

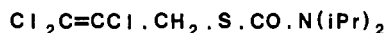
Rearrangement of *S*-2,3,3-Trichloroallyl

N,N-Diisopropylthiolcarbamate (Triallate) in Alcoholic Base

Treatment of triallate (*S*-2,3,3-trichloroallyl *N,N*-diisopropylthiolcarbamate) with methanolic potassium hydroxide solution yielded a white crystalline material whose structure, on the basis of spectroscopic data, is proposed as *cis*-*S*-2,3,3-trichloroprop-1-ene

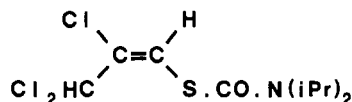
N,N-diisopropylthiolcarbamate. This compound when incorporated into Regina heavy clay at the 4, 2, and 1 ppm levels showed no herbicidal activity against wild oat seedlings.

Triallate (I) is used extensively for the control of wild oats in a variety of crops. During chemical degradation studies 0.5 g triallate was treated at room temperature with 10.0 ml of a 5% methanolic potassium hydroxide solution. On standing, a white precipitate separated out which, after filtration and washing with a small volume of methanol, yielded 0.2 g white crystals melting at 126–8° C. The melting point of triallate is 32–4° C. The unknown was very soluble in all common organic solvents but recrystallization from aqueous acetone resulted in a white semiamorphous solid with a melting point of 126–8° C.



I

The new compound has been tentatively identified as *cis*-*S*-2,3,3-trichloroprop-1-ene *N,N*-diisopropylthiolcarbamate (II).



II

Gas chromatographic analysis of a benzene solution of II under conditions previously reported for triallate (Smith, 1969) indicated a major peak with a relative retention time of 1.7 with respect to triallate.

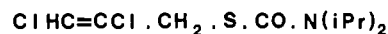
The mass spectrum of II indicates a molecular ion weight of 303, the presence of three chlorine atoms, and an *N,N*-diisopropylthiolcarbamate moiety, from which it may be concluded that II is isomeric with triallate. In addition, the mass spectrum indicated that the molecule contains one hydrogen atom that is easily abstractable, leading to a stabilized M-1 ion, and a series of ions derived therefrom.

The proton nmr spectrum of II (10% in CDCl_3) measured using a Varian A-60A spectrometer shows signals attributable to the 14 protons of the two isopropyl groups at $\delta = 1.33$ and $\delta = 3.82$ ppm (TMS internal standard), and two sharp singlets, each corresponding to 1 proton, at $\delta = 6.42$ and $\delta = 7.61$ ppm, respectively. In the spectrum of triallate (I), the $-\text{CH}_2$ protons appear as a singlet at 4.15 ppm. Thus the two nonisopropyl protons in II cannot be on the same or adjacent carbon atoms. No allylic coupling was observed between these two protons, which indicates that this coupling must be smaller than 0.3 Hz. This, however, is compatible with the range of +1 to -3 Hz generally noted for such couplings.

Using the empirical correlations of Pascual *et al.* (1966), the low field signal at $\delta = 7.61$ ppm can be assigned to an olefinic $-\text{ClC}=\text{CH}-\text{S}-$ proton. The calculated value for such a proton signal is $\delta = 7.60$ ppm, derived from a basic nonterminal olefinic proton peak at 5.28 ppm + 0.43 ppm for a *trans*- CHCl_2 grouping + 0.19 ppm for a *cis*-Cl + 1.70 ppm for a *gem*-S-CO- moiety.

The other line at $\delta = 6.42$ ppm is very close to the calculated value of 6.4 ppm for the proton in a $\text{CCl}_2\text{H}-\text{CCl}=\text{C}$ grouping. This figure being derived from $\delta = 5.3$ ppm, for the proton signal in CH_2Cl_2 , with estimated substituent effects of +0.4 ppm for the β -Cl and +0.70 ppm for the allylic C=C bond.

The infrared spectrum of II, run as a KBr disc, shows an olefinic $=\text{CH}$ stretch at 3020 cm^{-1} which is absent in triallate (I). The $=\text{CCl}$ stretch at $815-17 \text{ cm}^{-1}$ in triallate and in III (the closely related herbicide diallate) is found at 805 cm^{-1} in II with much reduced intensity. A new intense band at 712 cm^{-1} is found for II (absent in both diallate and triallate) which can be assigned to the aliphatic $-\text{CCl}$ stretch of the $-\text{CHCl}_2$ moiety of II. A medium intensity band at 860 cm^{-1} in the spectrum of II can be attributed to a $=\text{CH}$ -out-of-phase deformation stretch; this band appears at 872 cm^{-1} in the case of diallate (III), but is absent from the spectrum of triallate (I).



III

The assignment of the *cis* structure to II rests in part with the excellent fit between the nmr experimental and calculated chemical shifts. More important is the recently found generalization (Kloosterziel and Van Drunen, 1970) that base catalyzed double-bond migration proceeds *via* an energetically favored *cis* anion.

It was noted that II had no herbicidal activity against wild oat (*Avena fatua* L.) seeds germinated in moist Regina heavy clay treated at the 4, 2, and 1 ppm levels. At all three rates the percentage germination and subsequent growth were identical to those for seedlings grown in moist untreated clay. Under the same conditions, using Regina heavy clay treated with triallate at the above three rates, all of the wild oat seedlings died shortly after emergence.

ACKNOWLEDGMENT

Thanks are due to J. G. Saha of the Canada Department of Agriculture, Saskatoon, for providing the mass spectra.

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Received for review July 6, 1970. Accepted December 2, 1970.
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