

and yet accurate enough to prove whether a molecular compound exists.

A condensed procedure for this method of identification is as follows. Fuse together as nearly as possible equimolecular amounts of naphthalene and unknown, cool, recrystallize the melt from a little alcohol, and determine the melting point of the crystals.

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The Identification of Olefins as Dithiocyanates¹

BY O. C. DERMER AND GEORGE A. DYSINGER

The only general method of converting olefins into solid derivatives suitable for identifying them is the addition of nitrosyl chloride or oxides of nitrogen, and even the derivatives so obtained often must be changed into the more stable nitrolamines. A recent suggestion² that olefins be identified as addition products with osmium tetroxide can hardly be expected to improve the situation. Since Bruson and Calvert³ demonstrated the usefulness of thiocyanogen for identifying isoprene and 2,3-dimethylbutadiene-1,3, and since thiocyanogen is known to add to several olefins, including even ethylene, with the formation of crystalline solids,⁴ we thought it desirable to test the method further, particularly with aliphatic and alicyclic olefins.

Thiocyanogen was obtained either from sodium thiocyanate and cupric sulfate⁵ or by the action of bromine on plumbous thiocyanate.^{4a} Its addition to a number of common olefins produced two solid dithiocyanates already known and only two new solids: ethylene dithiocyanate, m. p. 90.0–90.5°; styrene dithiocyanate,^{3,4b,4c} m. p. 102.5–103.0°; cyclohexene dithiocyanate, m. p. 58.0–58.5°; and 3-methylcyclohexene-1 dithiocyanate, m. p. 69.5–70.0°. Most of the compounds tested yielded only oily dithiocyanates which were not further investigated; this group included propylene,⁶ butene-1, butene-2,⁷ 2-methylpropene-1,⁶ pentene-2,⁷ 1-methylbutene-2, caprylene, diiso-

(1) This is an abstract of a thesis submitted by Mr. Dysinger in partial fulfillment of the requirements for the degree of Master of Science at the Oklahoma Agricultural and Mechanical College in 1938.

(2) Criegee, *Angew. Chem.*, **51**, 519 (1938).

(3) Bruson and Calvert, *This Journal*, **50**, 1735 (1928).

(4) (a) Söderbäck, *Ann.*, **419**, 217 (1919); (b) Kaufmann and Liepe, *Ber. pharm. Ges.*, **33**, 139 (1923); (c) Kaufmann and Oehring, *Ber.*, **59**, 187 (1926); (d) Müller and Freytag, *J. prakt. Chem.*, **146**, 58 (1936).

(5) Kaufmann and Kuchler, *Ber.*, **67**, 944 (1934).

(6) Hagelberg, *ibid.*, **23**, 1086 (1890).

(7) Likhoshevstov and Butrimov, *Acta Univ. Voronegiensis*, **8**, No. 4, 86 (1935).

butene, *d*-limonene, pinene, diallyl, allyl alcohol,^{4b} and allyl bromide. All the derivatives, like thiocyanogen itself, have a disagreeable odor and an irritant action on the skin. It is likely that selenocyanogen, (SeCN)₂, would give derivatives with higher melting points,⁶ but the difficulty of obtaining metallic selenocyanates and the unpleasant characteristics of the reagent and derivatives make the usefulness of the method in qualitative organic analysis very doubtful.

Experimental

The olefins were either purchased from supply houses or synthesized by usual procedures. In Method A, about 10 g. of the olefin was added to a well-shaken suspension of 60 g. of sodium thiocyanate and 60 g. of anhydrous cupric sulfate in 150 ml. of glacial acetic acid. This mixture was allowed to stand overnight in the ice-box and was then filtered and diluted with much water. The product was removed by another filtration or by extraction with benzene, and if solid was recrystallized from dilute alcohol.

In Method B, the olefin was added to a suspension of 20 g. of plumbous thiocyanate in 100 ml. of thiophene-free benzene to which had been added 8 g. of bromine. The mixture was kept in an ice-bath in direct sunlight for about an hour or until its brown color disappeared. It was then filtered, the benzene evaporated, and the product purified as in Method A.

The methods seemed about equally useful, some olefins being treated by one, some by the other, and some by both. Cyclohexene dithiocyanate was prepared by Method A; it is a white crystalline compound, m. p. 58.0–58.5°, which was analyzed for sulfur.

Anal. Calcd. for C₆H₁₀N₂S₂: S, 32.25. Found: S, 32.36.

3-Methylcyclohexene-1 dithiocyanate, likewise made by Method A, forms white crystals melting at 69.5–70.0°.

Anal. Calcd. for C₉H₁₂N₂S₂: N, 13.21. Found: N, 12.96.

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Sodium Ethylene Carbide

BY O. C. DERMER AND CLARENCE LATHROP

In 1927 Walker¹ reported that when ethylene is passed over metallic sodium at 150°, a little of the ethylene is polymerized to a colorless oil, and the sodium turns white. To quote: "A white brittle solid was formed—sodium ethylene carbide—and the condensation of colorless oil decreases. Finally all the sodium is converted to this new brittle material which has no reaction with ethylene and the polymerization stops." These re-

(1) Walker, *J. Phys. Chem.*, **31**, 982–984 (1927).

sults have been cited among ethylene reactions by Egloff² but apparently have never had experimental confirmation.

As such a reaction would be of great interest in both synthetic work and theoretical discussions, we have attempted to produce it, but our efforts have been uniformly unsuccessful. Impure ethylene does yield a white solid when passed over or bubbled through molten sodium at 150°, but if the ethylene be purified by bubbling it through one or two test-tubes of the metal at this temperature, it does not react at all with more sodium. Such tarnishing of the metal as does then occur is due to air and moisture adsorbed on glass surfaces in the apparatus, for it can be diminished greatly by flaming the container tube and connections before use. The white solid that was formed in the scrubber tubes by the impure ethylene did not have the reactivity which would be expected of an organometallic compound of sodium. We were likewise unable to find any evidence of polymerization of the ethylene. Indeed, according to Walker's own data, little or no ethylene was consumed by polymerization or reaction with sodium, and the purity of the gas actually increased during the reaction.

(2) Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1937, p. 288.

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Refraction Data on Liquid C₃-Hydrocarbons

BY ARISTID V. GROSSE AND CARL B. LINN

One of us¹ recently has described the adaptation of the Abbé refractometer to low temperature measurements.

We have now completed measurements of the refractive indices for the D-line, at low temperatures, of *all known* C₃-hydrocarbons with the exception of cyclopropene.² (Very little is known about this hydrocarbon and none of its physical properties have ever been measured.) In order to obtain the molecular refractions we have determined, with Mr. R. C. Wackher, the still unknown densities of cyclopropane and allene.

In the following table the n_D and d_4^{25} (corrected to vacuum) of *propane*, *propene*, *cyclopropane*, *propyne* (allylene) and *propadiene* (allene) are recorded for the temperature range of -20 to -80° and also at their respective normal boiling points.

(1) A. V. Grosse, *THIS JOURNAL*, **59**, 2739 (1937).

(2) N. J. Demjanow and M. Dojarenko, *Ber.*, **56**, 2200 (1923).

The C₃-hydrocarbons show wide differences in their indices. These may be used advantageously for *analytical purposes* since binary mixtures of these hydrocarbons show with sufficient accuracy a straight line relationship. Particularly interesting cases are the propane-propene mixtures, obtained in catalytic dehydrogenation, or propyne-propadiene mixtures from isomerization studies.

The molecular refractions of these hydrocarbons are of interest since they are the lowest members of the series so far studied in the liquid state. The *Lorenz-Lorentz refractions* were calculated from the data of Table I for different temperatures and the values extrapolated to +20° are compared with values computed from Eisenlohr's atomic refractions in Table II. Molecular volumes are included for comparisons.

The experimental molecular refractions (extrapolated to +20°) are in as good agreement with the calculated values as can be expected in view of their large temperature coefficients. These variations with temperature are much greater than for higher molecular weight compounds, measured around room temperatures; however, from the standpoint of the theory of corresponding states this is at least partly to be expected, since the absolute position and range of our measurements cover about 20% of the total distance from absolute zero to the normal boiling point.

The only real deviation is observable in the case of cyclopropane. The difference, equalling 0.4 unit, evidently is due to the exaltation of the cyclopropane ring. This exaltation value is slightly less than the one obtained by L. Tschugajeff³ (=0.66) on strained or substituted cyclopropane derivatives (carone, thujene, etc.).

The sources of hydrocarbons were as follows:

Propane, from the Phillips Petroleum Company, c. p. grade, over 99% pure.

Propene, from the Matheson Company, c. p. grade, over 99% pure.

Cyclopropane, from the Mallinckrodt Chemical Company, over 99% pure.

Propyne, prepared by us by treating sodium acetylide with dimethyl sulfate.³

Propadiene, prepared for us by Dr. R. E. Schaad from 2,3-dibromopropane and zinc.⁴

Each hydrocarbon was purified carefully by fractionation on a low temperature Podbielniak column. Five cuts were taken on the plateau

(3) L. Tschugajeff, *Ber.*, **33**, 3122 (1900).

(4) G. Gustavson and N. Demjanow, *J. prakt. Chem.*, [2] **38**, 202 (1888).