[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, QUARTERMASTER RESEARCH AND ENGINEERING CENTER]

The Volatile Isothiocyanates in Fresh Cabbage[1]

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The presence of four thioureas in a mixture derived from the volatile isothiocyanates of fresh white cabbage has been indicated by paper chromatography and countercurrent distribution. The predominant component has been proved unequivocally to be allylthiourea by isolation of S-methyl-N-allylisothiuronium picrate, and the presence of 3-methylthiopropylthiourea has been established unambiguously by chromatography and infrared spectroscopy. Evidence is presented that two of the remaining constituents are 3-butenylthiourea and 3-methylsulfinylpropylthiourea. Estimates of the quantities of isothiocyanates present in fresh cabbage are given.

The nature of the isothiocyanates in various plants of the genus *Brassica* has been the subject of several recent investigations.[2,3] With few exceptions, the seeds, rather than the fresh parts of the plant, have been studied. The volatile isothiocyanates released from the thioglucosides in cabbage are believed to be of importance to the taste and odor of the fresh vegetable.[4] The presence of allyl isothiocyanate in the head of white cabbage and of allyl isothiocyanate and 3-butenyl isothiocyanate in the head of red cabbage has been indicated, on the basis of paper chromatographic evidence in only one solvent system, by Kjaer and co-workers.[2a]

In the present investigation, the fresh, wet tissues of white cabbage heads were macerated, subjected to enzymatic action for the liberation of the mustard oils from the thioglucosides, and extracted with *n*-hexane. The resultant solution of isothiocyanates was steam distilled and converted to thioureas. Paper chromatography indicated the presence of four thioureas, namely, allyl-, 3-methylthiopropyl-, 3-butenyl- and 3-methylsulfinylpropylthiourea.[5] The simultaneous occurrence of allyl and 3-methylthiopropyl isothiocyanates is reasonable since the former (or its glucoside) could be derived from the latter by the mere loss of methyl mercaptan.

Allylthiourea was separated from the mixture by countercurrent distribution. It was characterized by the formation of a crystalline derivative, S-methyl-N-allylisothiuronium picrate. The identity of the derivative with an authentic sample[6] was established by a mixed melting point determination, X-ray diffraction analysis and infrared spectra of the natural and synthetic compounds, giving the first unequivocal proof of the occurrence of allyl isothiocyanate in fresh cabbage leaves.

Evidence for 3-methylthiopropylthiourea was obtained by paper chromatography in four different solvent systems. By successive elution paper chromatography from two different solvent systems a sample was prepared which gave an identical infrared spectrum with that of an authentic sample. Because of the identification of 3-methylthiopropylthiourea, the tentative assignment of 3-methylsulfinylpropylthiourea to a paper chromatographic spot was made more reasonable. The coexistence of such compounds and the possibility of artifact formation has been discussed by Kjaer, *et al.*[3,7]

Spots were found on paper chromatograms for 3-butenylthiourea in three different solvent mixtures corresponding to those obtained from a synthetic sample.

The fallacy of using one system of paper chromatography for the identification of compounds was demonstrated by our initial results indicating the presence of *sec*-butylthiourea in the mixture.[8] The latter compound had been assigned tentatively to the spot at R_{Ph} 0.74 obtained in a chloroform–water system, since this isothiocyanate had been reported to occur in similar plant sources.[2,3] As later proved, this spot was due to 3-methylthiopropylthiourea.

A summary of the concentrations of the compounds identified is given in Table I.

TABLE I

ESTIMATED AMOUNTS OF ISOTHIOCYANATES IN FRESH CABBAGE

Isothiocyanate	Parts per million
Allyl	2.9
3-Methylthiopropyl	0.15
3-Butenyl	0.016
3-Methylsulfinylpropyl	Traces

Experimental

Extraction of Isothiocyanates.—One hundred pounds of cabbage,[9] *Brassica oleracea var. capitata alba* L. (Bonanza regular and Yellows resistant varieties), was shredded in a Hobart mixer and enzymatic action was allowed to take place at room temperature for 18 hours. After the addition of 55 l. of water and 11 kg. of sodium chloride, the resultant slurry was extracted three times by stirring with 15- to 20-l.

(1) Presented in part at the 134th National Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

(2) (a) K. A. Jensen, J. Conti and A. Kjaer, *Acta Chem. Scand.*, **7**, 1267 (1953); (b) A. Kjaer, J. Conti and K. A. Jensen, *ibid.*, **7**, 1271 (1953); (c) A. Kjaer and R. B. Jensen, *ibid.*, **10**, 1365 (1956); (d) M. G. Ettlinger and J. E. Hodgkins, THIS JOURNAL, **77**, 1831 (1955); (e) P. Delaveau, *Ann. pharm. franç.*, **14**, 765, 770 (1956); (f) M. A. Stahmann, K. P. Link and J. C. Walker, *J. Agr. Research*, **67**, 49 (1943).

(3) The natural isothiocyanates and the corresponding thioglucosides recently have been reviewed by A. Kjaer, "Encyclopedia of Plant Physiology," Vol. IX, Springer–Verlag, Berlin–Göttingen–Heidelberg, 1958, p. 71.

(4) E. J. Hewitt, D. A. M. Mackay, K. Konigsbacker and T. Hasselstrom, *Food Technol.*, **10**, 487 (1956).

(5) The names used in *Chemical Abstracts* for these compounds are 1-allyl-2-thiourea, 1-[3-(methylthio)-propyl]-2-thiourea, 1-(3-butenyl)-2-thiourea and 1-[3-(methylsulfinyl)-propyl]-2-thiourea.

(6) A. E. Dixon, *J. Chem. Soc.*, **83**, 550 (1903).

(7) A. Kjaer, R. Gmelin and I. Larsen, *Acta Chem. Scand.*, **9**, 1143 (1955).

(8) This observation corresponds to that of A. Kjaer, *et al.*[7] Dr. Martin G. Ettlinger and Mrs. C. Thompson have obtained an R_{Ph} value of 0.76 (by ascent) for 3-methylthiopropylthiourea rather than 0.82 (by descent) reported by Kjaer, *et al.*

(9) Obtained fron the Waltham Experiment Station of the University of Massachusetts through the courtesy of Professor Robert E. Young.

portions of *n*-hexane. The combined extracts (approximately 55 l.) were dried over anhydrous sodium sulfate, filtered and concentrated to 2.4 l. by distillation through a short column at atmospheric pressures. An eight-inch Fenske-type column[10] packed with glass helices was employed in the further concentration of this solution, in order to avoid possible loss of isothiocyanates. Concentration of a 231-cc. portion of the 2.4 l. of solution was continued at atmospheric pressure until, with the bath temperature raised to 105.5° and the temperature of the solution in the distilling flask at 88°, no more distillate was collected. The brown, viscous concentrate amounted to 6.8 g. Samples of the distillate gave no test for isothiocyanates with sodium azide–iodine solution.[11]

Vacuum Steam Distillation.—An all-glass vacuum steam distillation apparatus[12] was used. The concentrate from the hexane solution was steam distilled in 7- to 12-g. portions at a temperature of 35–36° and a pressure of 36–38 mm. After the distillation had been allowed to proceed for 4 hours, the distillate (*ca.* 60 cc.) was extracted with peroxide-free ether, and the condensing surfaces of the Dry Ice traps were thoroughly washed with ether. The combined ether extracts and washings were dried over anhydrous sodium sulfate and filtered.

Considerable non-volatile material remained as a viscous oil in the distilling flask after the steam distillation. When the distillation was continued for an additional period and the distillate tested for the presence of isothiocyanates by treatment with ammonia and subsequently with Grote reagent,[13] no color could be detected.

Conversion to Thioureas.—The ether solution from each portion of the vacuum steam distillation was treated with an approximately equal volume of methanol saturated with ammonia. After the solution had been allowed to stand at room temperature overnight, most of the solvent was removed on the steam-bath, and concentration to a dark brown, viscous oil was completed under reduced pressure. The total concentrate amounted to 740 mg. An ultraviolet absorption spectrum of this crude product in ethanol showed a maximum at 243 mμ characteristic of substituted thioureas.[14] Using a correction for non-specific absorption,[14] 146 mg. of thiourea, calculated as allylthiourea, was estimated to be present in the crude product by ultraviolet spectrophotometric analysis.

This material could be purified further by extraction with water. A 67-mg. sample was extracted four times with 2-cc. portions of water while being warmed in a bath at 65–70°. The combined extracts were concentrated at a bath temperature below 40° to a yellow-brown oil (22.2 mg.). The material remaining undissolved by water gave no blue color when tested for thioureas with Grote reagent.

Identification of Allylthiourea. (a) Paper Chromatography.—A portion of the water-soluble yellow-brown oil was examined by paper chromatography in a chloroform–water system,[15] using Grote reagent as a spray. Four spots were observed: a purple spot at the origin, an intense blue spot at R_{Ph} 0.25–0.27,[16] a blue spot at R_{Ph} 0.74 and a weak blue spot at R_{Ph} 0.61. The blue spot at R_{Ph} 0.25–0.27 corresponded to that of allylthiourea.[15] In a butanol–toluene–water (3:1:1) system,[17] a strong blue spot was observed at R_{Ph}0.90, corresponding to allylthiourea.

(b) **Countercurrent Distribution.**—On the assumption that the spots found in the chloroform–water chromatogram at R_{Ph} 0.25, 0.74 and 0.61 were due to allylthiourea, *sec*-butylthiourea and 3-butenylthiourea, respectively,[2a] a theoretical curve for a 60-transfer countercurrent distribution in a water–chloroform (1:2) system of a mixture of the compounds was calculated. Partition coefficients in the water–chloroform system were calculated by distributing weighed samples between equal volumes of solvents and determining the concentrations gravimetrically. A coefficient of 9.15 was found for allylthiourea and 1.64 for *sec*-butylthiourea. A value of 2.04 has been reported for 3-butenylthiourea.[2b] The curve showed that allylthiourea, with a maximum at tube 49, could be separated from the other two components. The individual curves of *sec*-butylthiourea and 3-butenylthiourea had maxima at tubes 27 and 30, respectively. A distribution of a known mixture of the thioureas in a 60-transfer Craig apparatus confirmed the theoretical curve. Although *sec*-butylthiourea and 3-butenylthiourea[18] were not separated, paper chromatographic examination of the tubes indicated that the maximum of *sec*-butylthiourea appeared at a lower tube number in the distribution.

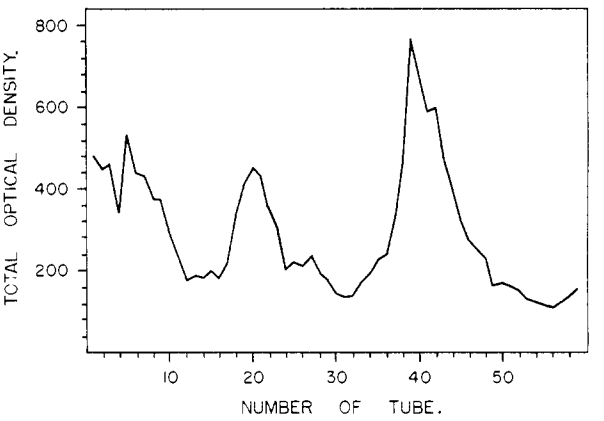

Fig. 1.—Distribution pattern of unknown mixture of thioureas. Total optical density refers to the volume of solution (cc.) × optical density at 240 mμ.

3-Methylthiopropylthiourea was reported to have a water–chloroform partition ratio of 1.35 by Kjaer and co-workers,[7] who had originally isolated the isothiocyanate from the seeds of *Iberis sempervirens* L. From this value, the position of the maximum of 3-methylthiopropylthiourea in the 60-transfer countercurrent distribution can be calculated to be at tube 24, and its location relative to the maxima of 3-butenylthiourea and allylthiourea is the same as that for *sec*-butylthiourea.

A 60-transfer distribution of a 102-mg. sample of the water-extracted, crude unknown mixture was carried out similarly. The stationary phase consisted of 10-cc. portions of water-saturated chloroform; 5-cc. portions of chloroform-saturated water were added as the upper phase. After the distribution had been completed, the contents of each tube were concentrated under reduced pressure in an atmosphere of nitrogen at a bath temperature below 45°. Each residue was dissolved in alcohol, and concentrations were determined by measuring optical densities at 240 mμ in a Beckman DU spectrophotometer. The curve obtained is shown in Fig. 1. Spot tests with Grote reagent were carried out for each of the tubes, and paper chromatograms in chloroform–water were made for selected fractions. From these results it was evident that the spot of R_{Ph} 0.74 began to appear at tube 16 and was strongest in the range from tube 19 to 24. The spot at 0.61 occurred in the tube 25 to 35 range. The 0.25–0.27 spot began to appear at tube 25, was strongest from tube 33 to 46, and disappeared at tube 52. The shift to lower tube numbers, as compared to the theoretical curve, was apparently a result of the presence of impurity in the unknown mixture. The strong absorption below tube 12 was not due to thioureas.

(c) **Isolation as S-Methyl-N-allylisothiuronium Picrate.**—Tubes 36–45, comprising the fraction believed to contain allylthiourea, were combined, concentrated to an oil and dissolved in 5 cc. of absolute ethanol. By measurement of the absorbance at 240 mμ, this solution was found to have a maximum concentration of 17.8 mg. of allylthiourea. To a 2.5-cc. portion (8.9 mg., 0.077 mmole, of allylthiourea) of the solution was added a solution of 114 mg. (0.84 mmole) of methyl iodide in 1 cc. of 95% ethanol. After this solution

(10) T. P. Carney, "Laboratory Fractional Distillation," The Macmillan Co., New York, N. Y., 1949, p. 111.

(11) F. Feigl, "Spot Tests," Vol. II, Elsevier Publishing Co., Houston, Tex., 1954, p. 302.

(12) A. E. Bailey and R. O. Feuge, *Ind. Eng. Chem., Anal. Ed.*, **15**, 280 (1943).

(13) I. W. Grote, *J. Biol. Chem.*, **93**, 25 (1931).

(14) A. Kjaer, J. Conti and I. Larsen, *Acta Chem. Scand.*, **7**, 1276 (1953).

(15) A. Kjaer and K. Rubinstein, *ibid.*, **7**, 528 (1953).

(16) R_{Ph} is defined as the ratio of the distance traveled by a compound to the distance traveled by phenylthiourea.

(17) This system was suggested to us by Dr. Martin G. Ettlinger, and the chromatographic technique was the same as described in ref. 15.

(18) Samples of 3-butenyl isothiocyanate were kindly supplied by Dr. M. G. Ettlinger and Dr. A. Kjaer.

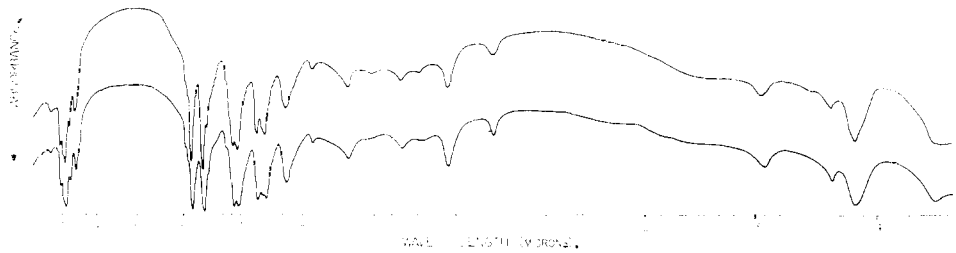

Fig. 2.—Infrared spectra: upper curve, eluted sample; lower curve, 3-methylthiopropylthiourea.

had been refluxed on the steam-bath for 10 minutes, it was treated with a solution of 17.5 mg. (0.077 mmole) of picric acid in 1.75 cc. of 95% ethanol. The resulting solution was concentrated under reduced pressure in an atmosphere of nitrogen to approximately 0.6 cc. A crystalline precipitate began to separate during the concentration. After the addition of 9 or 10 drops of water and thorough cooling, the precipitate was separated by centrifugation. The precipitate was extracted twice on the steam-bath with 1-cc. portions of water. The picrate precipitated from the filtered extracts as slender yellow needles. Recrystallization from 1 cc. of water yielded 8.6 mg., m.p. 146–147.5°.[19] A mixture of this product and S-methyl-N-allylisothiuronium picrate[6] prepared from authentic allylthiourea melted similarly at 145.5–147°.

An X-ray diffraction pattern of the product was identical to that of authentic S-methyl-N-allylisothiuronium picrate that had been crystallized similarly from water. A micro infrared spectrum[20] was also identical to that of the known compound.

Identification of 3-Methylthiopropylthiourea.—Because of the possibility that the spot at R_{Ph} 0.74 in chloroform–water might be due to 3-methylthiopropylthiourea rather than to *sec*-butylthiourea,[21] samples prepared by elution from paper chromatograms in chloroform–water were rechromatographed in three other solvent systems.

The paper (Whatman No. 1) used for the chromatograms to be eluted was prewashed twice with water, twice with ethanol, and twice with chloroform. Distilled water, distilled ethanol and spectrophotometric grade chloroform were used in the washing and in all subsequent work. A stock solution of 22.2 mg. of the water-extracted unknown mixture in 1 cc. of alcohol was prepared, and spots of 30–45 μl. of this solution were applied to the paper. Blank columns, one inch in width, were left on either side of the one-inch column containing the spot to be eluted. The chromatograms were developed by ascending chromatography in a chloroform–water system.[15] The position of the spot at R_{Ph} 0.74 was determined by excising and spraying the column containing the monitor spot. A strip, one inch or slightly less in width, then was cut across the blank columns and the column containing the spot to be eluted at the location indicated. This three-inch strip was suspended from a trough and eluted with ethanol by descending chromatographic irrigation in an alcohol-saturated atmosphere. A volume of 0.12–0.15 cc. of eluate was collected.

The eluates from two 30-μl. spots were combined, and an ultraviolet spectrum[22] of the solution showed the strong maximum at 244 mμ characteristic of substituted thioureas of this type.[14] The concentration, estimated from the corrected absorbance,[14] indicated that each of the 30-μl. spots contained 20.9 μg. of 3-methylthiopropylthiourea, equivalent to 7.7 mg. per 100 lb. of cabbage.

For rechromatography in other solvent systems, portions of the alcoholic eluate containing 30–32 μg. of 3-methylthiopropylthiourea were concentrated to approximately 20 μl. under reduced pressure in an atmosphere of nitrogen. The concentrates then were spotted on chromatograms in the usual way.

A comparison of the R_{Ph} and R_f values (Table II) demonstrated that the compound was not *sec*-butylthiourea and that it might indeed be 3-methylthiopropylthiourea.

TABLE II

PAPER CHROMATOGRAMS OF 3-METHYLTHIOPROPYLTHIOUREA

	Unknown sample	3-Methylthiopropylthiourea	*sec*-Butylthiourea
R_{Ph} in chloroform–water	0.74	0.76 (0.82)[a]	0.74
R_{Ph} in toluene–acetic acid–water (5:2:4)[b]	.46	.46	.64
R_f in heptane–butanol–formic acid (1:1:1)[c]	.12	.12	.26
R_{Ph} in benzene–ethanol–water (5:1:2)[b,d]	.67	.67	.74

[a] See ref. 6. [b] Suggested by Dr. Ettlinger. [c] J. Sjöquist, *Acta Chem. Scand.*, **7**, 447 (1943); see also ref. 7. [d] See also ref. 2e.

Proof that the compound was 3-methylthiopropylthiourea was obtained by infrared microspectroscopic analysis of a sample prepared by elutions from two successive paper chromatograms. A portion of the alcoholic eluate from the chloroform–water chromatograms representing 52 μg. of 3-methylthiopropylthiourea was concentrated to approximately 20 μl., as described above. The concentrate was spotted on a paper that had been previously washed with the organic layer of a toluene–acetic acid–water (5:2:4) mixture, in addition to the usual washings with water, alcohol and chloroform. After the chromatogram had been developed by ascending chromatography in a toluene–acetic acid–water (5:2:4) system,[23] a three-inch strip was excised at the location indicated by the monitor spot, and the strip was eluted with ethanol in the manner previously described. The eluate was evaporated to dryness in a lyophilization tube provided with a sintered glass cap.[24] To the tube was added 0.5 cc. of distilled water containing 1.5 mg. of potassium bromide, and the solution was lyophilized. A spectrum identical to that of known 3-methylthiopropylthiourea was obtained from a micro pellet pressed from the lyophilizate (Fig. 2). The sample of known 3-methylthiopropylthiourea was similarly prepared by lyophilization in potassium bromide solution. Eluted samples purified by chromatography in a chloroform–water system alone or by rechromatography in the same system did not give satisfactory spectra.

In model elution experiments on known samples, satisfactory spectra could be obtained from 20-μg. quantities, chromatographed in chloroform–water and eluted by the above procedure; 10-μg. quantities gave fairly satisfactory spectra. When water rather than alcohol was used as an eluting solvent, material that interfered with the spectra apparently was eluted. Elution by washing the paper briefly with alcohol rather than by chromatographic irrigation gave less satisfactory spectra. Considerable care in the purification of solvents and cleaning of glassware was required.

Identification of 3-Butenylthiourea.—The spot at R_{Ph} 0.61 in the chloroform–water system was tentatively regarded as representing 3-butenylthiourea by analogy to observations

(19) Kofler micro hot-stage; uncor.

(20) Spectra were taken in a Perkin-Elmer single-beam infrared spectrophotometer model 112, micro attachment model 85.

(21) A suggestion made by Dr. M. G. Ettlinger on the basis of his study of numerous samples of seeds of *Brassica*.

(22) Ultraviolet spectra were taken either in a Beckman model DU or a Cary 11 MS spectrophotometer.

(23) Table II, ref. *b*.

(24) We are indebted to Dr. W. B. Mason of the School of Medicine and Dentistry, University of Rochester, for the design of a very satisfactory tube for lyophilization.

TABLE III

PAPER CHROMATOGRAMS OF 3-BUTENYLTHIOUREA

	Unknown sample	3-Butenyl-thiourea
R_{Ph} in chloroform–water	0.61	0.61
R_{Ph} in benzene–ethanol–water (5:1:2)	.59	.58
R_f in heptane–butanol–formic acid (1:1:1)	.17	.18

reported previously.[2,3] By collecting eluates of the R_{Ph} 0.61 spot from a number of chloroform–water chromatograms, it was possible to obtain a quantity sufficient for rechromatography in other solvent systems. Eight 25-μl. spots of a solution of 24.6 mg. of the water-extracted unknown mixture (from 70 mg. of unextracted material) in 1 cc. of ethanol were chromatographed in a chloroform–water system, and the spots at R_{Ph} 0.61 were eluted by the method described above. The concentration, calculated[14] from an ultraviolet spectrum of the combined eluates which showed the characteristic maxima at 243 mμ, indicated that 16.2 μg. of 3-butenylthiourea had been eluted, equivalent to 0.86 mg. per 100 lb. of cabbage. For rechromatography in other solvent systems, portions of the eluate corresponding to 8 μg. of 3-butenylthiourea were concentrated and spotted, as described for 3-methylthiopropylthiourea. The chromatographic evidence for 3-butenylthiourea in three systems is shown in Table III.

Evidence for 3-Methylsulfinylpropylthiourea.—In order to study the spot that remained at the origin in the chloroform–water paper chromatogram, a chromatogram was run in a butanol–toluene–water (3:1:1) system.[17] It gave a new blue spot at R_{Ph} 0.35, which was close to that of 3-methylsulfinylpropylthiourea. With the identification of 3-methylthiopropylthiourea, this tentative assignment became more reasonable. 3-Methylsulfinylpropyl isothiocyanate[25,26] might have some volatility under the conditions employed in the vacuum steam distillation, or the sulfoxide could be formed as an artifact subsequent to the steam distillation.

Acknowledgments.—We wish to thank Dr. M. G. Ettlinger of The Rice Institute for his valuable suggestions and advice. We thank also Dr. G. Susich and Mr. A. King of the Microscopy Section of this Laboratory for the X-ray diffraction analyses, and Dr. J. D. Margerum and his associates of the Spectroscopy Section for assistance in determining the ultraviolet and infrared spectra.

(25) O. E. Schultz and R. Gmelin, *Arch. Pharm.*, **287**, 404 (1954).
(26) A. Kjaer and R. Gmelin, *Acta Chem. Scand.*, **10**, 1100 (1956).

NATICK, MASS.

[CONTRIBUTION FROM THE RESEARCH LABORATORIUM DR. C. JANSSEN]

The Synthesis of 2-R-3,3-Diphenyl-Δ^1-pyrrolines from 2,2-Diphenyl-4-bromobutyronitrile

BY PAUL J. A. DEMOEN AND PAUL A. J. JANSSEN

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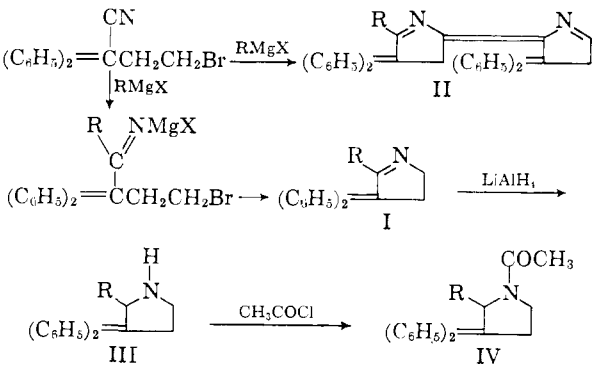
Different types of reaction products are obtained when an alkyl-, aryl- or aralkylmagnesium halide is allowed to react with 2,2-diphenyl-4-bromobutyronitrile under the conditions described. One series of reaction products consists of 2-substituted-3,3-diphenyl-Δ^1-pyrrolines, whereas the other series consists of higher melting products whose structure is discussed.

The most widely accepted method of synthesis of pyrrolines undoubtedly is the Grignard reaction between 4-chlorobutyronitriles and alkyl-, aryl- or aralkylmagnesium halides.[1–10] Little is known however about 3,3-disubstituted-Δ^1-pyrrolines.

Murray and Cloke[5] synthesized four (methyl-, ethyl-, *n*-propyl- and *n*-butyl-)2-phenyl-3-alkyl-3-phenyl-Δ^1-pyrrolines from 4-chloro-2-alkyl-2-phenylbutyronitriles and phenylmagnesium bromide. As a rule, they refluxed the Grignard reagent and the nitrile for eight hours in ether, and added the cooled mixture to liquid ammonia. After evaporation of the ammonia, the Δ^1-pyrrolines were isolated from the residue. Yields were: CH_3, 78%; C_2H_5, 70%; *n*-C_3H_7, 58%; *n*-C_4H_9, 35%. Except for the *n*-butylpyrroline, the compounds were solids. After a 6 months storage in a desiccator over phosphorus pentoxide, they changed to yellow resinous masses.



In this paper the products formed by the action of different alkyl-, aryl- or aralkylmagnesium halides on 2,2-diphenyl-4-bromo-butyronitrile are described. A typical general method was adopted,[2,3] and after suitable processing, the residual oily product was subjected to vacuum distillation. The phenomena described were observed on distillation: 1. In two cases (R = C_2H_5, *n*-C_3H_7) the distillate consisted of the expected substituted Δ^1-pyrroline I in yields between 22 and 65%, and the distillation residue after crystallization gave a pure compound with a higher melting point than the corresponding Δ^1-pyrroline. The yields were relatively low

(1) O. de Booseré, *Bull. soc. chim. Belg.*, **32**, 26 (1923).
(2) J. B. Cloke, THIS JOURNAL, **51**, 1174 (1929).
(3) L. C. Craig, H. Bulbrook and R. M. Hixon, *ibid.*, **53**, 1831 (1931).
(4) J. B. Cloke, L. H. Baer, J. M. Robbins and G. E. Smith, *ibid.*, **67**, 2155 (1945).
(5) J. V. Murray and J. B. Cloke, *ibid.*, **68**, 126 (1946).
(6) P. M. Maginnity and J. B. Cloke, *ibid.*, **73**, 49 (1951).
(7) G. G. Evans, *ibid.*, **73**, 5230 (1951).
(8) M. C. Kloetzel, J. L. Pinkus and R. M. Washburn, *ibid.*, **79**, 4222 (1957).
(9) J. H. Burckhalter and J. H. Short, *J. Org. Chem.*, **23**, 1278, 1281 (1958).
(10) D. W. Fuhlhage and C. A. VanderWerf, THIS JOURNAL, **80**, 6249 (1958).