These compounds, the first organic derivatives of azido-dithiocarbonic acid to be isolated, were formed by interaction of the alkyl or acyl halide and sodium azido-dithiocarbonate in acetone. They are white, crystalline compounds, stable at 0°, but decomposing more or less rapidly at higher temperatures into thiocyanates or isothiocyanates, sulfur and nitrogen. The crystallographic properties, melting points and solubilities of the compounds have been determined. Unlike certain of the inorganic azido-dithiocarbonates, the organic compounds show no photosensitivity, presumably because of the molecular character of their lattices.

The preparation of *p*-bromobenzoÿl isothiocyanate and its condensation products with alcohol and aniline is described.

ITHACA, NEW YORK

NOTES

The Rate of Rearrangement of Pinene to Dipentene.—The rate of disappearance of the optical activity of *d*-pinene upon heating has been measured by Smith.[1] His experimental results were treated by supposing that the reaction which occurred was a simple racemization, a view for which he presented some evidence. Recently it has been shown rather convincingly by Conant and Carlson[2] that the reaction Smith measured was the isomerization to dipentene. This substance is optically inactive and if the reaction went to completion the final rotation would be zero, just as in the supposed formation of the racemic mixture. The rate of the reaction, as calculated from the observed rotations, will not be the same in the two cases, and it is the purpose of this communication to point out how Smith's constants must be modified, if the reaction is actually an isomerization.

The equation appropriate to Smith's interpretation of the reaction was

$$\ln \alpha_1/\alpha_2 = 2k_1(t_2 - t_1) \qquad (1)$$

where α is a measured angle of rotation; but with the revised interpretation the rotation measures directly the amount of pinene remaining and we have

$$\ln \alpha_1/\alpha_2 = k_2(t_2 - t_1) \qquad (2)$$

This equation is of the same form as (1), and since Smith found that the values k_1 were constant, the values of k_2 will be constant also; clearly $k_2 = 2k_1$. That is, the correct first-order constants for the rearrangement are just twice the values reported by Smith.

It is still reasonable to suppose that this reaction occurs by a homogeneous unimolecular mechanism. Although it has lost some of its theoretical simplicity, since it can no longer be supposed that the heat of reaction is zero, it remains the only known example of a presumably unimolecular

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[1] Smith, THIS JOURNAL, **49**, 43 (1927).

[2] Conant and Carlson, *ibid.*, **51**, 3464 (1929).

rearrangement, since all the other first-order gas reactions are decompositions.

Contribution No. 256 from the
Gates Chemical Laboratory
California Institute of Technology
Pasadena, California

Louis S. Kassel[3]

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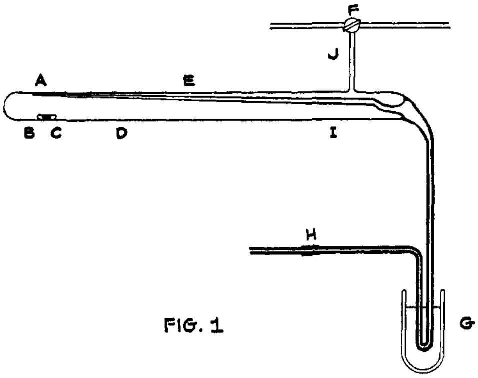

FIG. 1

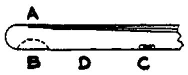

FIG. 2

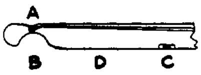

FIG. 3

A Capillary Gas Valve.—Having had occasion to withdraw many small samples of extremely pure chlorine from a large storage bulb without contaminating the main supply, the scheme in Fig. 1 was adopted. The outer tube D is of thin-walled 12-mm. tubing, 30-cm. long; the capillary E is less than 1-mm. bore, with thin walls. When a sample is to be collected in the reaction vessel which, together with tube D, has been evacuated, liquid air is applied at G. From this point on, H serves as a chlorine block, cotton wrapping around H being continually soaked with liquid air throughout all subsequent operations. The Dewar flask is then removed, and the chlorine in capillary G begins to melt. Current sent through an electromagnet held at point A, Fig. 1, causes the iron-cored glass capsule C to jump up and break the capillary at point A, and chlorine in G begins to distil over into the reaction vessel. C is then pulled out of the way, as in Fig. 2. When sufficient chlorine has been collected, F is shut, and a small flame applied momentarily at B. Since the pressure in D is less than one atmosphere, the thin tube immediately collapses as represented by the dotted curve in Fig. 2. The flame is now directed at A, and the capillary quickly sealed off as shown in Fig. 3. The blob of glass may be pulled off subsequently to give the appearance of Fig. 1 again. The capillary always breaks at point A-B where the strain of being sealed to D lies. Any gases given off from the momentary heating at B can be pumped out of D before opening F to the reaction vessel again; and none of these gases can pass into the storage bulb against the stream of chlorine which continually evaporates from G and flows into D through

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[3] National Research Fellow in Chemistry.

capillary E. The latter is sufficiently long to permit the withdrawal of about thirty samples, after which a new tube can be sealed on at I, and thirty more samples withdrawn. Stopcock F, treated with a special chlorine-resisting lubricant,[1] can be dispensed with, if necessary, by a slight modification of the scheme in Fig. 1, such as by sealing off the reaction vessel each time at a constriction at J.

This scheme is, of course, applicable to gases other than chlorine to replace other more complicated and less satisfactory devices. It has the advantage of repeated use without replacement. In other cases the liquid air trap may or may not have application, according to circumstances, and may be omitted at will.

CONTRIBUTION FROM THE
SCHOOL OF CHEMISTRY OF THE
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA
HUBERT N. ALYEA[2]

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A New Line in the Absorption Spectrum of Samarium.—During the course of work on the concentration of illinium it was noticed that an extremely faint line appeared at 5960 Å. in the absorption spectrum of supposedly pure samarium. No line at 5960 Å. has been reported for this element. As the material had been prepared by fractional crystallization of the double magnesium nitrates, the line could be attributed only to neodymium, europium, illinium or to samarium itself.

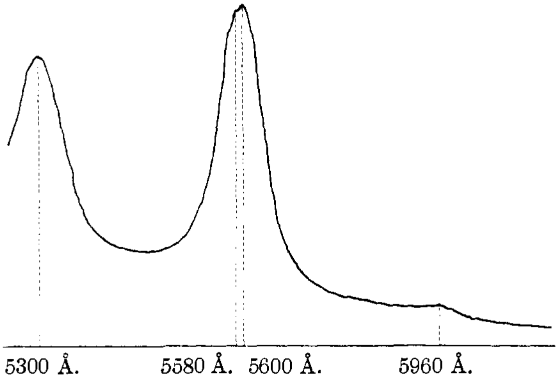

Fig. 1.—Microphotometric curve of part of the absorption spectrum of samarium nitrate, showing a new line at 5960 Å.

About two kilograms of rare earth oxide showing the line was, therefore, fractionally crystallized five hundred times as the double magnesium nitrate, and then one hundred times as the simple nitrate. During all this

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[1] H. N. Stephens, THIS JOURNAL, **52**, 635 (1930).

[2] National Research Fellow.

time the line at 5960 Å. remained at the same relative intensity to the other lines of samarium throughout the series. The only impurity eliminated was a faint trace of neodymium, the absorption bands of which appeared quite distinct from the line in question. It was, therefore, concluded that the line at 5960 Å. belonged to samarium and had escaped observation before owing to its extreme faintness.

The figure shows a microphotometric curve taken from part of the absorption spectrum of samarium nitrate photographed on a Hilger E1 quartz spectrograph as described elsewhere.[1] The solution, which was 6.0 *N* in samarium nitrate, was in a 15-cm. absorption cell. The temperature was 80°, as the line is more intense when the solution is hot. Some idea of the relative intensities of the new line and the one at 5600 Å. may be gained from the figure.

Contribution from the
Chemical Laboratory of the
University of Illinois
Urbana, Illinois

Pierce W. Selwood

Received January 30, 1930
Published May 8, 1930

The Standardization of Weights.—The accuracy of the Richards method[1] for the standardization of weights by substitution can be doubled by using the method of weighing by transposition. This latter method makes the use of a set of tare weights unnecessary, and involves no more time or difficulty than the Richards method. In fact, this is one operation to which the little-used transposition weighing seems peculiarly suited.

If the weights W_1 and W_2 are to be compared, W_1 is placed on the left pan and W_2 on the right and the zero point noted. The weights are then reversed and the difference, d, necessary to bring the pointer to the same zero point is noted. It can be shown readily that $W_2 - W_1 = d(l_2) \div (l_1 + l_2)$ where l_1 and l_2 are, respectively, the lengths of the beam to the left and to the right of the central knife edge. Since d is very small, any error introduced by assuming that $l_1 = l_2$ is entirely negligible, so $W_2 - W_1 = d/2$, where d may, of course, be either a positive or negative quantity. The method of calculating the corrections remains the same.

Variations in the relative lengths of the balance arms are not likely to occur during any one comparison, and variations between comparisons could not affect the value of $W_2 - W_1$ appreciably.

Contribution from the
Department of Chemistry
University of Michigan
Ann Arbor, Michigan

Philip F. Weatherill

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[1] Quill and Selwood with Hopkins, This Journal, **50**, 2929 (1928).

[1] T. W. Richards, *ibid.*, **22**, 144 (1900).