revision of Rossini's "best" combustion values[15] in terms of the presently accepted atomic weights and Jessup's corrected result[16] for the heat of combustion of the benzoic acid standard. The value for *n*-butyraldehyde was then deduced from this butyl alcohol datum on the assumption that Kistiakowsky's result[17] for the heat of dehydrogenation of ethyl alcohol to acetaldehyde can also be applied to the corresponding four-carbon compounds. In this latter case the heats of vaporization of the *n*-butyl alcohol and aldehyde were taken as 11.80 kcal.[15] and 7.90 kcal.,[18] respectively. Unfortunately, complete thermal data were not available for an analogous calculation in the case of *n*-heptaldehyde.

In general, the free energies so derived are probably reliable to within 0.08 kcal. per carbon atom, although in the case of *n*-butyraldehyde the error may possibly be twice this latter figure. While we shall not now resort to a detailed discussion of these results, it is noteworthy that the average change in molal free energy per $CH_2$ increment is here 1.43 kcal. in going from *n*-butyl alcohol to liquid cetyl alcohol as against a value of 1.21 kcal. previously found in the series of liquid normal paraffins.[9] It is also interesting to observe the difference of 7.33 kcal. in the molal free energies of *n*-butyraldehyde and methyl ethyl ketone, which is certainly real although one might intuitively expect approximately equal free energies for such isomers. Likewise, a comparison of these values for the several alcohols with those for the parent hydrocarbons[11] demonstrates that the introduction of the hydroxyl group produces an average lowering of 35 kcal. in the molal free energy for the production of a primary alcohol as against about 39 kcal. in the formation of the secondary alcohol, cyclopentanol.

STANFORD, CALIFORNIA

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[15] F. D. Rossini, *J. Research Natl. Bur. Standards*, **13**, 189 (1934).

[16] R. S. Jessup, *ibid.*, **36**, 421 (1946).

[17] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, THIS JOURNAL, **60**, 440 (1938).

[18] C. B. Longsworth, an unpublished research in the Stanford Laboratory.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

# The Preparation and Properties of Trifluoroiodoethene[1]

BY J. D. PARK, R. J. SEFFL[2] AND J. R. LACHER

RECEIVED JUNE 30, 1955

The preparation of perfluorovinyl iodide and its reaction with ethylene, vinyl fluoride, vinylidene fluoride, trifluoroethane 1,1-difluoro-2,2-dichloroethene and 1,1-difluoro-2-chloroethene is described and the structures of the resultant butenes are discussed. It has been found that the attacking perfluorovinyl free radical attaches itself to the variously substituted ethylenic carbon atoms in the order $CH_2 > \begin{matrix}CFH\\CHCl\end{matrix} > CF_2 > \begin{matrix}CCl_2\\CFI\end{matrix}$. The preparation of some fluorinated butadienes is described.

The new perfluorovinyl iodide has been synthesized from commercially available starting material. The first step in the synthesis involves the addition of hydrogen bromide to 1,1,2-trifluoro-2-chloroethene,[3] dehalogenation to trifluoroethene followed by reaction with iodine monochloride to give 1,1,2-trifluoro-1-chloro-2-iodoethane (I). This result is in accord with the observation by Haszeldine[4] that the negative substituent (in this case $Cl^-$) becomes attached to the $CF_2$ group in the molecule.

$CF_2{=}CFI$ (II) is prepared from I by treatment in a suspension of powdered potassium hydroxide in mineral oil. This particular medium was used rather than the traditional alcoholic potassium hydroxide since II reacts readily with alcoholic alkali to form ethers. The ultraviolet absorption spectrum of II shows a distinct band with the maximum at 258 mμ. This band is characteristic of aliphatic fluorinated iodides and Haszeldine[5] reports that the exact position of the band is dependent on the nature of the molecule.

## Free Radical Reactions of Perfluorovinyl Iodide—The Preparation of Some Fluorinated Butadienes

Perfluorovinyl iodide will react with other olefins such as ethylene, vinyl fluoride, vinylidene fluoride and trifluoroethene to form a linear 1:1 addition product in the presence of ultraviolet light as

$$CF_2{=}CFI + CX_2{=}CHX \longrightarrow CF_2{=}CFCHXCX_2I$$

where $X = H$ or F.

In accordance with a general mechanism as proposed by Haszeldine,[6] we propose the following mechanism for the reaction

$$\text{Initiation: } CF_2{=}CFI \longrightarrow CF_2{=}CF\cdot + I\cdot \quad (1)$$

$$\text{Propagation: } CF_2{=}CF\cdot + CX_2{=}CHX \longrightarrow CF_2CFCHXCX_2\cdot \quad (2)$$

$$\text{Chain transfer: } CF_2{=}CFCHXCX_2\cdot + CF_2{=}CFI \longrightarrow CF_2CFCHXCX_2I + CF_2{=}CF\cdot \quad (3)$$

It is to be noted that in step (1) the formation of a perfluorovinyl free radical is suggested. The existence of such a free radical has little precedent in the literature. With regard to other vinyl free radicals it is noted that Tickner and co-workers[7a,b]

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[1] Abstracted from a thesis by R. J. Seffl, submitted to the Graduate School of the University of Colorado in partial fulfillment of the requirements for the degree Doctor of Philosophy, June, 1954. Presented before the Fluorine Subdivision of the Division of Industrial and Engineering Chemistry, 126th Meeting of the American Chemical Society, N. Y. C., Sept. 12–17, 1954.

[2] E. I. du Pont Predoctoral Fellow in Chemistry, 1953–1954.

[3] J. D. Park, W. R. Lycan and J. R. Lacher, THIS JOURNAL, **73**, 711 (1951).

[4] R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952).

[5] R. N. Haszeldine, *ibid.*, 1764, 3761 (1953).

[6] R. N. Haszeldine, *ibid.*, 2856 (1949); **167**, 39 (1951); *Nature*, **165**, 152 (1950); *J. Chem. Soc.*, 3037 (1951).

[7] (a) A. W. Tickner, J. W. Hodgins and D. J. Leroy, *Can. J. Research*, **B26**, 619 (1948); (b) A. W. Tickner and D. J. Leroy, *J. Chem. Phys.*, **19**, 1247 (1951).

obtained the free radical $CH_2{=}CH\cdot$ from vinyl bromide and vinyl iodide and recently Lindsey and Ingraham[8] have postulated the intermediate formation of a cyclohexenyl free radical.

In step (2) of the reaction mechanism the attack by the free radical is upon the CXH group rather than the $CX_2$ group of the ethene. Haszeldine[9] in a study of the direction of addition of trifluoroiodomethane to unsymmetrical olefins has observed that the attacking free radical will go first to a $CH_2$ group, then to a CFH and finally to a $CF_2$ group. This order of addition has also been substantiated by Tarrant.[10] Accordingly, the addition products with vinyl fluoride, vinylidene fluoride and trifluoroethene should have the following structures: $CF_2{=}CFCH_2CHFI$ (III), $CF_2{=}CFCH_2CF_2I$ (IV) and $CF_2{=}CFCFHCF_2I$ (V). Further evidence of the structures as listed above is given by the fact that each of the above butenes reacted with potassium hydroxide to yield the respective butadiene. If the structures for IV and V were other than those written above, the dehydroiodination reaction could not have taken place.

When II was subjected to ultraviolet irradiation, a dimeric product containing iodine was formed. The presence of unsaturation in the product eliminated the possibility of the cyclic dimer, namely, 1,2-diiodo-1,2,3,3,4,4-hexafluorocyclobutane. The only other possible products from the reaction are 4,4-diiodoperfluorobutene-1 (VI) and 3,4-diiodoperfluorobutene-1 (VII). Since the product obtained did not react with zinc to form perfluorobutadiene, the dimer must have been the *gem*-diiodide (VI). This result is in agreement with work by Haszeldine,[11] Miller[12] and Henne[13] who showed that the attacking trifluoromethyl free radical will become attached to a $CF_2$ group in preference to a CFCl group.

The reaction of perfluorovinyl iodide with 1,1-difluoro-2,2-dichloroethylene and 1,1-difluoro-2-chloroethylene yielded 1,1,2,3,3-pentafluoro-4,4-dichloro-4-iodobutene-1 (VIII) and 1,1,2,4,4-pentafluoro-3-chloro-4-iodo-butene-1 (IX).

In summarizing, it has been found that an attacking perfluorovinyl free radical attaches itself to the variously substituted ethylenic carbon atoms in the following order: $CH_2 > CFH,CHCl > CF_2 > CFI,CCl_2$.

The utilization of the previously discussed free radical addition type of reaction has resulted in the preparation of the following butadienes: 1,1,2-trifluorobutadiene, 1,1,2,4-tetrafluorobutadiene, 1,1,-2,4,4-pentafluorobutadiene and hexafluorobutadiene.

## Experimental[14]

$CF_2Br{-}CFHCl$ and $CF_2{=}CFH$ were prepared by procedures previously reported.[3]

**Addition of Iodine Monochloride to Trifluoroethene.**—The addition of iodine monochloride to trifluoroethene was carried out in a high pressure autoclave under autogenous pressure. The reaction products were washed with 5% sodium bisulfite to remove any iodine or iodine monochloride, then with water, and dried over calcium sulfate. The product was distilled in a Vigreux column to give 170 g. of product boiling between 76.5 and 77.5° at 630 mm. Conversion to 1,1,2-trifluoro-1-chloro-2-iodoethane (I) was found to be 72%; molecular weight determinations by the Regnault method (calcd. for $C_2F_3HClI$: mol. wt. 244, found, 238) and molar refraction values (calcd., 29.10: found, 29.10).

*Anal.* Calcd. for $C_2F_3HClI$; C, 9.8; F, 23.3. Found: C, 9.9; F, 23.1.

The correctness of the structure assigned to I was further established by its conversion to perfluorovinyl iodide. This compound has physical properties entirely different from chlorotrifluoroethene which would have resulted had the iodine monochloride adduct been the 1,1,2-trifluoro-2-chloro-1-iodoethane isomer.

**Perfluorovinyl Iodide** ($CF_2{=}CFI$) (II).—The dehydrochlorination of I was carried out in a 200-ml. three-neck flask equipped with stirrer, dropping funnel and reflux condenser. The effluent gases from the reflux condenser were collected in a solid carbon dioxide–acetone cooled trap. About 48 g. (0.197 mole) of I was added dropwise to a suspension of 28 g. (0.5 mole) of powdered potassium hydroxide in 45 ml. of mineral oil under vigorous agitation. The mineral oil was maintained at 95° and the condenser heated to 35° to permit removal of the olefin from the reaction mixture. Stirring and heating were continued for four hours after the addition of I was completed to ensure complete removal of the olefin. The products obtained were transferred to a micro-distillation apparatus and distilled. The product II, distilled at 27.5 to 28.5° at 627 mm. and the conversion, based on starting materials was 76%. Physical properties and molar refraction values are given in Table I. The infrared spectrum displayed the presence of a C=C bond at 5.66 $\mu$.

*Anal.* Calcd. for $C_2F_3I$: C, 11.6; F, 27.4; mol. wt., 208. Found: C, 11.7; F, 27.2; mol. wt., 207.

**Preparation of Halogenated Butenes by the Reaction of Variously Substituted Ethylenes with** II.—The free radical addition reactions were carried out in a 5-l. Pyrex flask which was sealed off at the neck and fitted with a stopcock to permit the introduction and removal of the reactants and products. The ultraviolet light source was a Hanovia EH4 mercury arc tube and the reaction time in all cases was for a period of seven days.

In a typical reaction 21 g. (0.10 mole) of II and 4.2 g. (0.15 mole) of ethylene were charged to the reactor and irradiated for seven days. At the end of this period a liquid product highly colored with iodine was obtained. This crude product, 23 g., was distilled ina Metroware column. The product, 16.2 g. (67% of theory) distilled at 112° at 623 mm. and gave a positive test for unsaturation with potassium permanganate solution.

*Anal.* Calcd. for $C_4F_3H_4I$: C, 20.3; F, 24.5; mol. wt., 236. Found: C, 20.3; F, 24.7; mol. wt. (Regnault method), 229.

The following reactions were carried out in an analogous manner with the conversions as noted

$$CF_2{=}CFI + CH_2{=}CFH \longrightarrow CF_2{=}CFCH_2CFHI \quad \text{(III)} \quad 50\%$$

$$CF_2{=}CFI + CH_2{=}CF_2 \longrightarrow CF_2{=}CFCH_2CF_2I \quad \text{(IV)} \quad 24\%$$

$$CF_2{=}CFI + CF_2{=}CFH \longrightarrow CF_2{=}CFCFHCF_2I \quad \text{(V)} \quad 39\%$$

$$2CF_2{=}CFI \longrightarrow CF_2{=}CFCF_2CFI_2 \quad \text{(VI)} \quad 50\%$$

$$CF_2{=}CFI + CF_2{=}CHCl \longrightarrow CF_2{=}CFCHClCF_2I \quad \text{(IX)} \quad 4\%$$

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(8) R. V. Lindsey and J. N. Ingraham, THIS JOURNAL, **75**, 5613 (1953).

(9) R. N. Haszeldine, *J. Chem. Soc.*, 2504 (1952); 1199, 1592, 3565 (1953); R. N. Haszeldine, Abstracts of 112th Meeting of the American Chemical Society, Chicago, Illinois (September 1953), p. 35M.

(10) P. Tarrant and A. M. Lovelace, THIS JOURNAL, **77**, 768 (1955).

(11) R. N. Haszeldine and B. R. Steele, *Chemistry and Industry*, 684 (1951).

(12) W. T. Miller, Jr., and J. M. Howald, Abstracts of 122nd Meeting of the American Chemical Society, Atlantic City, N. J. (September, 1952), p. 12K.

(13) A. L. Henne and D. W. Kraus, THIS JOURNAL, **76**, 1175 (1954).

(14) All boiling points are uncorrected.

TABLE I

PHYSICAL PROPERTIES OF COMPOUNDS PREPARED

| Compound | Mol. wt. | B.p. °C. | B.p. Mm. | $n^{20}_D$ | $d^{20}_4$ | $MR_{obs.}$ | $MR_{calcd.}$ | $AR_F$ obsd. | $MR_{obsd.}$ | Analyses, % Carbon Calcd. | Analyses, % Carbon Found | Analyses, % Fluorine Calcd. | Analyses, % Fluorine Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CF_2ClCFHI$ | 244 | 77 | 630 | 1.4320 | 2.181 | 29.10 | 28.89 | 1.10 | 238 | 9.8 | 9.9 | 23.3 | 23.1 |
| $CF_2{=}CFI$ | 208 | 28 | 627 | 1.4143<br>(0°) | 2.284<br>(0°) | 22.70 | 23.50 | 0.74 | 207 | 11.6 | 11.7 | 27.4 | 27.2 |
| $CF_2{=}CFCH_2CH_2I$ | 236 | 112 | 623 | 1.4554 | 1.957 | 32.74 | 32.90 | 1.01 | 229 | 20.3 | 20.4 | 24.5 | 24.7 |
| $CF_2{=}CFCH_2CHFI$ | 254 | 107 | 633 | 1.4370 | 2.052 | 32.42 | 32.73 | 0.95 | .. | 18.9 | 18.8 | 29.9 | 29.8 |
| $CF_2{=}CFCH_2CF_2I$ | 272 | 92 | 633 | 1.4118 | 2.060 | 32.83 | 32.66 | 1.06 | .. | 17.6 | 17.4 | 34.9 | 35.1 |
| $CF_2{=}CFCFHCF_2I$ | 290 | 83 | 631 | 1.4006 | 2.103 | 33.47 | 32.59 | 1.18 | .. | 16.5 | 16.3 | 39.3 | 39.1 |
| $CF_2{=}CFCF_2CFI_2$ | 416 | 146 | 622 | 1.4794 | 2.522 | 46.80 | 45.39 | 1.26 | .. | 11.5 | 11.2 | 27.4 | 27.2 |
| $CF_2{=}CFCH{=}CH_2$ | 108 | 0.5 | 585 |  |  |  |  |  | 109 | 44.4 | 44.2 | 52.8 | 52.6 |
| $CF_2{=}CFCH{=}CFH$ | 126 |  |  |  |  |  |  |  | 130 | 38.1 | 38.0 | 60.3 | 60.6 |
| $CF_2{=}CFCH{=}CF_2$ | 144 | 10.2 | 630 |  |  |  |  |  | 146 | 33.3 | 33.0 | 65.9 | 65.7 |
| $CF_2{=}CFCF{=}CF_2$ | 162 | 3 | 627 |  |  |  |  |  | 161 |  |  |  |  |
| $CF_2{=}CFCF_2CCl_2I$ | 341 | 160 | 624 | 1.4635 | 2.232 | 42.11 | 42.74 | 0.98 |  | 14.1 | 14.4 | 27.8 | 27.7 |
| $CF_2{=}CFCHClCF_2I$ | 306 | 127 | 624 | 1.4391 | 2.177 | 37.52 | 37.03 | 0.93 |  | 15.7 | 15.5 | 31.0 | 31.0 |
| $CH_3CH_2OCF_2CFHI$ | 254 | 122 | 630 | 1.4189 | 1.839 | 34.88 | 34.91 | 1.02 |  | 18.9 | 19.0 | 22.4 | 22.2 |

$$CF_2{=}CFI + CF_2{=}CCl_2 \longrightarrow CF_2{=}CFCF_2CCl_2I \quad \text{(VIII)} \quad 5\%$$

The above butenes all reacted to give a positive test for unsaturation with dilute potassium permanganate solution. The physical properties and analyses of the various butenes are listed in Table I.

**Preparation of** $CF_2{=}CF—CH{=}CH_2$.—In a typical run 6.6 g. of 1,1,2-trifluoro-4-iodobutene-1 (III) was added dropwise to a suspension of powdered potassium hydroxide in 10 cc. of mineral oil. The reaction was carried out at 95° and the gaseous product was collected in a carbon dioxide–acetone cooled receiver. The condensed gas (1.4 g. or 52% of theory) had an experimental molecular weight of 109 (calcd. for $C_4F_3H_3$: mol. wt., 108) and a boiling point of 0.5° at 585 mm. pressure, and its infrared spectrogram compared very favorably with the authentic spectrogram for the diene[15] prepared from $CF_2ClCFCl–CH_2–CH_2I$.

**Preparation of** $CF_2{=}CH—CH{=}CFH$.—This diene was prepared in a similar manner noted above from $CF_2{=}CF—CH_2CHFI$. The product had an experimental molecular weight of 130 (calcd. for $C_4H_2F_4$: mol. wt., 126) and its infrared spectrogram displayed a doublet in the 5.70 μ region which is characteristic of a conjugated diene. Attempts to determine the boiling point of the diene were unsuccessful due to rapid polymerization which took place. (The analysis was carried out on a gas sample which had been distilled three times (pot to pot) in a vacuum system.)

**Preparation of** $CF_2{=}CF—CH{=}CF_2$.—This diene was prepared in a similar manner from $CF_2{=}CF—CH_2CF_2I$. It had a boiling point of 10–11° at 630 mm. pressure and an experimentally determined molecular weight of 145 (calcd. for $C_4F_5H$: mol. wt., 144).

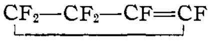
Similar results (somewhat poorer yields) were obtained by the dehalogenation of $CF_2{=}CF—CHClCF_2I$ with zinc at 95°. The infrared spectrum displayed a doublet characteristic of dienes at 5.60–5.80 μ.

**Preparation of** $CF_2{=}CF—CF{=}CF_2$.—The dehydroiodination of $CF_2{=}CF—CFH—CF_2I$ yielded perfluorobutadiene (2 g. 67% of theory) which was condensed in a Dry Ice–acetone cooled trap. It had an experimentally determined molecular weight of 161 (calcd. for $C_4F_6$: mol. wt. 162) and a reflux boiling point of 2.5–3° at 630 mm. The infrared spectrogram of this diene was identical with the spectrogram of the authentic $CF_2{=}CF—CF{=}CF_2$ obtained from M. W. Kellogg Co. of Jersey City, New Jersey.

The physical properties of the dienes and the experimental molecular weights are given in Table I along with the analytical data.

**Reactions of Butenes with Zinc.** (a) **4,4-Diiodoperfluorobutene-1** (VI).—1.0 g. of this compound did not react with 2 g. of zinc in 2 cc. of absolute ethanol. On the basis of this result the butene was assigned the structure VI rather than VII.

(b) **4,4-Dichloro-4-iodoperfluorobutene-1** (VIII).—3.0 g. of this compound was treated with 1 g. of zinc dust in 10 cc. of dioxane. The reaction temperature was 95° and heating was continued for 4 hours. At the end of this period no liquid had collected in the cold trap (expected b.p. of $CF_2{=}CF—CCl{=}CF_2$ about 50–60°) and analysis of the zinc halide showed no chloride to be present. On the basis of this lack of reactivity with zinc the butene is assigned the structure VIII rather than the isomer 1,1,2,4,4-pentafluoro-3,3-dichloro-4-iodobutene-1.

**Thermal Dimerization of** $CF_2{=}CFI$.—About 34 g. of $CF_2{=}CFI$ was placed in a Carius tube 2.5 × 30 cm. and sealed. This tube was then heated at 170–180° for 24 hours. The following products were obtained: 9.7 g. of unchanged $CF_2{=}CFI$, 7 g. of a low boiling liquid and a considerable amount of solid iodine. The low boiling liquid was identified as  CF₂—CF₂—CF=CF with a boiling point of −4° and a freezing point of −59.3 to −60.5°.

**Grignard Formation.**—About 3.0 g. of Mg was placed in a 300-ml. three-neck flask equipped with stirrer, reflux condenser and dropping funnel. A Dry Ice–acetone cooled trap was attached to the condenser. A stream of oxygen-free nitrogen was passed through the system and the pot flamed to remove any traces of moisture. About 100 ml. of diethyl ether was added to the Mg and 27 g. of $CF_2{=}CFI$ was placed in the dropping funnel. A crystal of iodine was added to aid in initiating the reaction and a small amount of $CF_2{=}CFI$ was added to the Mg and ether. The stirred reaction mixture was warmed to reflux and the Grignard formation began in a short while. The reaction mixture was cooled to 0° and the balance of the $CF_2{=}CFI$ added slowly. After complete consumption of the Mg the reaction mixture was hydrolyzed by the addition of 25 cc. of 6 *N* hydrochloric acid. The hydrolysis of the Grignard reagent resulted in a vigorous reaction and 2.5 g. (22% of theory based on conversion to $CF_2{=}CFH$) of liquid was condensed in the Dry Ice trap. This liquid was subjected to a molecular weight determination and proved to be $CF_2{=}CFH$ (calcd. for $C_2F_3H$: mol. wt., 82; found, 82). The temperature of the reaction mixture was raised to 29° and an additional amount (about 2 g.) of $CF_2{=}CFH$ was obtained. Attempts to treat $CF_2{=}CFI$ with NaCN, $CH_3COOK$ and $CH_3COOAg$ in the hope of replacing the iodine atom with the respective anions have been unsuccessful.

**Preparation of** $CH_3CH_2OCF_2CFHI$.—Reaction of $CF_2ClCFHI$ and ethanol yielded the ether which distilled at 121.5–123.5° with slight decomposition, or at 36° at 17 mm. pressure. The identity of the ether $CH_3CH_2OCF_2CFHI$ was established by molar refraction values (calcd., 34.90; obsd., 34.88) $n^{20}_D$ 1.4189, $d^{20}_4$ 1.8387 and by analysis.

**Hydrolysis of** $CH_3CH_2OCCF_2.CFHI—CH_3CH_2OCF_2CFHI + H_2SO_4 \rightarrow CH_3CH_2OCOCFHI + HF$.—The hydrolysis was carried out by adding 90% $H_2SO_4$ to 4.5 g. of the ether according to the method of Tarrant and Young.[16] The acid CFHICOOH which was isolated was subjected to repeated recrystallization until a consistent melting point of 78.5–

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(15) D. A. Rausch, Ph.D. Thesis, University of Colorado, 1953.

(16) J. A. Young and P. Tarrant, THIS JOURNAL, **72**, 1860 (1950).

79.0° was obtained. (Swarts[17] reports 74°.) Anhydrous ammonia was passed into the $CCl_4$ solution of the ester to give the amide $CFHICONH_2$ melting at 93.0° (Swarts reports 92.5°).

Infrared spectra were taken with a Perkin-Elmer Model 12 C spectrophotometer. A Beckman quartz spectrophotometer, Model D.U., was used for the ultraviolet spectrum.

**Acknowledgment.**—We wish to thank Dr. P. M. Dean of this University for the analytical data, and the Minnesota Mining and Manufacturing Company of St. Paul, Minnesota, for partial support of this work in the form of a grant-in-aid.

BOULDER, COLORADO

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[17] F. Swarts, "Organic Fluorine Compounds: A Review," Mem. Couronnes, *Acad. roy. Belg.*, **61**, 94 (1901); *Chem. Zentr.*, **74**, 12 (1903).

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[CONTRIBUTION FROM LOS ALAMOS SCIENTIFIC LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# Preparation and Some Properties of $HAu(CN)_2$[1]

BY R. A. PENNEMAN, E. STARITZKY AND L. H. JONES

RECEIVED OCTOBER 6, 1955

The existence of $HAu(CN)_2$ has been suggested in the literature, for example, in the work of Bassett and Corbet[2] on $KAu(CN)_2$, but the compound was not isolated. The preparation of a dilute solution ($10^{-3}$ *M*) of the analogous compound, $HCu(CN)_2$, by the dissolution of CuCN in aqueous HCN has been reported.[3] These workers found that $HCu(CN)_2$ behaved like a strong acid, having the limiting equivalent conductance, $\Lambda_\infty$ 389.

Our interest in $HAu(CN)_2$ arose from a discussion[4] concerning work of L. H. Jones on the polarized infrared spectrum of $KAu(CN)_2$.[5]

## Experimental

The preparation of $HAu(CN)_2$ is achieved readily by passage of a solution containing $KAu(CN)_2$ through a column containing $H^+$-form Dowex-50 resin. In a typical experiment, 1 g. of $KAu(CN)_2$ was dissolved in 15 ml. of water and passed slowly through a resin column (1.5 cm. i.d. × 13 cm.), previously washed to *p*H 6 with water. When $HAu(CN)_2$ appeared in the eluate, the *p*H dropped abruptly.

A purer preparation (containing only negligible AuCN) was obtained when a saturated solution containing equivalent amounts of $KAu(CN)_2$ and KCN was passed through the resin so that both $HAu(CN)_2$ and HCN were produced. Under these conditions, less decomposition occurred when the solution was evaporated.

Colorless crystals of $HAu(CN)_2$ were deposited when a drop of solution was evaporated rapidly in a stream of dry air at room temperature. A microchemical test for potassium was negative. $HAu(CN)_2$ is readily soluble in water. If the solid is heated to 120° it alters rapidly, forming AuCN; decomposition is slower at 103°.

Preparations were examined with the polarizing microscope, with infrared spectroscopy and by X-ray.

The crystals of $HAu(CN)_2$ examined were small, had poorly developed faces, and gave irregular extinctions in crossed polarized light. Observed extinction angles and interference figures make it probable that $HAu(CN)_2$ crystallizes in the monoclinic system. The crystals are optically biaxial positive with a large axial optic angle (estimated $2V_Z = 70°$) and with very strong dispersion of optic axes $r > v$. The principal refractive indices are $n_X = 1.95$; $n_Z = 1.96$; $n_3 = 1.98$.

The infrared spectrum of an aqueous solution of $HAu(CN)_2$ has a strong absorption peak at 2147 $cm.^{-1}$, as does aqueous $KAu(CN)_2$. A sample of solid $HAu(CN)_2$, dried on polythene film, showed absorption bands at 2146 and 399 $cm.^{-1}$. Neither the bending frequencies nor a hydrogen stretching frequency for solid $HAu(CN)_2$ were observed at path lengths up to 0.5 mm. Thicker samples were too opaque to infrared radiation to obtain their spectra. Solid $KAu(CN)_2$ shows absorption peaks at 2141 and 427 $cm.^{-1}$ (see reference 5). These peaks correspond to the asymmetric C–N stretching and asymmetric C–Au–C stretching vibrations, respectively. This indicates that probably the Au–C force constant is lower in solid $HAu(CN)_2$ than in solid $KAu(CN)_2$. In solid $KAu(CN)_2$ the peak at 2141 $cm.^{-1}$ has a much higher extinction coefficient than the analogous peak of solid $HAu(CN)_2$ at 2146 $cm.^{-1}$. This indicates that although $HAu(CN)_2$ is highly ionized to $H^+$ and $Au(CN)_2^-$ in aqueous solution, in the solid it is probably essentially un-ionized, thus greatly decreasing the extinction coefficient.

A sample of $HAu(CN)_2$ gave a powder X-ray diffraction pattern in which no lines characteristic of $KAu(CN)_2$ or of AuCN were recognized (see Table I). After 20 minutes heating at 120° in the open capillary, the residue gave an X-ray diffraction pattern characteristic of AuCN and no other recognized lines.

TABLE I

PARTIAL POWDER X-RAY DIFFRACTION PATTERN OF $HAu(CN)_2$

| *d* (A.)[a] | *I*/*I*₁[b] | *d* (A.)[a] | *I*/*I*₁[b] |
|---|---|---|---|
| 8.67 | 100 | 2.286 | 5 |
| 4.76 | <5 | 2.160 | 10 |
| 4.49 | <5 | 1.921 | <5 |
| 4.36 | <5 | 1.745 | 5 |
| 4.30 | 30 | 1.729 | 5 |
| 3.35 | <5 | 1.618 | <5 |
| 3.02 | 45 | 1.510 | 5 |
| 2.94 | <5 | 1.441 | 5 |
| 2.88 | 20 | 1.392 | <5 |
| 2.70 | 5 | | |

[a] Philips 114.6 mm. diameter powder camera, Straumanis mounting ($CuK\alpha$) = 1.5418 A. [b] Relative peak intensities above background from densitometer measurements.

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