Dipole Moment and Structure Assignments of *cis*- and *trans*-Chloroiodoethene

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Received April 5, 1971

Van de Walle and Henne[1] prepared the geometric isomers of chloroiodoethene by absorption of acetylene gas by a solution of ICl in aqueous HCl. The isomers were resolved as azeotropic components by fractionally distilling the product mixture with an equal weight of 1-propanol. Their structural assignments were based on the relative rates of dehydrohalogenation with alcoholic KOH. Since trans elimination is faster than cis,[2] the faster isomer was assigned *cis*-chloroiodoethene (*i.e.*, hydrogen and iodine trans). The physical properties of the isomers (Table I) are consistent with this structural assignment. However, dielectric constants (ϵ) and dipole moments ($\bar{\mu}$) reported by Errera[3] are anomalous with respect to the Van Arkel dipole rule[4] (Table II) (*i.e.*, the isomer with the higher dipole moment has the higher value for each physical property).

TABLE I
PHYSICAL PROPERTIES OF CHLOROIODOETHENE[1]

	Trans	Cis
Bp of propanol azeotrope, °C	87.5–88.5	93.6–94.0
Bp, °C	113–114	116–117
Fp, °C	−41.0	−36.4
d^{0}_{4}	2.1355	2.2399
d^{15}_{4}	2.1048	2.2080
n_D	1.57146	1.58288
Rel reaction rate with KOH	0.55	1.00

TABLE II
DIELECTRIC PROPERTIES OF CHLOROIODOETHENE OF ERRERA[3]

	Trans	Cis
ϵ	2.95	2.72
$\bar{\mu}$, D	1.27	0.57

In view of the electronegativity of chlorine and iodine, one would expect the dipole moment of the cis isomer to be greater than that of the corresponding trans isomer. This anomaly could be explained on the grounds that iodine may be electron donating rather than withdrawing. However, as pointed out by Eliel,[5] this seems unlikely in view of the fact that the dipole moment of *p*-chloroiodobenzene closely corresponds to the difference of the dipole moments of chlorobenzene and iodobenzene rather than the sum of these moments. It would seem that either the structures or the dipole moments of the chloroiodoethene isomers have been misassigned.

Both isomers were prepared in our laboratory by iodination of *cis*- and *trans*-chlorovinylmercuric chloride[6] and by the direct addition of iodine monochloride to acetylene.[1] Structure assignments were made from a study of the ir C–H out-of-plane bending frequencies and in particular, the nmr AB coupling constants. A second-order analysis of the AB spectra of the high- and low-boiling isomers of chloroiodoethene shows $J_{AB} = 5.8$ and 13.5 Hz, respectively. The molecular spectra clearly confirm the original dehydrohalogenation kinetic assignments of Van de Walle and Henne[1] (Table I). The spectral data also enable us to conclude that the iodination of chlorovinylmercuric chloride proceeds with retention of configuration. The dipole moments of the *trans*-chloroiodoethene in benzene and cyclohexane are 0.549 ± 0.006 and 0.519 ± 0.006 D, respectively. Since these values agree in magnitude with the moment Errera[3] reported for the cis isomer (Table II), we conclude that the measurements were assigned to the wrong isomer.

Experimental Section

Measurements.—Thin layer chromatograms were obtained on silica gel G with methanol solvent using iodine vapor for detection. Vapor phase chromatograms were recorded with a Perkin-Elmer 154L vapor fractometer equipped with a 3 mm × 1.53 m column of 8% di-*n*-nonyl phthalate on 90–100 mesh Ankron ABS with a helium flow rate of 20 ml/min and column temperature of 115°. Ultraviolet spectra were obtained with a Beckman Model DBG spectrophotometer. Infrared spectra were measured with a Perkin-Elmer 337 spectrometer. The nmr spectra were recorded with Varian Models A-56/60 and A-60 spectrometers. Mass spectra were obtained with a Consolidated Electrodynamic Corp. CEC 21-104 spectrometer. Gc–mass spectra were recorded on a Finnigan Corp. Series 3000 system at 70 eV. The dipole moments were obtained from dielectric measurements made with a dielectrometer constructed in our laboratory. This instrument utilizes a circuit similar to that developed by Chien.[7] A Model 2TN20LV dielectric cell (purchased from Balsbaugh Laboratories, Duxbury, Mass.) was modified so that samples could be transferred into or out of the cell without disassembling or moving it. All dielectric constant measurements were made in cyclohexane or benzene at 25.00 ± 0.05°. Density measurements were made with a Sartorius Model 2743 balance and a 25-ml volumetric flask. The dipole moments were calculated from a least-squares analysis of dielectric and density data by the Hedestrand procedure,[8] ignoring atomic polarizations.

Materials.—Reagent grade benzene, cyclohexane, and *p*-xylene were purified by conventional methods.[9] Dielectric solvents were stored over type 4A molecular sieve under nitrogen in brown bottles and were distilled weekly. Analytical grade diethyl ether was purchased from Eastman Organic Chemicals. Iodine monochloride was purchased from Alfa Inorganics. The propanol, benzoyl peroxide, cadmium iodide, iodine, iodine monochloride, and mercuric chloride were Baker Analyzed reagent grade. Acetylene was purchased from local suppliers and scrubbed with a 30% solution of $HgCl_2$ in aqueous HCl.

The isomers of chloroiodoethene were prepared by two independent methods, I and II.

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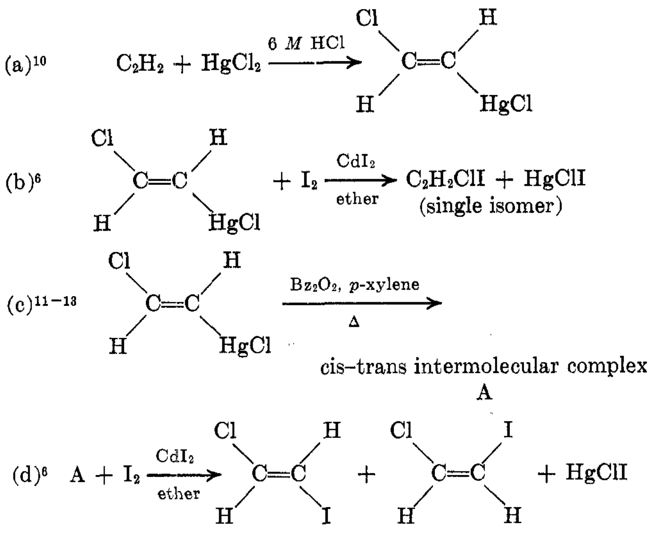
Method I



trans-**2-Chlorovinylmercuric Chloride (Ia).**[10]—The product was recrystallized from chloroform: mp 122° (lit.[12] 123°); tlc R_f 0.52; uv max (EtOH) 212 nm (lit.[14] 212 nm); ir (KBr pellet) 3050–3100 (CH), 1570 (C═C), 940 cm^{-1} (CH, trans).

trans-**Chloroiodoethene (Ib).**[6]—The product was vacuum distilled from HgClI and CdI_2: bp 113° (755 mm) (lit.[1] 113–114° (760 mm) (trans), 116–117° (cis)]; vpc retention time 1.12 min; ir (KBr) 3080 (CH), 1545 (C═C), 1600 and 1630 (Fermi resonance of the C═C fundamental at 1545 and the first overtone of the strong band at 797), 902 cm^{-1} (CH, trans); nmr (acetone-d_6, TMS) δ 6.57 ppm (AB, δ^0 10.7 Hz, J_{AB} = 13.5 Hz); mass spectrum *m/e* 188 ($C_2H_2ClI^+$) with prominent P + 2 at 190, characteristic of Cl, 61 (base), and 63 ($C_2H_2Cl^+$).

Cis–Trans Intermolecular Complex of Chlorovinylmercuric Chloride (Ic).[11-13]—*trans*-Chlorovinylmercuric chloride was isomerized in dry *p*-xylene with benzoyl peroxide catalyst at 95° for 10 hr. The hot mixture was filtered. The filtrate was cooled to give (75%) the complex (A) which was recrystallized from CCl_4: mp 74.5° (lit.[11,13] 76°); tlc R_f 0.73; uv max (EtOH) 211 nm; ir (KBr pellet) 3000–3075 (CH), 1585 (C═C), 930 (CH trans), and 692 cm^{-1} (CH, *cis*); nmr spectrum is identical with that reported by Wells and Kitching.[12]

cis- **and** *trans*-**Chloroiodoethene (Id).**[6]—The iodination of the intermolecular mercury complex (A) was carried out by a modification of the method of Beletskaya, Reutov, and Karpov.[6] Ten grams of the complex (A) and 8.40 g (0.0331 mol) of I_2 with 0.5 g of CdI_2 catalyst were stirred for 36 hr in 100 ml of diethyl ether. After removing the ether by distillation, the reaction mixture was treated with an equal volume of 1-propanol, and the azeotropic mixture of the *cis*- and *trans*-chloroiodoethene was resolved by distillation on a spinning-band column. The 87.5–88.5° fraction was found to contain the trans isomer, with properties identical with those of the product of Ib. The 93.6–94.0° fraction contained the cis isomer: vpc retention time 1.36 min; nmr (acetone-d_6, TMS) δ 6.81 ppm (AB, δ^0 4.4 Hz, J_{AB} = 5.8 Hz); gc–mass spectrum is identical with the spectrum of the trans isomer. The preparation was not sufficiently pure for ir or dielectric measurements.

Method II[1]

$$C_2H_2 + ICl \xrightarrow{6\,M\ HCl} C_2H_2ClI + \text{other products}$$

A mixture of *cis*- and *trans*-chloroiodoethene was prepared by the direct addition of iodine monochloride to acetylene as described by Van de Walle and Henne.[1] The vpc retention times, nmr AB spectra, and gc–mass spectra of the cis and trans isomers were found to be identical with those of the products of reactions Ib and Id.

The dielectric constant and density data used for the calculation of the dipole moment of *trans*-chloroiodoethene in benzene and cyclohexane are summarized in Table III.

TABLE III
DIELECTRIC CONSTANT AND DENSITY OF *trans*-CHLOROIODOETHENE

Benzene			Cyclohexane		
N_2	d	ϵ	N_2	d	ϵ
0.00980	0.8781	2.280	0.01088	0.7826	2.036
0.01429	0.8831	2.282	0.01443	0.7851	2.039
0.02037	0.8906	2.286	0.02011	0.7922	2.042
0.03080	0.9027	2.290	0.03066	0.8034	2.048
0.03630	0.9095	2.293	0.04107	0.8148	2.054

Benzene: $\alpha = 0.469, \beta = 1.19$; $P_{2\infty} = 35.0$ CC; $\epsilon_1 = 2.276, d_1 = 0.8663$

Cyclohexane: $\alpha = 0.580, \beta = 1.08$; $P_{2\infty} = 35.0$ CC; $\epsilon_1 = 2.030, d_1 = 0.7703$

Registry No.—*trans*-2-Chlorovinylmercuric chloride, 1190-78-9; *trans*-chloroiodoethene, 28540-81-0; *cis*-chloroiodoethene, 31952-74-6.

Acknowledgment.—This research was supported by the Council for Faculty Research, Eastern Illinois University.

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O-Triphenylmethylhydroxylamine (Trityloxyamine), a Useful O-Protected Form of Hydroxylamine

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Received June 23, 1971

In connection with other work, a protected form of hydroxylamine was required in which substitution would be rigorously restricted to the nitrogen atom and which would be soluble in aprotic solvents.[1] It was also necessary that the protecting group be readily cleaved under mild acidic conditions. This report describes the preparation and some properties of *O*-triphenylmethylhydroxylamine (trityloxyamine), $(C_6H_5)_3CONH_2$, an O-protected hydroxylamine which fulfills these requirements.

Acylation of the amine function of hydroxylamine does not usually require protection of the hydroxyl group. The conditions under which such reactions are usually carried out give the *N*-acyl derivative as the only isolable product. Jencks[2] has described a number of cases, however, wherein certain acylating agents under controlled conditions can give high yields of the *O*-acyl derivative. Evidently, *O*-acylhydroxylamines are often the initial product. Unless the conditions of the reaction and work-up are carefully controlled, rearrangement to the more stable *N*-acyl form occurs.

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(1) The preparation of solutions of free hydroxyamine of appreciable concentration usually requires the use of aqueous or alcoholic solvents due to the polar characteristics of hydroxylamine and the salts from which it is usually prepared.

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