

both at 25 and at 100°: at 25°, 97–98.0% strontium chromate by titration; at 100°, 96.7%.

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### The Identification of Polynitro Aromatic Compounds as Addition Compounds with Naphthalene<sup>1</sup>

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Although polynitro aromatic compounds are not rare in industry and are common derivatives for identifying other aromatic compounds, there is no systematic procedure for their own identification. As a class they can be detected by color reactions,<sup>2</sup> but their derivatives generally owe their existence to the reactivity of some other functional group in the molecule. If no such group is present, recourse must be had to either (a) reduction, which is difficult to control and frequently yields polyamines requiring acylation to make them suitable derivatives, or (b) further nitration, which may be impossible.

In view of the well-known excellence of picric acid and other polynitro aromatic compounds as reagents for identifying condensed-ring aromatic compounds, the reverse procedure, suggested by Mulliken<sup>3</sup> and Clarke<sup>4</sup> and more explicitly by Reichstein<sup>5</sup> and Coghill and Sturtevant,<sup>6</sup> seemed worth systematic extension. The attractiveness of the method was increased by a literature search, which showed that 39 polynitro compounds of the 47 that had been studied form complexes with naphthalene. We retained naphthalene as the reagent because of this prior use and because it is universally available and easy to purify.

We chose for study polynitro compounds which either are commercially available and therefore

commonly encountered, or are themselves derivatives used in qualitative organic analysis. In each case the polynitro compound-naphthalene system was investigated by an application of cooling-curve technique to the method used by Baril and Hauber<sup>7</sup> for hydrocarbon picrates. If the curve for the equimolecular mixture indicated compound formation, the stability of the supposed compound toward recrystallization was tested. If recrystallization caused decomposition, we usually considered it necessary to construct the whole melting point-composition diagram, since a plateau on the cooling curve might represent merely the crystallization of a eutectic mixture at the fifty mole per cent. point.

Of the seventeen new derivatives thus found and described in Table I, all but four can be recrystallized without decomposition. Even these four can be used in qualitative analysis; but inasmuch as the molecular weight must be known before an equimolecular mixture can be made, this method without recrystallization is merely confirmatory

TABLE I  
NEW DERIVATIVES OF POLYINITRO COMPOUNDS

M. p., °C. (corr.)	Polynitro compound	M. p. of C <sub>10</sub> H <sub>8</sub> deriv., °C. <sup>a</sup> (corr.)
62	Isoamyl 3,5-dinitrobenzoate <sup>b</sup>	46–47
63	2,6-Dinitrophenol <sup>c</sup>	58–58.5
68	2,4,6-Trinitroanisole	69–70 <sup>f</sup>
79	2,4,6-Trinitrophenetole	39
86	2,4-Dinitrophenetole	41 <sup>d</sup>
86.5	3,5-Dinitro- <i>o</i> -cresol	94
88	1-Iodo-2,4-dinitrobenzene <sup>e</sup>	66–67
89	2,4-Dinitroanisole	50
93	Ethyl 3,5-dinitrobenzoate	75 <sup>f</sup>
98	Ethyl 3,5-dinitrosalicylate	78 <sup>d,f</sup>
106	2,4-Dinitro-6-cyclohexylphenol	73–74
106	3,5-Dinitroanisole	69 <sup>d</sup>
117	3-Chloro-2,4,6-trinitrophenol	127
119	2,4,6-Trinitrobenzaldehyde <sup>e</sup>	136.5
123	3,5-Dinitroguaiacol	94
147	2,4-Dinitroresorcinol	165
171	2,4,2',4'-Tetranitrobenzyl <sup>g</sup>	136 <sup>d,f,h</sup>

<sup>a</sup> Capillary melting points are given unless otherwise stated. The melting points from cooling curves are generally about 2° lower. <sup>b</sup> Ref. 5. <sup>c</sup> Eastman Kodak Co. product. <sup>d</sup> Value obtained from the cooling curve only; compound could not be recrystallized without decomposition. <sup>e</sup> Körner, *Gazz. chim. ital.*, **4**, 323 (1874). <sup>f</sup> Result verified by melting point-composition diagram. <sup>g</sup> Braun and Rawicz, *Ber.*, **49**, 802 (1916). <sup>h</sup> Compound may melt incongruently; the temperature-composition curve was not determined accurately enough to decide the question. <sup>i</sup> Asahina and Shinomiya, *J. Chem. Soc. Japan*, **59**, 341 (1938), reported 54° for this m. p.

(7) Baril and Hauber, *THIS JOURNAL*, **53**, 1087 (1931).

(1) This is an abstract of a thesis submitted by R. B. Smith in partial fulfillment of the requirements for the degree of Master of Science at the Oklahoma Agricultural and Mechanical College in 1938. Nearly all this material was presented at the Milwaukee meeting of the American Chemical Society, September, 1938.

(2) Houben, "Die Methoden der organischen Chemie," G. Thieme, Leipzig, 3rd edition, Vol. IV, 1924, pp. 190–192.

(3) Mulliken, "A Method for the Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1916, Suborder II, various pages.

(4) Clarke, "A Handbook of Organic Analysis," Edward Arnold and Company, London, 1928, pp. 240–241.

(5) Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926); Sutter, *ibid.*, **21**, 1266 (1938).

(6) Coghill and Sturtevant, "An Introduction to the Preparation and Identification of Organic Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1936, p. 202.

and requires previous supporting evidence. Twenty-nine polynitro compounds yielded no 1:1 complexes with naphthalene: 2,4-dinitrobenzaldehyde, 2,4-dinitrodiphenyl ether, 2,4-dinitrodiethylaniline, 2,4-dinitromesitylene, 2,6-nitrohydroquinone-4-acetate, 2,4-dinitrobenzyl acetate, 1-*t*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene, 2,4-dinitrobenzyl alcohol, 2,4-dinitroacetanilide, 2,2'-dinitrobiphenyl, 4,5-dinitroveratrole, 2,6-dinitrohydroquinone, 2,4-dinitro-1-naphthol, 2,3,4,6-tetranitrophenol, 3,4,5-trinitroveratrole, 2,4-dinitro-1-naphthol-7-sulfonic acid, 2,4-dinitrodiphenylamine, 2,4,2',4'-tetranitrobiphenyl (eutectic at about 85 mole % naphthalene), picramic acid, 2,4,2',4'-tetranitrodiphenylmethane (eutectic at about 90 mole % naphthalene), 1,8-dinitronaphthalene, 2,4-dinitrophenylacetic acid, 2,4-dinitrophenylhydrazine, 3,3'-dinitrobiphenyl, 3,5-dinitrobenzoic acid, 1,3,8-trinitronaphthalene, 2,4,6-trinitrobenzoic acid, 4,4'-dinitrobiphenyl.

Although the method of identification outlined in this paper is not general in application, it has compensating desirable features. It is simple, rapid, and inexpensive, and it gives derivatives from which the only possible impurities, the original reagents, usually may be removed by recrystallization.

The attempt to deduce rules correlating structure of a polynitro compound with its ability to yield a stable complex is beset with difficulties. Although it is clear that polynitrophenols usually give stable derivatives, which in many cases even melt higher than either of their constituents, there are several exceptions. Phenolic ethers mostly resemble the phenols in behavior, but the complexes are much less stable. At the other extreme are polynitro amines, which rarely yield compounds with naphthalene.<sup>8</sup> Our results on 2,4-dinitromesitylene and 1-*t*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene confirm earlier reports<sup>9</sup> of the hindering effect of methyl groups situated between nitro groups on the ability of the latter to cause compound formation.

As might have been predicted for polynuclear compounds, at least two nitro groups must be present on each ring if addition compounds are to be formed<sup>10</sup>; but their relative positions on a ring

are also of consequence. In particular, nitro groups ortho to each other both seem to diminish in ability to promote reaction. This is obvious in the cases of *o*-dinitrobenzene and 3,4-dinitrotoluene,<sup>11</sup> and may explain the failure of 2,3,4,6-tetranitrophenol, 2,3,4,6-tetranitroaniline,<sup>12</sup> and the polynitroveratroles to yield complexes; but the generalization fails to account for the activity of 2,3,4-trinitrotoluene, 4,5,6-trinitro-*o*-cresol, and several polynitrochlorobenzenes.<sup>13</sup>

The preponderance of high-melting polynitro compounds among those which formed no addition products suggests that the dominant factor is not structure, but melting point, of the polynitro compound; and of course high melting point connotes lowered mutual solubility of naphthalene and the polynitro compound.

### Experimental

The naphthalene used was a commercially resublimed sample which we recrystallized from alcohol. The other principal reagents were prepared or otherwise obtained as shown in Table I.

The apparatus employed for determining cooling curves was patterned after that of Washburn.<sup>14</sup> To avoid the need of a specially constructed Dewar flask, three test-tubes of different sizes were fitted together concentrically by cork stoppers. The thermometer, which served also as a stirrer, was supported loosely in the small central tube by another cork stopper.

Ten millimoles each of naphthalene and the polynitro aromatic compound were fused together and transferred to the central tube of the apparatus. The whole apparatus was heated until the material melted, and then allowed to cool slowly, supercooling of the melt being minimized by stirring and seeding. It was thus possible to obtain reproducible cooling curves, on which plateaus parallel to the time axis were considered evidence of compound formation. The thermometer was calibrated in the apparatus by using compounds of known purity and melting points: diphenylamine, naphthalene, and benzoic acid.

The compounds indicated to exist were recrystallized, usually from the minimum amount of alcohol, and then examined under the microscope for homogeneity. If dissociation had occurred, we used Rheinboldt's "thaw-point" technique<sup>15</sup> to learn the form of the melting point-composition curve, since this is a rapid semi-micro method

*ibid.*, 1108 (1936)] have shown that mononitro compounds containing electron attracting groups in both meta positions can yield addition compounds. Since Hammick and Hellicar<sup>9b</sup> claim this kind of reinforcing influence for chlorine, we have examined the behavior of 3,5-dichloronitrobenzene and found it to give no 1:1 compound with naphthalene. Evidently the electron attracting power of chlorine is not so great as that of the groups employed by Bennett.

(11) Kremann and Rodinis, *Monatsh.*, **27**, 125 (1906).

(12) Davis and James, *Aberystwith Studies*, **4**, 213 (1922).

(13) Beilstein, "Handbuch der organischen Chemie," Verlag von J. Springer, Berlin, 4th edition.

(14) Washburn, *Ind. Eng. Chem.*, **16**, 275 (1924).

(15) Rheinboldt, in Houben, "Die Methoden der organischen Chemie," G. Thieme, Leipzig, 3rd ed., Vol. I, 1925, p. 1169.

(8) Compare Buehler, Hisey and Wood, *THIS JOURNAL*, **52**, 1939 (1930).

(9) (a) Efremov and Tikhomirova, *Ann. inst. anal. phys. chim.*, **4**, 65 (1928); (b) Hammick and Hellicar, *J. Chem. Soc.*, 761 (1938).

(10) Cf. Hertel and Kurth, *Ber.*, **61**, 1650 (1928). No exceptions involving polynitro compounds are known, but Bennett and co-workers [Bennett and Willis, *ibid.*, 266 (1929); Bennett and Wain,

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 Dithiocyanates<sup>1</sup>

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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 suggestion<sup>2</sup> that olefins be identified as addition products with osmium tetroxide can hardly be expected to improve the situation. Since Bruson and Calvert<sup>3</sup> 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,<sup>4</sup> we thought it desirable to test the method further, particularly with aliphatic and alicyclic olefins.

Thiocyanogen was obtained either from sodium thiocyanate and cupric sulfate<sup>5</sup> or by the action of bromine on plumbous thiocyanate.<sup>4a</sup> 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,<sup>3,4b,4c</sup> 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,<sup>6</sup> butene-1, butene-2,<sup>7</sup> 2-methylpropene-1,<sup>6</sup> pentene-2,<sup>7</sup> 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,<sup>4b</sup> 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)<sub>2</sub>, would give derivatives with higher melting points;<sup>6</sup> 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 10 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 C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>S<sub>2</sub>: 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 C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub>: N, 13.21. Found: N, 12.96.

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## Sodium Ethylene Carbide

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In 1927 Walker<sup>1</sup> 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).