

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

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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

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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).