

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*-bromobenzoyl isothiocyanate and its condensation products with alcohol and aniline is described.

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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 Carlson² 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

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

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

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

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

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.

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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

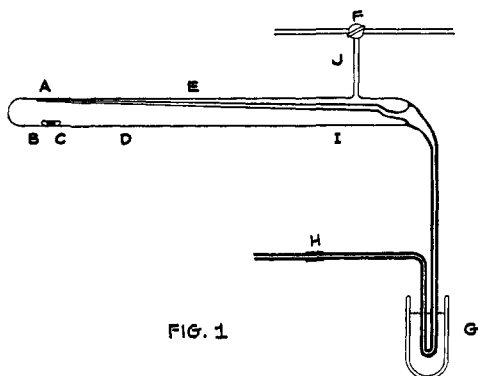


FIG. 1

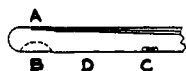


FIG. 2



FIG. 3

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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