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THE PREPARATION OF *SYM.*-DIPHENYLCARBAZIDE

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Sym.-diphenylcarbazide has come into considerable use for the detection of various metallic radicals, particularly chromium.¹ On attempting to prepare this compound by heating urea with an excess of phenylhydrazine, it was found difficult to obtain products from different runs having uniform melting points. Moreover, the melting points given in the literature vary between 151 and 171°.²

The melting point of 163–164° has been given frequently and a product melting sharply at this point (uncorrected) was often obtained in our

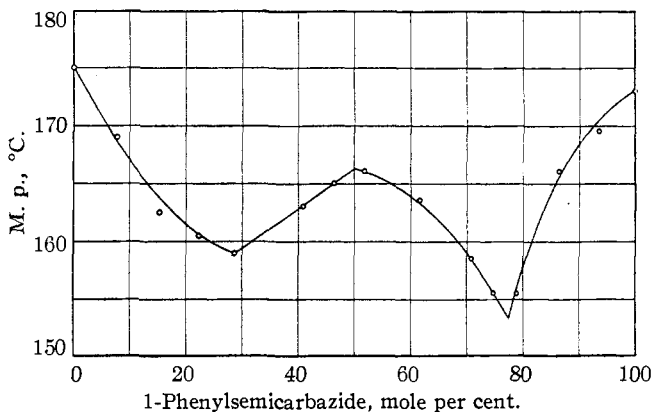


Fig. 1.—Melting-point curve of mixtures of *sym.*-diphenylcarbazide with 1-phenylsemicarbazide.

work. It was found that this substance is an addition compound of one mole of *sym.*-diphenylcarbazide with one mole of 1-phenylsemicarbazide. This was shown by analysis, by determining the melting points of mixtures of known percentages of pure *sym.*-diphenylcarbazide and 1-phenylsemicarbazide, and also by the fact that the melting point of the double compound is lowered when mixed with either pure diphenylcarbazide or pure phenylsemicarbazide, but not when mixed with an intimate mixture of equimolar portions of these two compounds. Because of the slow de-

¹ Stover, *THIS JOURNAL*, 50, 2363 (1928).

² (a) Skinner and Ruheman, *Ber.*, 20, 3372 (1887), m. p. 161° (see ref. 2 h.); (b) Fischer, *ibid.*, 22, 1935 (1889), m. p. 163–164°; (c) Heller, *Ann.*, 263, 272 (1891), m. p. 163°; (d) Cazeneuve and Moreau, *Bull. soc. chim.*, [3] 23, 53 (1900), m. p. 169–170°; (e) Oddo, *Atti. accad. Lincei*, [5] 12, 435 (1903), m. p. 168–169°; (f) Metzger and Zons, *J. Ind. Eng. Chem.*, 4, 493 (1912), m. p. 150–151°; (g) Barnebey and Wilson, *THIS JOURNAL*, 35, 157 (1913), m. p. 163.5°; (h) Bamberger, Padova and Ormerod, *Ann.*, 446, 285 (1925), m. p. 171°.

composition of all the materials at the melting point it was not possible to determine cooling curves accurately and all melting points were determined by the capillary tube method. For the same reason the mixed melting points had to be determined on material that was intimately ground together rather than on fused material. Because of the wide range of the melting points of the mixtures, the figures given in the table are the temperatures at which the material first definitely wet the side of the capillary tube. This point could be checked readily on separately prepared mixtures within 1° . The experimental results are given in the accompanying tables and graph and show a possible explanation of the discrepancy in the melting points recorded in the literature where 1-phenylsemicarbazide is a possible product. Cazeneuve and Moreau^{2d} note that an alteration in the appearance of *sym.*-diphenylcarbazide takes place at 151° but that this is not the melting point. We have noted at times a similar change at about 158° (corr.) but the true melting point of the pure material is quite sharp.

ANALYSES

	M. p. (corr.), $^\circ\text{C}$.	Calcd. C, %	Found	Calcd. H, %	Found
<i>Sym.</i> -diphenylcarbazide ($\text{C}_{18}\text{H}_{14}\text{N}_4\text{O}$)	175-175.5	64.46	64.00 64.09	5.79	5.88 5.88
1-Phenylsemicarbazide ($\text{C}_7\text{H}_9\text{N}_3\text{O}$)	173-173.5	55.63	55.87 55.69	5.96	6.11 6.04
Double compound of <i>sym.</i> -diphenylcarbazide and 1-phenylsemicarbazide ($\text{C}_{20}\text{H}_{20}\text{N}_7\text{O}_2$)	166-166.5	60.05	60.22 60.44	5.88	5.86 5.94

MELTING POINTS OF MIXTURES OF *sym.*-DIPHENYLCARBAZIDE AND 1-PHENYLSEMICARBAZIDE

1-Phenylsemicarbazide Weight, %	Mole, %	M. p. (corr.), $^\circ\text{C}$.	1-Phenylsemicarbazide Weight, %	Mole, %	M. p. (corr.), $^\circ\text{C}$.
0	0	175	50	61.5	163.5
5	7.8	169	60	70.6	158.5
10	15.1	162.5	65	74.8	156
15	22.1	160.5	70	78.9	156
20	28.5	159	80	86.4	166
30	40.8	163	90	93.5	169.5
35	46.2	165	100	100.0	173
40	51.6	166			

In order to purify the *sym.*-diphenylcarbazide prepared from urea and phenylhydrazine, it is necessary to extract the crude product with boiling distilled water repeatedly and with vigorous stirring until the melting point no longer changes. Although 1-phenylsemicarbazide is quite soluble in hot water, it is only slowly extracted from the double compound. During this process a red color develops, even when the water used for extraction has been boiled previously to remove dissolved air. This color is readily removed by washing with small portions of cold acetone, followed by a final crystallization from acetone. The product thus obtained contains one mole of acetone of crystallization, which is best removed by adding cold benzene to the dried product,

heating to boiling, allowing to cool and filtering. Neither 1-phenylsemicarbazide nor the double compound forms an addition product with acetone.

By using the method of Cazeneuve and Moreau,^{2d} who reacted phenylhydrazine with diphenyl carbonate or guaiacol carbonate instead of urea, no 1-phenylsemicarbazide is formed and the necessity for this troublesome purification is eliminated. Because it is available commercially, guaiacol carbonate is more suitable than diphenyl carbonate, although the latter gives slightly better yields. The original procedure of Cazeneuve and Moreau has been modified so that the *sym.*-diphenylcarbazine is more readily isolated in a pure state, and so that the guaiacol formed in the reaction and the excess phenylhydrazine are recovered in good yields. The same procedure has been used with equal success in runs using as much as 8 moles of guaiacol carbonate.

Preparation of *Sym.*-Diphenylcarbazine.—A mixture of 54.8 g. (0.2 mole) of guaiacol carbonate and 86.4 g. (0.8 mole) of phenylhydrazine is heated in an oil-bath at 160–165° (thermometer in liquid) for two hours with occasional shaking. The mixture is poured out into an open dish and after it has cooled it is stirred until crystallization begins. It is allowed to stand for several hours at 15° to allow complete crystallization and is then worked to a paste and extracted repeatedly with benzene until entirely free of phenylhydrazine and guaiacol. The pure white product melts at 175–175.5° (corr.) and the yield is 34–35 g., or 70–72% of the calculated amount.

Recovery of Phenylhydrazine and Guaiacol.—The benzene extracts obtained above are combined and dry hydrogen chloride passed in until the mixture becomes too pasty for good mixing. The phenylhydrazine hydrochloride is filtered with suction and thoroughly washed with benzene. The combined filtrates are treated again with hydrogen chloride and the process is repeated until the precipitate becomes distinctly pink. Hydrogen chloride is then passed in until nothing further precipitates, and the red and sometimes sticky solid that is formed is filtered and discarded. The combined crops of phenylhydrazine hydrochloride are practically white and weigh 53 g. (0.37 mole), which is almost the calculated amount recoverable. The pure free base was obtained from the hydrochloride in 80% yields.

The benzene solution, after the removal of all material that can be precipitated with hydrogen chloride, is distilled from a steam-bath at reduced pressure to remove the benzene, and the residue distilled *in vacuo*. There is obtained in this way 19 g. of guaiacol (70% of the calculated amount), boiling at 103–105° at 22 mm., m. p. 26–28°.

Summary

1. It has been found that compound formation takes place between *sym.*-diphenylcarbazine and 1-phenylsemicarbazide, and this is offered as a possible explanation of the discrepancy in the melting points of *sym.*-diphenylcarbazine recorded in the literature.

2. A satisfactory method for the preparation of pure *sym.*-diphenylcarbazine is given.

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