[Contribution from Research Laboratories, Goodyear Tire and Rubber Company]

ACTION OF NASCENT THIOCYANOGEN UPON ISOPRENE AND DIMETHYLBUTADIENE

By Herman A. Bruson and William A. Calvert

Received February 27, 1928 Published June 5, 1928

The identification of certain low boiling, unsaturated hydrocarbons which yield only liquid addition products with the halogens or hydrogen halides is often a matter of considerable difficulty. Especially is this true of isoprene which readily undergoes substitution, polymerization and resinification upon treatment with bromine or hydrogen bromide. By the use of hypochlorous or hypobromous acids Mokijewski[1] obtained crystalline addition compounds of isoprene which serve as characteristic derivatives.

In attempting to prepare a derivative which would be more stable it occurred to us to treat both isoprene and its methyl homolog, 2,3-dimethylbutadiene, with thiocyanogen. Söderbäck[2] and Kaufmann[3] as well as Challenger and others[4] have observed that thiocyanogen adds to the unsaturated bonds of organic compounds in a manner analogous to bromine and forms, in many cases, well defined, crystalline addition products. However, no mention is made concerning the action of thiocyanogen upon unsaturated hydrocarbons containing two reactive double bonds as exemplified by the butadienes.

When a solution of thiocyanogen prepared by the method of Söderbäck[2] from lead thiocyanate and bromine in anhydrous benzene, was allowed to react in excess at 0° with either isoprene or 2,3-dimethylbutadiene, addition took place, but only traces of crystalline reaction products could be isolated. Polymerization of the thiocyanogen to the insoluble compound $(SCN)_x$ apparently occurred before any appreciable addition to the hydrocarbon was effected.

However, by generating the thiocyanogen in the nascent state according to the method of Kaufmann and Oehring[5] addition took place smoothly at 5°, isoprene and dimethylbutadiene yielding beautiful, crystalline compounds of sharp melting point. The analysis of these addition products indicated that only one mole of $(SCN)_2$ added to one mole of hydrocarbon despite the fact that a slight excess of thiocyanogen was available for completely adding to both double bonds. No tetrathiocyanate could be isolated under the conditions employed.

[1] Mokijewski, *Chem. Z.*, **19**, 2254; *Chem. Zent.*, **70**, I, 590 (1899).

[2] Söderbäck, *Ann.*, **419**, 217 (1919); **443**, 142 (1925).

[3] Kaufmann, *Ber. deut. pharm. Ges.*, **33**, 139 (1923).

[4] Challenger, Smith and Paton, *J. Chem. Soc.*, **123**, 1046 (1923); Challenger and Bott, *ibid.*, **127**, 1039 (1925).

[5] Kaufmann and Oehring, *Ber.*, **59**, 187 (1926).

We have not investigated the mode of addition, that is, whether it is 1,2 or 1,4. The behavior of butadiene[6] and of isoprene[7] with bromine and hydrogen bromide would indicate that the addition of $(SCN)_2$ would by analogy also occur preferentially in the 1,4-position, although in view of the recent work of Farmer, Lawrence and Thorpe[8] some doubt is cast upon the infallibility of 1,4-addition in the case of butadiene.

The addition product of thiocyanogen with isoprene and with dimethylbutadiene is a useful, characteristic derivative for purposes of identification and for further synthetic work.

Experimental

Isoprene and $(SCN)_2$.—The isoprene was prepared by passing the vapors of limonene over a glowing platinum spiral *in vacuo.*[9] The crude isoprene (b. p. 33–40°) thus obtained was allowed to stand over barium peroxide for ten days to remove amylenes and was then fractionated using a three-foot Vigreaux column with baffles. The fraction boiling at 33–34° was used.

Ten cc. of isoprene (7 g.) dissolved in 35 cc. of glacial acetic acid was added to a solution of 36 g. of sodium thiocyanate dissolved in 335 cc. of glacial acetic acid, and into the cooled mixture at 5–6° a solution of 11 cc. of bromine dissolved in 65 cc. of glacial acetic acid was slowly allowed to drop, the thiocyanate solution meanwhile being vigorously stirred. The room was darkened so that a minimum of polymerization of the thiocyanogen would occur.

After addition of the bromine solution, which should take about fifteen minutes, the stoppered mixture was allowed to stand in the ice chest for twelve hours. The yellow precipitate of polymerized thiocyanogen was filtered off and washed with 50 cc. of glacial acetic acid, the washings being combined with the filtrate, which was then diluted with twice its volume of water and made alkaline by the addition of excess solid sodium carbonate. A yellowish, waxy material separated. It was skimmed off, washed with cold water, then dissolved in 50 cc. of cold benzene and filtered. The filtrate when added to 100 cc. of cold ligroin and stirred crystallized in glistening plates. The slightly yellowish crystals were purified by bone-blacking once in hot benzene and recrystallizing twice from benzene–ligroin mixture; yield of pure product, 4 g.

The pure dithiocyano addition product of isoprene formed colorless, glistening platelets, m. p. 76–77° (corr.). It is very soluble in cold benzene, chloroform, acetone, ether and alcohol, somewhat less soluble in glacial acetic acid and only slightly soluble in petroleum ether or cold ligroin. For analysis the compound was dried in high vacuum at 35°.

Anal. Subs., 0.2166 required 23.5 cc. of 0.1 N H_2SO_4 (Kjeldahl); 0.1240 gave 0.3166 g. of $BaSO_4$ (Carius). Calcd. for $C_7H_8S_2N_2$: S, 34.77; N, 15.21. Found: S, 35.00; N, 15.19.

Mol. wt. (Cryoscopic in benzene; $K = 51$). Subs., 0.1052, 0.1976; benzene, 16.16. ΔT, 0.182°, 0.335°. Calcd.: 184. Found: 182.4, 186.4.

The compound possesses a faint, disagreeable odor; its solutions cause blistering of the skin and its dust creates a sickening metallic taste in the mouth when inhaled.

---

[6] Thiele, *Ann.*, **308**, 339 (1899).

[7] Staudinger and others, *Helv. chim. acta*, **5**, 743, 756 (1922).

[8] Farmer, Lawrence and Thorpe, *J. Soc. Chem. Ind.*, **47** [4] 101 (1928).

[9] Staudinger and Klever, *Ber.*, **44**, 2215 (1911).

Dimethylbutadiene and $(SCN)_2$

The 2,3-dimethylbutadiene was prepared by the catalytic dehydration of anhydrous pinacone, according to the method of Kyriakides[10] employing hydrobromic acid. After purification and fractionation, it boiled at 67–60°

Twenty cc. (15 g.) of dimethylbutadiene dissolved in 75 cc. of glacial acetic acid was added to 500 cc. of glacial acetic acid containing 72 g. of dissolved potassium thiocyanate, and into the cooled mixture at 6° a solution of 18.6 cc. of bromine in 110 cc. of glacial acetic acid was allowed to drop slowly with stirring. After standing for twelve hours in the ice chest, the precipitate was filtered off and washed with water to remove acetic acid and inorganic salts. It was dried by washing with alcohol and ether, then boiled with 100 cc. of benzene and filtered hot through a hot water funnel. The yellow, insoluble $(SCN)x$ remains behind on the filter. The filtrate upon cooling crystallized in yellowish needles which were bone-blacked in boiling benzene and allowed to recrystallize. For analysis the compound was redissolved in boiling ethyl acetate and upon cooling crystallized in well formed, colorless, odorless, rhombohedrons; yield, 5 g. of pure product; m. p. 130° (corr.).

It is very difficultly soluble in boiling alcohol, ether or acetone, but dissolves in hot benzene, chloroform and ethyl acetate. It was dried in a high vacuum at 75° for analysis.

Anal. Subs., 0.1290 required 13.3 cc. of 0.1 N H_2SO_4 (Kjeldahl); 0.1342 gave 0.3159 g. of $BaSO_4$ (Carius). Calcd. for $C_8H_{10}S_2N_2$: S, 32.31; N, 14.14. Found: S, 32.27; N, 14.43.

Summary

Isoprene and dimethylbutadiene each add one molecule of thiocyanogen to form well defined, crystalline addition products which may be used to characterize these hydrocarbons.

AKRON, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

HEXA-TERTIARY-BUTYLETHYNYLETHANE

BY PAUL L. SALZBERG WITH C. S. MARVEL

RECEIVED MARCH 1, 1928 PUBLISHED JUNE 5, 1928

The observed cases of dissociation of hexa-substituted ethanes have been limited to compounds containing at least two aryl groups attached to each of the carbon atoms which tend to separate and become trivalent. Consequently it has seemed logical to attribute the weak character of the ethane linkage to some properties of the neighboring aromatic nuclei, such as size (steric hindrance), weight and degree of unsaturation.

It has been suggested several times that the substitution of unsaturated aliphatic radicals for the hydrogen atoms of ethane might also weaken the central carbon–carbon bond. An indication of the similarity between the unsaturation of an acetylenic linkage and of a benzene nucleus has

---

[10] Kyriakides, THIS JOURNAL, **36**, 991 (1914).