Synthesis of 4-Iodo- and 4-Thiocyanatobutynyl Carbamates

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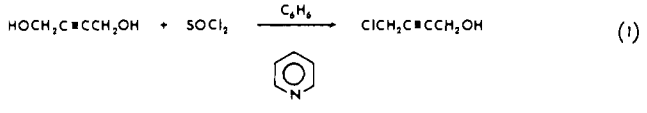
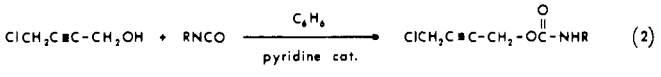
By a known procedure, five new thiocyanatobutynyl and two new iodobutynyl carbamates were prepared and characterized. Per cent yields, melting points, elemental analyses, and infrared data are given.

IN A RECENT United States patent (*2*), Hopkins describes the preparation and use of 4-thiocyanato-2-butynyl carbamates as plant growth regulators. The authors have had the occasion in a recent program with the Department of the Army at Ft. Detrick to prepare some more of these compounds and the iodo analogs. The procedure used was essentially that of Hopkins—Equations 2 (*3*) and 3 (*2*). Equation 1 was that of Bailey and Fujiwara (*1*):



(1)



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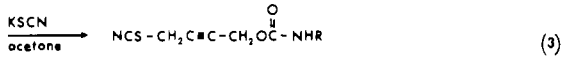

(3)

The compounds obtained were all crystalline solids with over-all yields ranging from 12 to 51%. An itching skin rash similar to that produced by poison ivy was developed in handling 4-iodo-2-butynyl 2′,5′-dichlorocarbanilate, and probably all of these compounds are potential vesicants. The infrared spectra of these compounds showed characteristic N—H stretch at 2.90μ (bonded) – 3.07μ. Aliphatic C—H stretch was seen at 3.38–3.51μ while aromatic C—H appeared at 3.20–3.25μ. In all but two cases, no C≡C stretch was seen. This absorption appeared very weakly at 4.49μ in the case of 4-iodo-2-butynyl 2′,5′-dichlorocarbanilate and at 4.55μ for 4-iodo-2-butynyl *p*-methoxycarbanilate. Characteristic —SCN vibration appeared at 4.62μ for both thiocyanato compounds prepared. Carbonyl stretching frequency was observed at 5.83—5.91μ, but 4-iodo-2-butynyl 2′,5′-dichlorocarbanilate exhibited this vibration at 5.72μ. Substitution patterns were determined in the region 11.41–12.40μ and were consistent in all cases with the depicted structures. One compound, 4-iodo-2-butynyl *N*-(*n*-octyl)carbamate, was analyzed by NMR, using a Varian Associates A-60 proton magnetic resonance spectrometer. Table I shows the results of that analysis.

Table I. NMR Analysis of 4-Iodo-2-butynyl *N*-(*n*-octyl)carbamate

Chemical Shift, P.P.M.	Rel. Peak Area	Theo. No. of Hydrogen	Assignment
0.88 (distorted triplet)	15	15	$CH_3(CH_2)_6$—
1.30 (broad singlet)			
3.21 (quartet)	2	2	—CH_2N—
3.73 (triplet)	1.7	2	—CH_2I
4.70 (triplet)	2.9	3	—OCH_2—;—NH—
5.11 (broad singlet)			

EXPERIMENTAL

All starting materials were obtained commercially as reagent or practical grade and were used without further purification. Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin Elmer Model 137 spectrophotometer. Compounds were examined as cast films from chloroform on sodium chloride plates.

1-Chloro-2-butyn-4-ol. This intermediate was prepared by the method of Bailey and Fujiwara (*1*). The compound was isolated in 36% yield as a caramel colored liquid, b.p. 98–100° C./20 mm. and n_D^{25} 1.4999. The literature reported b.p. 50° C./0.5 mm. and n_D^{25} 1.4980. Vapor phase chromatography showed the product to be 97.5% pure with no starting 1,4-butynediol remaining. The following illustrates the method of preparation of the compounds listed in Table II. The method illustrated is applicable to the other compounds in the table.

4-Iodo-2-butynyl *N*-methylcarbamate. By the method of Hopkins *et al.* (*3*), a 500-ml. four-necked reaction flask was charged with 8.2 grams (0.143 mole) of methyl isocyanate and 15.4 grams (0.143 mole, corrected for impurities) of 1-chloro-2-butyn-4-ol in 225 ml. of benzene. A catalytic amount of pyridine was added, and the reaction mixture was heated to reflux with stirring for 3 hours. At the end of this time, the reaction mixture was concentrated at the water pump to yield a crude white solid. After it had been dried, this material was refluxed with an equimolar amount of potassium iodide in acetone to give, after filtration and concentration of the filtrate, 8 grams (22%) of an orange solid, m.p. 37–40° C. In some cases, recrystallization from ethanol or petroleum ether was required to obtain the compound in high purity (Table II).

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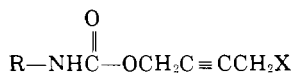
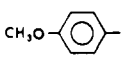
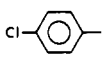
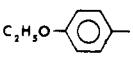
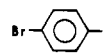
Table II. Characterization of Carbamates and Carbanilates



Compound	R	X	M.P., °C.	Yield, %	Analysis
4-Iodo-2-butynyl *N*-methylcarbamate	CH_3—	—I	37–40	22	Calcd. C, 28.4; H, 3.2; N, 5.5 Found C, 28.3; H, 3.0; N, 5.3
4-Iodo-2-butynyl *N*-(*n*-octyl)carbamate	n-C_8H_{17}—	—I	47.5–51	51	Calcd. C, 44.5; H, 6.3; N, 4.0 Found C, 44.0; H, 6.0; N, 4.0
4-Iodo-2-butynyl *p*-methoxycarbanilate		—I	93.5–95.5[a]	32	Calcd. C, 41.7; H, 3.5; N, 4.1 Found C, 41.9; H, 3.4; N, 3.9
4-Iodo-2-butynyl *p*-chlorocarbanilate		—I	133–133.5[a]	32	Calcd. C, 37.8; H, 2.6; N, 4.0 Found C, 38.1; H, 2.6; N, 3.8
4-Iodo-2-butynyl 2′,5′-dichlorocarbanilate		—I	60–62[a]	17	Calcd. C, 34.4; H, 2.1; N, 3.6 Found C, 33.9; H, 1.7; N, 3.5
4-Thiocyanato-2-butynyl *p*-ethoxycarbanilate		—SCN	86–89[b]	38	Calcd. C, 57.9; H, 4.9; N, 9.6 Found C, 57.8; H, 4.6; N, 9.6
4-Thiocyanato-2-butynyl *p*-bromocarbanilate		—SCN	128–129	12	Calcd. C, 44.3; H, 2.8; N, 8.6 Found C, 44.3; H, 2.8; N, 8.4

[a] Recrystallized from ethanol. [b] Recrystallized from petroleum ether.

ACKNOWLEDGMENT

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(3) Hopkins, T.R., Neighbors, R.P., Strickler, P.D., Phillips, L.V., *J. Org. Chem.* **24**, 2040 (1959).

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Resin Acid Composition of Pine Oleoresins

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The resin acid composition of the oleoresins and rosins from various species of pines is reported. The data indicate that the source of some oleoresins can be identified by their composition.

THE USE of gas chromatography for the analysis of resin acids was first reported in 1959 by Hudy (*5*). Gas chromatography was used in this work to analyze the acid fraction of pine oleoresins and rosin. The resin acid composition varies considerably from one species to another, and proper selection of the source of oleoresin or rosin can substantially increase the yield of desired acids in work involving the isolation of pure resin acids. From Tables I and II, the pine oleoresin or rosin from which a certain resin acid can best be isolated can be determined. For example, French rosin has twice as much pimaric acid as American rosin, and Greek rosin contains none at all. Isopimaric acid accounts for 21% of the acids in slash pine oleoresin (*Pinus elliottii*) but only 10% of the acids present in longleaf oleoresin (*Pinus palustris*) and only a trace in loblolly oleoresin (*Pinus taeda*).

Table III lists the physical constants of the resin acids and their methyl esters that were studied in this work.