

Other compounds such as furfuryl alcohol and propionic, 2-furoic, and lactic acids, because of their polarity, tend to be slowly eluted during liquid chromatography and consequently are found in many fractions. In a complex and difficult study of this nature involving many fractionation steps and several different investigators these findings are understandable.

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## Preparation and Herbicidal Activity of the Vinylbenzyl Esters of Various Thio- and Dithiocarbamic Acids

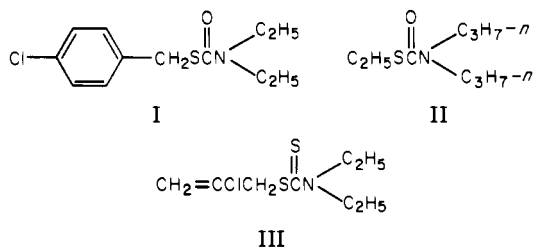
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The vinylbenzyl esters of 14 thio- and dithiocarbamic acids were prepared from vinylbenzyl chloride, carbon oxysulfide, or carbon disulfide, and a secondary amine. These materials were tested for both pre- and postemergent herbicidal activity. The greatest herbicidal activity was manifested with a preemergent application of these chemicals on grassy plants. Compounds with the thiocarbamate moiety (-NCOS-) were found to be more herbicidally active than those containing the dithiocarbamate moiety (-N-CS<sub>2</sub>-). An estimation was made of the influence of the vinyl moiety on the herbicidal activity, and it was found to depress this activity when contrasted to the unsubstituted benzyl derivatives.

Certain thio- and dithiocarbamate esters are employed as selective herbicides in various food crops. As a class,

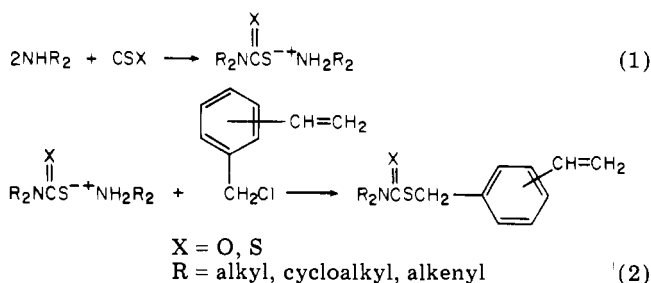
Ag-Products Research, Dow Chemical U.S.A., Walnut Creek, California 94598.

they are particularly known for their preemergent herbicidal activity on grassy plants. Benthio carb (I), EPTC (II), and CDEC (III) are examples of thio- and dithiocarbamate esters which are presently being utilized as selective herbicides. The availability of vinylbenzyl chloride prompted us to prepare some thio- and dithio-



carbamate esters of this material as potential herbicides (Giacobbe and Norton, 1975) as other benzyl thiocarbamates are reported as herbicides (Aya et al., 1972; Harman and D'Amico, 1963; Maeda, 1972). It was also our intention to try and determine the effect of the vinyl moiety on the herbicidal activity. This paper describes the preparation, herbicidal activity, and an estimation of the influence of the vinyl moiety on the herbicidal activity of various thio- and dithiocarbamate esters derived from vinylbenzyl chloride.

The thio- and dithiocarbamates were prepared by reaction of a secondary amine and carbon disulfide or carbon oxysulfide to form an amine salt (eq 1), which was then



allowed to react with vinylbenzyl chloride to form the amine hydrochloride and the thio- or dithiocarbamate (eq 2). The carbon disulfide or carbon oxysulfide was employed in excess to ensure complete reaction. All compounds (1 through 14) in Table I were prepared by this route and proceeded smoothly with the exception of 8 which was hindered by polymer formation.

These compounds were tested in a greenhouse for preemergent and postemergent herbicidal activity. The greenhouse temperature was maintained in the range of 18–29 °C, and daylight was supplemented with Gro-lux fluorescent illumination to provide a constant 16-h photoperiod. The compounds were initially tested on five grasses: *Avena fatua* (wild oats), *Setaria glauca* (yellow foxtail), *Echinochloa crusgalli* (barnyardgrass), *Digitaria sanguinalis* (crabgrass), and *Sorghum halepense* (johnson grass). The chemicals were applied in a 50% aqueous acetone emulsion containing 0.1% Tween 20. For the preemergence test, the chemical emulsion was drenched on the surface of soil in pots seeded 0.5 in. below the surface at a rate equivalent to 10 lb/acre. A 4000-ppm solution of the emulsion was sprayed to run-off to the foliage of 2–4-in. tall seedlings for the postemergence test. The plants were allowed to grow for 2 weeks and then evaluated in comparison with untreated plants. Visual ratings were made with 0 indicating no visible effects and 100 indicating dead plants. The results of these tests are shown in Table I.

These tests indicated that the compounds (1 to 14) were indeed grass herbicides, and that the greatest activity was manifested with a preemergence application of the chemical. Several other relationships are also apparent from these data; namely, the greatest preemergent activity was found when the amine moiety contained four to six carbon atoms. Also, compounds containing the thio-

carbamate ( $-\text{C}(=\text{O})\text{S}-$ ) moiety were more active than those analogues with the dithiocarbamate ( $-\text{C}(=\text{S})\text{S}-$ ) moiety.

The next problem was to determine the effect of the vinyl moiety on preemergent herbicidal activity. This was accomplished by simultaneously testing diethyl and diisopropylbenzyl carbonothioate (Harman and D'Amico, 1963) with compounds 1 and 3. The preemergence test procedure was exactly as described earlier, with the exceptions that the chemicals were applied at five rates (8, 4, 2, 1, and 0.5 lb/acre) on eight grasses: *Setaria italica* (German millet), *Sorghum bicolor* (sorghum), *Setaria viridis* (green foxtail), *Setaria faberi* (giant foxtail), *Setaria glauca* (yellow foxtail), *Sorghum halepense* (johnson grass), *Digitaria sanguinalis* (crabgrass), and *Echinochloa crusgalli* (barnyardgrass).

The results from the test designed to determine the effect of the vinyl moiety on the preemergence herbicidal activity were obtained by calculating the concentration (pounds/acre) of the chemical needed to inhibit the average growth of the eight grasses in the test by 50% ( $\text{GR}_{50}$ ). This was accomplished by using a probit analysis on the average herbicidal activity for all eight grasses at each of the five application rates. These results are shown in Table II.

Two conclusions are evident from the data in Table II. Compounds containing the diethylamine moiety are approximately two–three times more herbicidally active than those analogues derived from diisopropylamine. Also, thiocarbamates with an unsubstituted benzyl ring are approximately three–five times more herbicidally active than those substituted with a vinyl moiety.

One can speculate as to the reasons why the thiocarbamates containing diethylamine and an unsubstituted benzyl moiety were found to have enhanced herbicidal activity. There is evidence that the sulfoxides of the thiocarbamates are more herbicidally active than thiocarbamates themselves (Casida et al., 1974). We observed that the preparation of thiocarbamates derived from diisopropylamine required longer reaction times than those derived from diethylamine (see Experimental Section). This difference was ascribed to the increased steric encumbrance created by the two isopropyl groups as compared to two ethyl groups. Hence, this same steric encumbrance may retard the biological oxidation of the sulfur atom to its sulfoxide with a concomitant decrease in herbicidal activity.

The decreased herbicidal activity found with the carbamates containing the vinyl moiety is more difficult to rationalize. However, the increased lipophilicity (perhaps the compounds have gone beyond an optimum value) and potential soil-binding sites with the molecules containing the vinyl moiety may offer two explanations for the observed results.

#### EXPERIMENTAL SECTION

The gas chromatography data were collected on an F&M Model 500 instrument (column: 5% 410 silicone gum on Chromosorb Q 60/80, 2 ft × 1/8 in. i.d., glass; detector, 375 °C; helium pressure, 30 psi; oven, linear temperature increase at 11 °C/min from 50 to 300 °C). The vinylbenzyl chloride component was eluted at 109–115 °C (9.5–10 min) and all products (1 through 14) were eluted between 195 and 260 °C (between 17 and 24 min). Proton NMR spectra were recorded using a Varian A-60 recording spectrometer. Chemical shifts are reported as parts per million ( $\delta$ ) relative to tetramethylsilane. Infrared spectra were recorded using a Perkin-Elmer Model 257 recording spectrometer or a Perkin-Elmer Model 457 recording spectrometer.

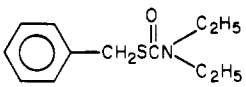
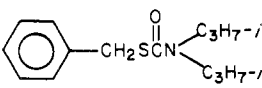
Table I. Compounds Prepared and Their Herbicidal Activity

Compd no.	Structure	Test	Biol. act. on grasses, preemergence at 10 lb/acre; post- at 4000 ppm					Formula anal.
			Wild-oats	Fox-tail	Barnyard-grass	Crab-grass	Sorghum	
1		Pre Post	90 60	98 70	98 70	80 55	95 0	C <sub>16</sub> H <sub>23</sub> NOS C, H, N
2		Pre Post	25 25	80 55	75 55	100 0	0 0	C <sub>16</sub> H <sub>23</sub> NS <sub>2</sub> H, N, C <sup>a</sup>
3		Pre Post	90 60	98 75	100 75	85 20	98 40	C <sub>14</sub> H <sub>19</sub> NOS C, H, N
4		Pre Post	20 0	70 0	90 0	50 0	80 0	C <sub>14</sub> H <sub>19</sub> NS <sub>2</sub> C, H, N
5		Pre Post	75 45	50 60	98 70	85 40	90 20	C <sub>16</sub> H <sub>21</sub> NOS C, H, N
6		Pre Post	0 0	0 20	0 20	0 0	0 0	C <sub>16</sub> H <sub>21</sub> NS <sub>2</sub> C, H, N
7		Pre Post	75 0	98 0	98 0	90 0	98 0	C <sub>16</sub> H <sub>19</sub> NOS C, H, N
8		Pre Post	0 0	0 0	0 0	0 0	0 0	C <sub>16</sub> H <sub>19</sub> NS <sub>2</sub> C, H, N
9		Pre Post	50 50	95 80	95 85	70 30	85 0	C <sub>12</sub> H <sub>15</sub> NOS C, H, N
10		Pre Post	0 85	0 25	0 70	0 100	0 0	C <sub>12</sub> H <sub>15</sub> NS <sub>2</sub> C, H, N
11		Pre Post	95 40	98 50	98 50	90 70	85 20	C <sub>16</sub> H <sub>23</sub> NOS C, H, N
12		Pre Post	0 0	25 0	40 0	0 0	0 0	C <sub>16</sub> H <sub>23</sub> NS <sub>2</sub> C, H, N
13		Pre Post	100 25	100 75	100 75	100 25	100	C <sub>16</sub> H <sub>23</sub> NOS C, H, N
14		Pre Post	0 0	20 0	30 0	0 0	0 0	C <sub>16</sub> H <sub>23</sub> NS <sub>2</sub> C, H, N
15		Pre <sup>b</sup> Post	95 0	95 100	95 85	100 90		

Benthiocarb

<sup>a</sup> Calcd: 65.48. Found; 64.7. <sup>b</sup> Tested at 20 lb/acre.

Table II

Compound	Herbicidal act. <sup>a</sup> GR <sub>50</sub> , lb/acre
	0.1
8	0.5
	0.3
1	0.9

<sup>a</sup> See text for details.

The vinylbenzyl chloride (VBC) is a monomer of the Dow Chemical Company which is a mixture of the meta (60%) and para (40%) isomers of vinylbenzyl chloride. It is not possible to separate the vinylbenzyl chloride isomers nor compounds 1 through 14 by gas chromatography on

the instrument used for this work; therefore, the assumption was made that the products obtained were of the same meta (60%) and para (40%) isomer composition as the vinylbenzyl chloride. All amines were freshly distilled.

**Supplementary Material Available:** Details of the synthetic procedures and physical properties for the new compounds discussed (9 pages). Ordering information is given on any current masthead page.

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## Synthesis and Spectroscopic and Gas Chromatographic Behavior of Isomeric Chlorinated Terphenyls

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The synthesis and spectroscopic and chromatographic properties of 22 polychlorinated terphenyl (PCT) isomers are reported. Diazo coupling of a biphenylamine with an excess of a symmetrical chlorobenzene gave a single chloroterphenyl product; coupling with unsymmetrical chlorobenzenes gave mixtures which in some cases could be purified and identified by the wavelength of their characteristic ultraviolet absorption spectra. Chlorine substitution in the para position gives a characteristic bathochromic shift of the  $\lambda_{max}$  whereas substitution in the ortho positions gives a hypsochromic shift to these values. The gas-liquid chromatographic retention times of the PCT isomers increased with increasing chlorine content, whereas the relative molar electron capture responses tended to be highest with 4-chloro substitution and whereas ortho substitution (2 and 6 positions) gave the lowest response values. Availability of synthetic PCT isomers thus permits comparative evaluation of the environmental and biological impact of PCTs which have already been identified as pollutants.

Polychlorinated terphenyls (PCTs) are industrial chemicals with applications similar to those of the polychlorinated biphenyls (PCBs). PCT residues have been identified in the eggs and fatty tissue of herring gulls (Zitko et al., 1972), Rhine River water, oysters, eel, and human fat (Freudenthal and Greve, 1973; Doguchi and Fukano, 1975), paperboard samples (Thomas and Reynolds, 1973), and silo wall scrapings, silage, and cows' milk (Fries and Marrow, 1973). Chromatographic analysis indicated that this PCT corresponded to commercial Aroclor 5460, a mixture of ortho-, meta-, and para-chlorinated terphenyl isomers (Putnam et al., 1974). It is difficult to investigate the biological properties of a complex mixture and we therefore report the synthesis and chromatographic properties of 22 chlorinated terphenyl isomers. 4-

Chloro-*p*-terphenyl is readily prepared from the corresponding commercially available 4-nitro-*p*-terphenyl and the remaining isomers were all synthesized by the diazo coupling of a biphenylamine and a halobenzene (Cadogan, 1962). In coupling reactions where more than one product was formed the structures were confirmed by spectroscopic and photochemical methods.

#### MATERIALS AND METHODS

**Chemicals.** The following compounds were obtained commercially: 1,3-dichlorobenzene, 1,2,3-trichlorobenzene (BDH); 1,2-dichlorobenzene (Anachemia); *p*-terphenyl (Eastman); 4-nitro-*p*-terphenyl, 4-aminobiphenyl, 2-aminobiphenyl, 1,2,4,5-tetrachlorobenzene, 1,2,3,4,5-pentachlorobenzene (Aldrich); 1,3,5-trichlorobenzene (Baker); 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, isoamyl nitrite (Matheson Coleman and Bell); 4-amino-4'-chlorobiphenyl hydrochloride (Burdich and Jackson); 1,2,3,5-tetrachlorobenzene (Schuchardt, Munchen).

**Thin-Layer Chromatography.** Preparative and analytical thin-layer chromatography (TLC) was carried out on glass plates (20 × 20 cm, 20 × 50 cm, and 20 × 100 cm) coated with MN-Kieselgel G/UV<sub>254</sub> silica at a

Guelph Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada (B.C., S.S., L.O.R.), Milieuchemie, University of Amsterdam, Amsterdam, The Netherlands (O.H.), and Environment Canada, Biology Station, St. Andrews, New Brunswick, Canada (V.Z.).