before the pK_a measurements were made. The fractions collected for pK_a measurements boiled over less than a 1° range.

Dimethylaminoacetonitrile. A commercial sample of glycolonitrile was cooled to 0° in a heavy walled flask and saturated with dimethylamine. The latter was generated by dropping a concentrated aqueous solution of the hydrochloride onto pellets of sodium hydroxide. After the flask was tightly stoppered, it was removed from the ice bath and allowed to warm up to room temperature. On standing for 4 to 6 hr. the reaction mixture was fractionally distilled. The product boiled at 135–136° at atmospheric pressure.

β-Aminopropionitrile. Four hundred milliliters of an ice cold 28% aqueous solution of ammonia and 100 ml. of ice cold acrylonitrile were mixed in a heavy walled liter flask. After the flask was securely stoppered, it was allowed to warm up and remain at room temperature for several days. It was then fractionally distilled under reduced pressure. The product boiled at 89°/23 mm. Aminoacetonitrile polymerizes quite rapidly so that it was titrated immediately after preparation.

Measurements of pK_a values. The amine solutions titrated were between 0.05 and 0.10 molar. Hydrochloric acid ($0.183M$) was used as the titrant. The equivalence point was taken at the maximum $\frac{d(pH)}{d(ml)}$ from the titration curves. Activity coefficients were taken at unity so that the $pK_a = pH$ at half neutralization. The pH measurements were made with a Beckmann pH meter, industrial model, using glass and saturated calomel electrodes at 29 ± 1°. A conservative estimate of the total error involved in these measurements is 0.1 pK_a unit in the cases of cyanamide and diethylcyanamide. For the other compounds it is closer to 0.05 pK_a unit.

Acknowledgment. We are indebted to the American Cyanamid Co., New York, N. Y., for gifts of the following chemicals: cyanamide, diethylcyanamide, β-isopropylaminopropionitrile, β-dimethylaminopropionitrile, and β,β′-dicyanodiethylamine.

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Chlorination of 1,1-Difluoro-2,2-dichloroethane

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Received July 25, 1957

Henne and Ladd[1] reported that photochemical chlorination of 1,1-dichloro-2,2-difluoroethane (I) at room temperature yields, as the only monochlorination product, 1,1-difluoro-2,2,2-trichloroethane (II). Since the other possible monochlorination product, 1,1-difluoro-1,2,2-trichloroethane (III), and II should have nearly identical boiling points, Henne and Ladd[1] characterized their product by dehalogenation with zinc, wherefrom only 1-fluoro-2,2-dichloroethylene (IV) (b.p. 35°) was isolated.

$$\underset{\text{I}}{CHF_2CHCl_2} + Cl_2 \xrightarrow{h\nu} \underset{\text{II}}{CHF_2CCl_3}$$

$$\underset{\text{II}}{CHF_2CCl_3} + Zn \longrightarrow \underset{\text{IV}}{CHF{=}CCl_2}$$

The photochemical chlorination of spectroscopically pure I, prepared by the method of Swarts,[2] was recently carried out in this laboratory using a procedure similar to that of Henne and Ladd.[1] The chlorination apparatus described by Muskat and Northrup[3] was used wherein the reaction mixture was heated under reflux (60–70°) and the chlorine was introduced into the vapor between the reflux condenser and the reflux boiler. A General Electric Photoflood No. RFL2 was used as the light source.

The monochlorination product (b.p. 72°) was separated by distillation and subjected to mass spectrometric and infrared analyses. The mass spectrum of pure III, prepared after Henne and Ladd[1] by fluorination of pentachloroethane with antimony trifluoride, was available. Henne and Ladd established the structure of III by zinc dehalogenation, which gave 2-chloro-1,1-difluoroethylene (V) (b.p. −17°). A quantitative comparison of the spectrum of pure III with that of the monochlorination product of I revealed that the latter contained 56 mole % III.[4] The remainder was assumed to be II, as there was no evidence for the presence of I or 1,1-difluoro-1,2,2,2-tetrachloroethane (VI). Thus, approximately equivalent amounts of the two isomers were produced and the reactivities of the two hydrogens of I were approximately equal at the reaction temperature (60–70°). These results will necessitate a slight modification of the theory advanced by Hauptschein and Bigelow.[6]

$$CCl_3CHCl_2 \xrightarrow{SbF_3} \underset{\text{III}}{CF_2ClCHCl_2}$$

$$\underset{\text{III}}{CF_2ClCHCl_2} + Zn \longrightarrow \underset{\text{V}}{CF_2{=}CHCl}$$

The mass spectrometric analysis was carried out at a high potential so that considerable bond rupture occurred. Table I gives a comparison of the major peaks in the mass spectra of pure I, III, and VI with the monochlorination product of I. The strong peaks of the mixture at m/e = 83, 85, and 87 are due to III, whereas those at m/e = 51, 117, 119, 133, and 135 are due to II. The peaks at m/e

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(1) A. L. Henne and E. C. Ladd, *J. Am. Chem. Soc.*, **58**, 402 (1936).

(2) F. Swarts, *Chem. Zent.*, **I**, 13 (1903).

(3) I. E. Muskat and H. E. Northrup, *J. Am. Chem. Soc.*, **52**, 4043 (1930).

(4) A discussion of the factors involved and the methods of quantitative analysis by mass spectrometer has been given by Barnard.[5]

(5) G. P. Barnard, *Modern Mass Spectrometry*, The Institute of Physics, London, 1953, chapter 7.

(6) M. Hauptschein and L. A. Bigelow, *J. Am. Chem. Soc.*, **73**, 5591 (1951).

TABLE I

Comparison of Mass Spectra

m/e	CF_2HCHCl_2[a] I	$CF_2ClCHCl_2$[a] III	CF_2ClCCl_3[b] VI	Mixture	Ion	Expected for[c] CHF_2CCl_3
51	16.3	0.6	0.09	10.2	CHF_2^+	1
82	1.6	2.0	27.6	6.0	CCl_2^+	s
83	100.0	100.0	0.4	100.0	$CHCl_2^+$	—
84	1.7	2.4	17.7	4.9	CCl_2^+	s
85	64.3	77.4	43.4	74.9	$CHCl_2^+$ CF_2Cl^+	—
87	10.5	14.4	13.8	13.7	$CHCl_2^+$ CF_2Cl^+	—
117	1.6	0.41	100.0	26.1	CCl_3^+	1
119	0.3	0.25	94.9	24.2	CCl_3^+	1
121	—	0.08	30.5	7.6	CCl_3^+	1
132	0.1	0.6	14.6	1.1	$C_2F_2Cl^+$	s
133	2.7	19.2	0.36	46.7	$C_2F_2HCl_2^+$	1
134	21.5	0.75	9.4	3.9	$C_2H_2F_2Cl_2^+$ $C_2F_2Cl_2^+$	s
135	2.1	12.1	0.19	29.6	$C_2HF_2Cl_2^+$	1
136	13.6	0.3	1.5	2.0	$C_2F_2HCl_2^+$ $C_2F_2Cl_2^+$	s
167	—	0.02	97.9	4.0	$C_2F_2Cl_3^+$	s
169	—	0.06	93.6	4.0	$C_2F_2Cl_3^+$	s
171	—	0.04	29.8	1.3	$C_2F_2Cl_3^+$	s

[a] Peak strength relative to m/e at 83 = 100. [b] Peak strength relative to m/e at 117 = 100. [c] "1" indicates a major peak predicted, "s" a minor peak predicted.

= 133 and 135 particularly indicate the presence of II.

The infrared spectrum of the mixture confirmed the presence of III and indicated the presence of another compound which was neither I nor VI. The weak peaks at m/e = 134, 136, 167, 169, and 171 in the mass spectrum of the mixture could be due to small amounts of I and VI in the mixture. However, as is indicated in Table I, all of the fragments could be derived from II so there is no reason to assume, by necessity, that I or VI are present. Conversely, there is no reason to assume that I and VI are entirely absent either.

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Synthesis and Configuration of *cis*-8-Methylhydrindane

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Received August 1, 1957

In connection with the determination of the skeletal structure of picrotoxinin we have described a synthesis of DL-*cis*-5-isopropyl-8-methylhydrin-4,6-diene (picrotoxadiene);[3] we now wish to detail the observations made in a repetition of part of this synthesis with optically active materials. Although an extension of this work will make possible the assignment of absolute configuration in the picrotoxin series the results herein are sufficient to allow such assignment for an important reference compound, *cis*-8-methylhydrindane, as well as some of its ketonic derivatives.

Cis-2-methyl-2-carboxycyclopentane-1-acetic acid (I),[4] prepared *via* 2-methyl-2-carbethoxycyclopentylidenecyanoacetic ester,[3,5] was resolved with the aid of its brucine salt; after twenty-one recrystallizations of this salt from water the rotation ($[\alpha]_D^{21}$ +37°) of the regenerated acid showed no further increase. Partially resolved (−) acid was obtained from the mother liquors. The remaining transformations (to IX) indicated in the diagram were carried out in a manner similar to that described previously for the corresponding racemic series; the compounds were characterized by their infrared spectra, in all cases identical with those of the racemic series. The optically active bicyclic hydrocarbon (X) was prepared from IX by the Huang-Minlon modification of the Wolff-Kishner reduction.

The assignment of the *cis* configuration in this series has rested on the obtention by Errington and

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[2] Present address: Lederle Laboratories, Pearl River, N. Y. Abstracted from the Ph.D. Thesis of Elliott Cohen, Columbia University, 1956.

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