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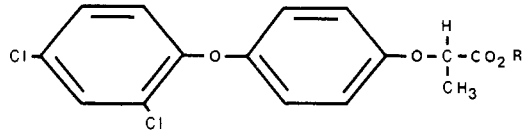
Esterification of the Hydrolysis Product of the Herbicide Dichlorfop-Methyl in Methanol

The acid formed by alkaline hydrolysis of the herbicide dichlorfop-methyl [methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propionate] was characterized spectroscopically. In methanolic solution, at 25 °C this acid underwent complete esterification within 14 days. At 60 °C methylation was faster and complete within 24 h.

Dichlorfop-methyl [I, R = CH_3; methyl 2-(4-(2,4-dichlorophenoxy)phenoxy)propionate] will be used on the



I

Canadian prairies at rates of 1.12 kg/ha as a postemergence treatment for the control of annual grasses in wheat, flax, and rape. Herbicidal esters are known to undergo hydrolysis to their respective acids in moist soils (Burcar et al., 1967; McKone and Hance, 1972; Smith, 1972, 1976; Beynon et al., 1974). Thus, the acid (I, R = H) derived from dichlorfop-methyl was required for soil persistence and degradation studies. This communication reports the preparation of the acid together with the interesting and anomalous reaction of dichlorfop acid whereby it undergoes complete methylation in methanolic solution at room temperature.

MATERIALS AND METHODS

Dichlorfop Acid. A commercial formulation (10 ml) of dichlorfop-methyl (Hoechst Aktiengesellschaft, Frankfurt, Germany) was hydrolyzed at room temperature by treatment with 40 ml of a 50% aqueous methanolic solution containing 4 g of potassium hydroxide. After 24 h the reaction mixture was diluted with 150 ml of water and extracted with 3 × 100 ml portions of ether to remove any unhydrolyzed ester and ether-soluble impurities. The aqueous phase was then acidified with 20 ml of 12 N hydrochloric acid and shaken with 2 × 100 ml volumes of ether. The combined ether extracts were dried over anhydrous sodium sulfate and evaporated, using a rotary evaporator, to yield a red oil. The oil was dissolved in a mixture of ether and *n*-hexane, from which it crystallized as a pink amorphous solid with a melting point of 100–102 °C.

Methanol. Distilled in glass methanol was used in these studies, obtained from Caledon Laboratories Ltd. (Georgetown, Ontario, Canada).

Methylation. A 2 mg/ml solution of the acid was prepared in methanol and 1.0-ml aliquots were measured into 1-ml capacity silylation tubes fitted with screwcaps. Tightly sealed duplicate vials were then incubated at 25 ± 1 °C and 60 ± 2 °C when 20-μl aliquots were removed at regular intervals and added to 100-ml portions of *n*-hexane. After vigorous shaking, the ester content was determined gas chromatographically by comparing the ester peak heights from 5-μl injections with those from an ester standard prepared by treating a 20-μl sample from each vial at every sampling period with diazomethane, using the procedure described by Rivers et al. (1970).

Spectra. Mass spectra were determined using a Finnigan 1015 mass spectrometer utilizing a solid probe for direct insertion.

Gas Chromatographic Analysis. The gas chromatograph used was a Hewlett-Packard 7610A equipped with a nickel electron-capture detector. The 2 m × 3 mm i.d. glass column was packed with a mixture of 2% QF-1 and 3% DC-200 on 60–80 mesh Gas-Chrom Q. Carrier gas was argon containing 5% of methane at a flow rate of 40 ml/min. Injector, column, and detector temperatures were 240, 210, and 300 °C, respectively. Under these conditions the dichlorfop-methyl had a retention time of 2.4 min.

RESULTS AND DISCUSSION

The dichlorfop acid was identified by the fact that it could be remethylated to dichlorfop-methyl and from spectroscopic considerations. The mass spectrum indicated a molecular ion weight of 326 (equivalent to $C_{15}H_{12}O_4Cl_2$) and the presence of 2 chlorine atoms. Ion

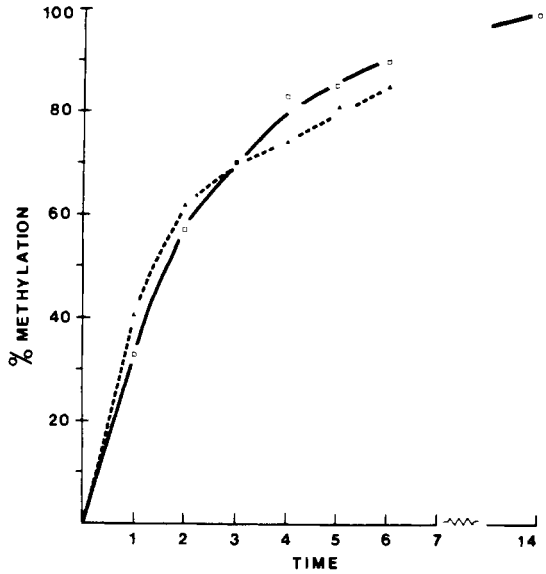


Figure 1. The percentage methylation of 2 mg of dichlorfop acid in 1 ml of methanol with time at 60 °C (▲- - -▲, abscissa in hours) and 25 °C (□- - -□, abscissa in days).

fragments with masses of 282 and 253, each containing 2 chlorine atoms, were also observed. The mass spectra of the parent dichlorfop-methyl and the remethylated acid were identical and showed a molecular ion weight of 340 (2 chlorine atoms) with ion fragments of masses of 282 and 253, both of which contained 2 chlorine atoms. No ion mass weights of 326 were observed. From these data the hydrolysis product was characterized as the acid (I, R = H).

From experiments in which a methanolic solution of dichlorfop acid had been used, it became apparent that with time there was a decrease in the acid concentration which was accompanied by formation of dichlorfop-methyl, the latter being identified by gas chromatographic and mass spectral analysis. This observation prompted a more detailed study of the fate of dichlorfop acid in methanolic solution.

The average results from duplicate experiments on the esterification of dichlorfop acid in methanol at two temperatures with time are summarized in Figure 1, from which it is seen that at 60 °C, methylation is rapid and 85% complete in 6 h. Reaction was complete within 24 h. At 25 °C, esterification is slower with approximately 30% occurring over a 24-h period. After 6 days at 25 °C, about 90% of the acid had undergone methylation, while methylation was complete within 14 days.

Thus, it was confirmed that dichlorfop acid in methanol can undergo complete methylation at room temperature. This is anomalous as the esterification of organic acids by alcohols at room temperature is generally insignificant and even at high temperatures does not normally go to completion but rather reaches an equilibrium. Horner et al. (1974) have reported that the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) on being heated under reflux with methanol (1.7 g in 10 ml) reached an equilibrium with the methyl ester when 52% esterification had occurred.

Separate experiments showed that the dichlorfop acid did not undergo any detectable esterification at room temperature in ethanol or 1-butanol over a 14-day period, indicating that the ethyl and *n*-butyl esters are either not formed under these conditions or are formed much more slowly than the methyl ester.

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Mercury in Chicken Eggs

Methylmercuric chloride (MeHgCl) and ethylmercuric chloride (EtHgCl) in approximately equivalent concentrations were isolated from the alkaline hydrolysates of chicken eggs purchased on the retail market. The mercury (Hg) from the two alkylmercuric compounds in 19 samples collected during 1973–1975 averaged 0.04 ppm. The range was 0.02 to 0.10 ppm. Comparative assays with an atomic absorption spectrophotometric method (AA) for six samples indicated that a large proportion of Hg was present as these two alkylmercuric compounds. Data are reported on the increase from 0.02 to 10.0 ppm of EtHg compounds, with no increase in MeHg compounds in eggs laid over a 32-day period by one hen fed approximately 1 mg of Hg per day as a grain coated with Ceresan M (ethylmercury *p*-toluenesulfonanilide).

The chemical form of mercury (Hg) determines its biological effect or toxicity. Elemental Hg is the least toxic, and alkylmercuric compounds are the most toxic. Other chemical forms of Hg in compounds with fungicidal properties, the inorganic Hg^{2+}, alkoxyalkylmercuric, and arylmercuric compounds, have toxicities between these two extremes. The low level of Hg in eggs has made it difficult to determine its chemical form. The 33 egg samples included in the Food and Drug Administration survey of the mercury content of food in 1970, 1971, and 1972 (Simpson, 1974) contained <0.002 to 0.005 ppm of Hg. Except in special circumstances, most of the Hg in foods other than