difluoride (2.0 g, 29% yield) was eluted with a 1:1 pentane-methylene chloride mixture. No evidence of the other isomer was indicated by fluorine nmr of the crude product before chromatography. Spontaneous decomposition of a purified sample was noted after standing for 10 days at 25°.

Anal. Calcd for $C_9H_8F_2$: C, 70.12; H, 5.23. Found: C, 69.74; H, 4.98.

1,2-Difluoroacenaphthene.—The olefin (6.0 g, 39 mmoles) was fluorinated in a manner described above at −78° with 44 mmoles of F_2. Care was taken to ensure that the partial pressure of F_2 was maintained below 40 mm. Upon removal of the solvent the colorless oil was immediately chromatographed at 15° on anhydrous silica gel with 4:1 pentane-methylene chloride. The first fractions contained 0.82 g (11% yield) of *trans*-1,2-difluoroacenaphthene, mp 40.5-42.5°. This fraction was contaminated with 1,1,2-trifluoroacenaphthene which proved impossible to remove completely.

Continued elution with 4:1 pentane-methylene chloride afforded 2.60 g (35% yield) of *cis*-1,2-difluoroacenaphthene, mp 105° (petroleum ether, bp 60-80°). Spectral details are discussed in the results section.

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[1] This work was sponsored under Army Ordnance Contract DA-01-021 ORD-11878 (Z) Modification No. 15.

[2] (a) W. T. Miller, J. O. Stoffer, G. Fuller, and A. C. Currie, *J. Am. Chem. Soc.*, **86**, 51 (1964). (b) A. Yu. Yakubovich, S. M. Rozenshtein, and V. A. Ginsberg, U.S.S.R. Patent 162,825; *Chem. Abstr.*, **62**, 451*g* (1965). (c) A. Y. Yakubovich, V. A. Ginsberg, S. M. Rozenshtein, and S. M. Smirnov, U.S.S.R. Patent 165,162; *Chem. Abstr.*, **62**, 9018*g* (1965).

[3] R. F. Merritt and J. K. Ruff, *J. Am. Chem. Soc.*, **86**, 1392 (1964); *J. Org. Chem.*, **30**, 328 (1965).

[4] (a) E. R. Alexander and A. Mudrak, *J. Am. Chem. Soc.*, **73**, 59 (1951). (b) L. Fieser and J. Cason, *ibid.*, **62**, 432 (1940).

[5] Trademark of Union Carbide Corp.

[6] Trademark of Minnesota Mining and Manufacturing Co. The grease must be thoroughly purged of unsaturated volatile impurities by heating at 125° at 0.01 mm for 12 hr.

[7] All elution chromatographic columns were fitted with water jackets through which coolant was passed during the separations.