[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-DITHIOCARBONIC ACID. V. ALKYL AND ACYL DERIVATIVES[1,2,3]

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WITH MICROSCOPICAL STUDIES BY C. W. MASON

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The marked photosensitivity of certain compounds of azido-dithiocarbonic acid with strongly electropositive elements or radicals, particularly the cesium, rubidium and tetramethylammonium salts, has been attributed[1c,1d] to a tendency on the part of these substances to undergo a reversible, superficial photolysis which results in the liberation, *in situ*, of certain metallic atoms or radicals in the crystal lattice. The hypothesis thus formulated serves also to explain the action of light in accelerating the decomposition of the solid inorganic azido-dithiocarbonates thus far studied. Discharge of the anions yields free azido-carbondisulfide, $SCSN_3$, which is known[2g] to undergo spontaneous thermal decomposition at ordinary temperatures into thiocyanogen, sulfur and nitrogen.

Photolytic action of the type thus assumed to take place during the illumination of the inorganic salts already investigated, all of which are believed to crystallize in the form of ionized lattices, could scarcely be expected to occur in the case of organic derivatives of azido-dithiocarbonic acid, which would, in all probability, in the solid state, take the form of molecular lattices. An important incentive to the preparation and study of these derivatives, none of which has yet been described, is therefore furnished by the possibility of investigating compounds of this type from the viewpoint of the hypothesis under consideration.

A second incentive is afforded by the desire to investigate the influence of various substituents for hydrogen upon the velocity of thermal decomposition of azido-dithiocarbonic acid,[2a] and upon the nature of the products of such decomposition. It is by no means a foregone conclusion

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[1] For the earlier articles of this series see (a) Smith and Wilcoxon with Browne, THIS JOURNAL, **45**, 2604 (1923); (b) Browne and Smith, *ibid.*, **47**, 2698 (1925); (c) Browne and Audrieth, *ibid.*, **49**, 917 (1927); (d) Audrieth, Smith and Browne, *ibid.*, **49**, 2129 (1927).

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[3] This paper was presented at the St. Louis Meeting of the American Chemical Society in April, 1928. Manuscript received April 9, 1929, but withheld from publication by the author.

that organic derivatives of various types should decompose in a manner strictly analogous to that characteristic of the inorganic salts. It is entirely possible, for example, that in certain cases normal thiocyanates, and in others isothiocyanates, might be obtained as products of thermal decomposition.

In the present article are described the methyl, benzyl, benzohydryl, triphenylmethyl, benzoyl and *p*-bromobenzoyl derivatives of azido-dithiocarbonic acid.

Preparation.—Attempts to obtain alkyl and aryl azido-dithiocarbonates by direct condensation of the organic azides with carbon disulfide by a method analogous to that used in preparing the inorganic derivatives[2f] did not prove successful. Formation of the azido-dithiocarbonates evidently involves the transfer of electrons from the azide *ion* to a molecule of carbon disulfide, or, more specifically, to one of the sulfur atoms of the disulfide, with consequent condensation of the two radicals: $N_3^- + CS_2 = SCSN_3^-$. Since the organic azides are not dissociated to an appreciable degree, the electronic transfer does not take place.

The general method finally adopted for the preparation of the compounds to be described involves the interaction, in acetone, of the alkyl or acyl halide and sodium azido-dithiocarbonate, in accordance with the equation:

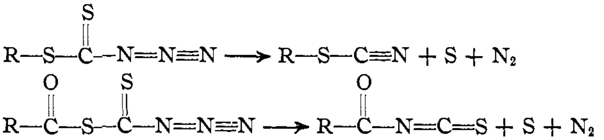
$$RCl + NaSCSN_3 = NaCl + RSCSN_3$$

With the bromides, with triphenylmethyl chloride and with the acyl chlorides the reaction proceeds rather rapidly at room temperature. In the case of less reactive chlorides, the use of higher temperatures is precluded by the instability of the products. The precipitated metallic halide is removed by filtration, and if the product is but slightly soluble in acetone, the precipitate is treated with chloroform to extract the azido-dithiocarbonate.

General Properties.—All of the organic azido-dithiocarbonates studied were obtained as white, crystalline compounds which undergo at room temperature a slow spontaneous decomposition, with ultimate quantitative formation of the corresponding thiocyanate or isothiocyanate,[4] sulfur and nitrogen:

[4] The *normal* thiocyanates were invariably obtained as decomposition products of the alkyl azido-dithiocarbonates. In view of the circumstance that no normal acyl thiocyanate has as yet been isolated, it is not surprising that isothiocyanates, only, have been obtained by decomposition of the acyl derivatives. It is entirely possible, however, that the normal thiocyanate is in each case formed at first, as an intermediate product, but that, as suggested by Wheeler and Merriam[5] for the case of esters in which "the group R is strongly negative the product immediately undergoes a molecular rearrangement into the form RNCS (when R is the group C_6H_5CO-, etc.)."

[5] Wheeler and Merriam, THIS JOURNAL, **23**, 285 (1901).



$$R{-}S{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}N{=}N{\equiv}N \longrightarrow R{-}S{-}C{\equiv}N + S + N_2$$

$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}S{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}N{=}N{\equiv}N \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N{=}C{=}S + S + N_2$$

The velocity of this decomposition is sufficiently retarded at low temperatures to permit the storage of samples of the products at 0° for several weeks without appreciable deterioration.

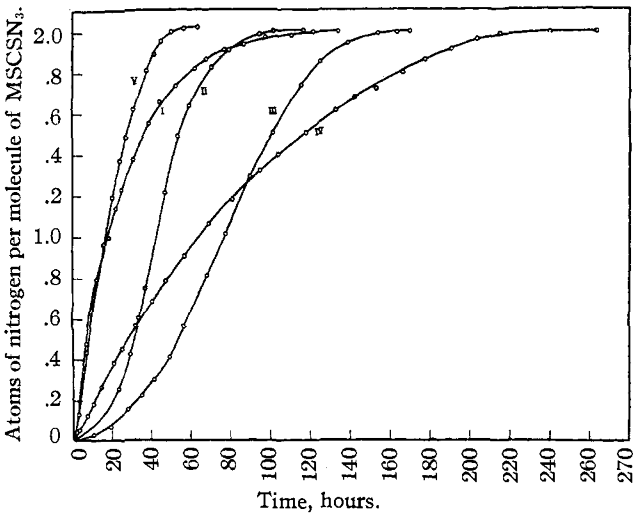


Fig. 1.—Nitrometric decomposition of derivatives of azidodithiocarbonic acid at 40°. I, CH_3SCSN_3; II, $(C_6H_5)_2CHSCSN_3$; III, $C_6H_5CH_2SCSN_3$; IV, $(C_6H_5)_3CSCSN_3$; V, $C_6H_5COSCSN_3$.

The course of the isothermal decomposition of five compounds has been investigated nitrometrically at 40°. The data obtained are recorded graphically in Fig. 1. From these data the compounds may be listed in the approximate order of increasing stability as follows: $C_6H_5CO- < (C_6H_5)_2CH- < CH_3- < C_6H_5CH_2- < (C_6H_5)_3C-$. The benzyl and benzohydryl derivatives obviously undergo autocatalytic decomposition. The methyl- and phenyl-substituted methylazido-dithiocarbonates manifest a relative degree of stability reminiscent of the behavior of the substituted ammonium salts, of which the disubstituted derivative invariably differs from the mono-, tri- and tetra-substituted compounds in various physical properties, such as electrical conductivity.

Melting-point determinations were made with the aid of the Maquenne block,[6] an apparatus designed especially for use with substances which, like those under investigation, "melt with decomposition." Comparison

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[6] Houben-Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, **1921**, Vol. I, 2d ed., p. 734.

of the results obtained by this procedure with the melting points determined by the usual method, using a capillary tube (in an electrically heated Thiele apparatus), shows that the latter are usually lower in the case of compounds that undergo appreciable decomposition during fusion (see Table I).

Unlike the inorganic salts of the azido acid, the organic derivatives are not particularly explosive. They "puff" mildly when held in the flame, or when heated rapidly on a metal plate. Furthermore, on exposure to illumination they show no photosensitivity and undergo no coloration. This affords support to the photolytic theory mentioned in an earlier paragraph.

The results of qualitative determinations of the solubility of the compounds at room temperature in various non-aqueous solvents are presented in Table I. All of the organic derivatives studied were found to be insoluble in water and to be very soluble in chloroform.

TABLE I

MELTING POINTS AND SOLUBILITIES OF ORGANIC AZIDO-DITHIOCARBONATES

V = very soluble; M = moderately soluble; S = slightly soluble

R—$SCSN_3$ R =	Melting points, °C. Maquenne-block method	Capillary-tube method	Acetone	EtOAc	EtOH	MeOH	Ether	C_6H_6	CS_2	$CHCl_3$	CCl_4
CH_3—	32	34	V	V	M	M	M	V	V	V	V
$C_6H_5CH_2$—	64.5	66	V	V	S	S	M	M	V	V	M
$(C_6H_5)_2CH$—	67.5	67	V	V	M	M	M	V	V	V	V
$(C_6H_5)_3C$—	132 (dec.)	102–104 (dec.)	S	S	S	S	S	M	M	V	M
C_6H_5CO—	119–120 (dec.)	92–94 (dec.)	S	S	S	S	M	M	M	V	M
p-BrC_6H_4CO—	127 (dec.)	99–101 (dec.)	S	S	S	S	S	S	M	V	M

Analysis.—The amount of nitrogen evolved during thermal decomposition of the compounds was determined in each case by slowly heating the sample, mixed with sand to minimize the danger of explosion, in a bulb attached to a nitrometer. The results obtained were invariably somewhat high, as it was not feasible to introduce a correction for the vapor tension of the thiocyanate formed as a product of the reaction. The sulfur was determined as barium sulfate after conversion to a soluble sulfate by ignition with sodium peroxide in a Parr bomb.

Methyl Azido-dithiocarbonate, CH_3SCSN_3.—The product, which was obtained by the interaction of methyl bromide and sodium azido-dithiocarbonate in acetone, was purified by recrystallization from chloroform. It is slowly attacked by concentrated aqueous alkalies.

Anal. (a) Subs., 0.1855, 0.2498: $BaSO_4$, 0.6485, 0.8759. Calcd. for $C_2H_3N_3S_2$: S, 48.14. Found: S, 48.02, 48.16. (b) Subs., 0.4148, 0.2623: N_2 (corr.), 71.4, 44.7 cc. Calcd. for CH_3SCSN_3: N_2, 1 mole. Found: N_2, 1.023, 1.013.

Under the microscope the crystals appear to consist of thick, four-sided prisms which are rhomb-shaped in cross section. The acute angle of the rhomb is about 75°. The terminal pinacoid is perpendicular to the prism faces. All prism views exhibit parallel extinction; end views of the prisms reveal a very small extinction angle, about 1–2°. The angle of the acute bisectrix parallel to the elongation with 2V is about 65°. The crystals are optically negative and exhibit strong double refraction. They are probably of monoclinic symmetry.

Benzyl Azido-dithiocarbonate, $C_6H_5CH_2SCSN_3$.—The interaction of benzyl chloride and sodium azido-dithiocarbonate in acetone at room temperature required for its completion approximately twenty-four hours. The precipitated sodium chloride was filtered off and a small amount of water was added to the filtrate. The crude benzyl derivative which separated on cooling with ice and salt was purified by recrystallization from chloroform.

Most reagents cause primary decomposition of the azido-dithiocarbonate to form the thiocyanate, which then exhibits its own characteristic reactions. Thus, boiling with nitric acid brings about oxidation to benzaldehyde; the prolonged action of aqueous alcohol causes hydrolysis. Benzyl thiocyanate was obtained readily by heating the azido-dithiocarbonate in a suitable organic solvent (absolute alcohol) and removing the precipitated sulfur. The solution after concentration deposited crystals of benzyl thiocyanate, m. p. 41°.

Anal. (a) Subs., 0.1705, 0.1640: $BaSO_4$, 0.3768, 0.3675. Calcd. for $C_8H_7N_3S_2$: S, 30.64. Found: S, 30.35, 30.78. (b) Subs., 0.2021, 0.4856: N_2 (corr.), 21.62, 52.47 cc. Calcd. for $C_7H_7SCSN_3$: N_2, 1 mole. Found: N_2, 1.000, 1.010. (c) Dumas total nitrogen determination. Subs., 0.2611: N_2 (corr.), 42.5 cc. Calcd. for $C_8H_7N_3S_2$: N, 20.1. Found: N, 20.4.

Benzyl azido-dithiocarbonate crystallizes in prisms of monoclinic symmetry, showing the forms 1 0 0, 1 1 0, 0 1 1 and 1 0 1. Extinction is parallel to the plane of symmetry, and oblique in this plane at an angle of 7°. The crystals are biaxial, positive, 2V about 80°, $v < r$. The axial plane is transverse of the prisms. Double refraction is moderately strong.

Benzohydryl Azido-dithiocarbonate, $(C_6H_5)_2CHSCSN_3$.—The interaction of benzohydryl bromide[7] and sodium azido-dithiocarbonate in acetone was complete after about half an hour. After filtering to remove the precipitated sodium bromide, addition of water caused a yellow liquid to separate. This was dissolved in a mixture of petroleum ether and benzene and the solution was dried over anhydrous sodium sulfate. Upon cooling with ice and salt, benzohydryl azido-dithiocarbonate separated in small colorless crystals.

Anal. (a) Subs., 0.1113, 0.1340: $BaSO_4$, 0.1877, 0.2201. Calcd. for $C_{14}H_{11}N_3S_2$: S, 22.47. Found: S, 22.55, 22.56. (b) Subs., 0.4212, 0.5428: N_2 (corr.), 34.42, 42.68 cc. Calcd. for $C_{13}H_{11}SCSN_3$: N_2, 1 mole. Found: N_2, 1.017, 1.025.

The substance, recrystallized from xylene, forms prisms and elongated tablets, the opposite edges of which are beveled, and the ends obtusely pointed (120°). These tablets are frequently shortened to thick rhomb-shaped plates, the four vertices of which are beveled. Prism views exhibit parallel extinction; the rhombs, symmetrical extinction. End views show oblique extinction, about 45°.

Good biaxial interference figures are obtainable, which indicate that the acute bisectrix is inclined to the pinacoid of the tablets. The axial plane is parallel to the acute diagonal of the rhombs. Double refraction is strong, positive, with 2V about 60°,

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[7] The chloride reacted much more slowly, and for this reason was not as satisfactory as the bromide in this preparation.

and $r < v$ marked (or else inclined dispersion). Refractive indices were not determined on account of solubility in the standard immersion liquids. The oblique extinction of the end views of the prisms and tablets, and tilted position of the optic axes indicate that the plane symmetry of the crystals lies crosswise of them (parallel to the acute diagonal of the rhombs), and that they belong to the monoclinic system.

Triphenylmethyl Azido-dithiocarbonate, $(C_6H_5)_3C\text{-}SCSN_3$.—When triphenylmethyl chloride and sodium azido-dithiocarbonate were brought together in acetone, the ester was precipitated rapidly, together with sodium chloride. This precipitate was air-dried, and was extracted with chloroform, in which the triphenylmethyl ester is soluble. After concentrating and cooling, the solution deposited colorless crystals of triphenylmethyl azido-dithiocarbonate.

Anal. (a) Subs., 0.2743, 0.2348: $BaSO_4$, 0.3483, 0.3004. Calcd. for $C_{20}H_{15}N_3S_2$: S, 17.74. Found: S, 17.44, 17.57. (b) Subs., 0.3868, 0.3746: N_2 (corr.), 24.16, 23.37 cc. Calcd. for $C_{19}H_{15}SCSN_3$: N_2, 1 mole. Found: N_2, 1.008, 1.006.

The substance crystallizes in bipyramids and tablets of orthorhombic symmetry. The tablets possess end angles of about 120°. All views exhibit symmetrical extinction. The axial plane is parallel to the base of the pyramidal forms; 2V is large ($> 70°$). The crystals are optically positive.

Allyl Azido-dithiocarbonate, $C_3H_5SCSN_3$.—This substance was obtained by interaction of allyl bromide and sodium azido-dithiocarbonate in acetone. Because of the instability and the difficulty of purification of the resulting product, no attempt was made to study it carefully. It apparently undergoes fairly rapid decomposition, since the characteristic odor of allyl isothiocyanate was very marked in all of the samples that were prepared.

Benzoyl Azido-dithiocarbonate, $C_6H_5COSCSN_3$.—This acyl derivative was prepared by the interaction of benzoyl chloride and sodium azido-dithiocarbonate, either in aqueous solution or in acetone. The latter medium is preferable, since the reaction is practically instantaneous in this solvent. The product was purified by recrystallization from chloroform.

Anal. (a) Subs., 0.1845, 0.2115: $BaSO_4$, 0.3810, 0.4348. Calcd. for $C_8H_5ON_3S_2$: S, 28.72. Found: S, 28.36, 28.24. (b) Subs., 0.2997, 0.2212: N_2 (corr.), 30.11, 22.33 cc. Calcd. for $C_7H_5OSCSN_3$: N_2, 1 mole. Found: N_2, 1.002, 1.006.

Benzoyl azido-dithiocarbonate is hydrolyzed by hot aqueous potassium hydroxide solution with the formation of potassium benzoate and potassium azido-dithiocarbonate. The formation of benzoyl isothiocyanate by the thermal decomposition of the benzoyl derivative is shown by the fact that the purified decomposition residue combines with alcohol to form ethyl benzoylthiocarbamate, $C_6H_5CO\text{—}NH\text{—}CS\text{—}OC_2H_5$, and with aniline to form α-phenyl-β-benzoylthiourea, $C_6H_5CO\text{—}NH\text{—}CS\text{—}NHC_6H_5$.[8] Apparently the strongly negative character of the benzoyl group causes the normal thiocyanate first formed to undergo immediately an intramolecular rearrangement to the isothiocyanate.

Benzoyl azido-dithiocarbonate crystallizes in the form of thin, oblique-ended plates, belonging to the monoclinic system; acute angles, 63°; obtuse angles, rarely truncated. When precipitated directly under the microscope, crystals are obtained in which the axial plane is inclined 21° to the longer edges of the plates, in the direction of the diagonal connecting their obtuse angles. Recrystallization from xylene alters the habitus so that the other two edges of the plates are longer, resulting in an apparent extinction angle of 6° instead of 21°. Seen edgewise the plates exhibit parallel extinction. They are optically negative, with 2V about 75–80°. The refractive index for vibrations in the

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[8] Miquel, *Ann. chim. phys.*, [5] **11**, 321, 334 (1877).

axial plane is about 1.50; for vibrations transverse to this the refractive index is estimated to be about 1.75.

***p*-Bromobenzoyl Azido-dithiocarbonate**, $BrC_6H_4COSCSN_3$.—This compound was precipitated, together with sodium chloride, by the interaction of *p*-bromobenzoyl chloride[9] and sodium azido-dithiocarbonate in acetone. The product was purified by recrystallization from chloroform.

p-Bromobenzoyl azido-dithiocarbonate crystallizes from chloroform or xylene in tiny rhomb-shaped plates or oblique-ended prisms. These exhibit oblique extinction, dispersed, at an angle of about 7–8°; some views show parallel extinction. It probably crystallizes in the monoclinic system.

Anal. (a) Subs., 0.2280, 0.1870: $BaSO_4$, 0.3503, 0.2857. Calcd. for $C_8H_4ON_3BrS_2$: S, 21.22. Found: S, 21.10, 20.98. (b) Subs., 0.2580, 0.3497: N_2 (corr.), 19.44, 25.95 cc. Calcd. for $C_7H_4OBr—SCSN_3$: N_2, 1 mole. Found: N_2, 1.016, 1.001.

The reactions of the *p*-bromobenzoyl derivative are strictly analogous to those of the benzoyl compound. Boiling with aqueous potassium hydroxide solution hydrolyzes the substance to form potassium *p*-bromobenzoate and potassium azido-dithiocarbonate; thermal decomposition yields nitrogen, sulfur and *p*-bromobenzoyl isothiocyanate, which was identified by its melting point and by the preparation of its condensation product with alcohol and with aniline. Since *p*-bromobenzoyl isothiocyanate had not previously been prepared and described in the literature, it was necessary, for purposes of identification, to synthesize not only the isothiocyanate but also its condensation product with alcohol and with aniline. These are briefly described below.

***p*-Bromobenzoyl Isothiocyanate**, BrC_6H_4CONCS.—This substance was readily obtained by the interaction of *p*-bromobenzoyl chloride and sodium thiocyanate in acetone. Recrystallization of the crude product from chloroform gave a colorless crystalline solid, m. p. 55°.

Anal. Subs., 0.2395, 0.2453: $BaSO_4$, 0.2242, 0.2323. Calcd. for C_8H_4ONBrS: S, 13.2. Found: S, 12.9, 13.0.

Ethyl *p*-Bromobenzoylthiocarbamate, $BrC_6H_4CO\text{-}NH\text{-}CS\text{-}OC_2H_5$.—This derivative was prepared by direct combination of ethyl alcohol with *p*-bromobenzoyl isothiocyanate. It crystallizes from aqueous alcohol in fine, colorless needles, m. p. 99°.

Anal. Subs., 0.2097, 0.2119: $BaSO_4$, 0.1675, 0.1690. Calcd. for $C_{10}H_{10}O_2NBrS$: S, 11.1. Found: S, 11.0, 11.0.

α-Phenyl-β-(*p*-bromobenzoyl)-thiourea, $BrC_6H_4CO\text{-}NH\text{-}CS\text{-}NHC_6H_5$.—This compound was produced by direct combination of aniline and *p*-bromobenzoyl isothiocyanate. Recrystallization from aqueous alcohol yielded a colorless crystalline solid, m. p. 151°. It is very soluble in chloroform, toluene and aniline; it crystallizes from the latter in the form of fine, elongated prisms.

Anal. Subs., 0.2648, 0.1810: $BaSO_4$, 0.1827, 0.1245. Calcd. for $C_{14}H_{11}ON_2BrS$: S, 9.6. Found: S, 9.5, 9.5.

Summary

The methyl, benzyl, benzohydryl, triphenylmethyl, benzoyl and *p*-bromobenzoyl azido-dithiocarbonates have been prepared and described.

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[9] *p*-Bromobenzoyl chloride may be prepared in good yield by the long continued action of an excess of thionyl chloride upon *p*-bromobenzoic acid, although the reaction is unusually slow. When 25 g. of thionyl chloride (0.21 mole) and 16 g. of the acid (0.08 mole) were refluxed for 120 hours, the yield of purified *p*-bromobenzoyl chloride, after one crystallization from petroleum ether, was 15 g. (85% of the calculated amount).

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 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).