filtered), λ (K_{α}) = 1.5418 Å, radiations were employed and measurements were corrected for film shrinkage. An interesting feature of the unit cell data is the presence of four molecules per cell in anhydrous lupanoline. Since the maximum number of asymmetric units per cell in $P2_1$ is 2, two molecules of lupanoline must occupy one set of general positions and two molecules must occupy another set of general positions. The asymmetric unit, therefore, may be considered as comprising two molecules of lupanoline.

X-ray powder diffraction data are shown in Table III. The photographs were taken with Co radiation (λ (K_{α}) = 1.790 Å), filtered with Fe foil, in a camera of 114.6 mm. diameter, and with Straumanis film mounting. The longest interplanar spacing measurable with the apparatus used (i.e., the 'cut-off') was 20 Å. Film shrinkage corrections were < 0.2% and were not applied. Relative intensities (I/I_1) were estimated visually. Lines having values of d > 3.8 Å have been indexed on the basis of the single crystal data given in Table II.

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SYNTHESIS OF C¹⁴ LABELED DDT

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Barry (1) described a method for preparing DDT which involved the coupling of acetic anhydride with chlorobenzene by the use of aluminum chloride catalyst to yield p-chloroacetophenone. The 1-(p-chlorophenyl)-2,2,2-trichloroethanone, which was obtained by direct chlorination of p-chloroacetophenone, yielded the corresponding alcohol on reduction with aluminum isopropoxide in dry isopropyl alcohol. The alcohol was condensed with chlorobenzene to give DDT.

This note describes the adaptation of this method to the preparation of C¹⁴ labeled DDT.

EXPERIMENTAL

The complete synthesis was carried out with inactive materials and the biological toxicity of the product was compared with an authentic sample of the insecticide. The biological tests showed that the probability of the two materials being different was approximately 1 in 100. It may be concluded that the materials were practically identical so far as their biological effects in these tests were concerned. A mixed melting point of the two materials remained unchanged.

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Preparation of Sodium Acetate-1-C¹⁴

Labeled barium carbonate was prepared by the technique described by Henneberry and Baker (2). Forty milliliters of sodium carbonate (C¹⁴) solution, having an activity of 0.211 mc. per ml., along with 203 mgm. of inactive sodium carbonate, was added to 50 ml. of saturated barium hydroxide solution. The water and alcohol used to wash the barium carbonate were combined and set aside for measurement of radioactivity (A). The yield of barium carbonate (C¹⁴) was 1.976 gm.

Labeled sodium acetate was prepared from the barium carbonate following the procedure of Van Bruggen *et al.* (5). The barium carbonate (1.976 gm.) was transferred to the reaction vessel by means of acetone (B) which was subsequently evaporated. At the end of the reaction the ether and residual carbon dioxide were removed by a stream of nitrogen gas. The flushing gas was bubbled through 1N sodium hydroxide (C). The residue (D), left in the reaction vessel after the acetic acid had been removed by distillation, was also kept for measurement of radioactivity. The yield of anhydrous sodium acetate was 0.6080 gm.

Preparation of Acetic Anhydride-1-C¹⁴ and p-Chloroacetophenone-carbonyl-C¹⁴

A mixture of sodium acetate-1-C¹⁴ (0.6080 gm.) and *p*-toluene sulphonyl chloride (1.62 gm.) was heated at 180-200°C. for 30 min. This method of preparing acetic anhydride from sodium acetate was described briefly by Shantz and Rittenberg (4). The acetic anhydride which distilled off (residue E) was heated at 100°C. for 18 hr. with anhydrous aluminum chloride (2.4 gm.) and chlorobenzene (1.40 gm.). At the end of this heating period, ice (4 gm.) and concentrated sulphuric acid (4 ml.) were added and the temperature was reduced to 50-60°C. The *p*-chloroacetophenone-carbonyl-C¹⁴ was recovered from the reaction mixture by steam distillation (residue F). It was extracted from the aqueous layer (G) with ether and was distilled under reduced pressure. The ether forerun and the residue were combined and kept for measurement of radioactivity (H).

Preparation of 1-(p-Chlorophenyl)-2,2,2-trichloroethanol-1-C¹⁴

The 1-(p-chlorophenyl)-2,2,2-trichloroethanone-1-C¹⁴, which was obtained by the chlorination at 210°C. of labeled p-chloroacetophenone, was mixed with anhydrous isopropanol (8 ml.) and aluminum isopropoxide (2.16 gm.). The temperature of the reaction mixture was maintained sufficiently high to remove the acetone as it was formed. When a negative test (2,4-dinitrophenylhydrazine reagent) for acetone in the distillate was noted, the reaction mixture was refluxed for 15 min. and the distillation was then continued. The cycle of distillation, refluxing, and distillation, was repeated until the test for acetone in the distillate (I) was no longer positive. Ice (3 gm.), followed by concentrated sulphuric acid (3 ml.), was added to the reaction mixture and the product was extracted with ether and then was distilled under reduced pressure. The residue (J) was kept for measurement of radioactivity.

Preparation of 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane-1-C¹⁴

Chlorobenzene (0.6 gm.) and sulphuric acid (3.84 ml., 99.1% pure) were added to the flask which contained the labeled 1-(p-chlorophenyl)-2,2,2-

trichloroethanol. The reaction vessel was surrounded by an ice bath and the reactants were stirred for six hours. The reaction was quenched by the addition of ice (1 gm.) and the DDT was extracted with four 5-ml. portions of chloroform. The acid layer (K) was kept for measurement of radioactivity. The DDT solution was evaporated (distillate L) to dryness at 60° at 1 mm. The crude DDT was purified by three successive recrystallizations from ethanol. There was obtained 197 mgm. of DDT melting at 108°-108.7° (corr.) and having a specific activity of 62,000 counts per min. per mgm. The mother liquors (M), from the recrystallization, were combined and set aside for measurement of radioactivity.

The oxidation mixture of Lindenbaum et al. (3) was found to be inadequate for the complete combustion of DDT. Reproducible results were obtained when 20 ml. of a solution containing 69 gm. of chromic trioxide, 200 ml. of fuming sulphuric acid (30% SO₃), and 100 ml. of syrupy phosphoric acid was used for each sample.

The residues, distillates, washings, etc., which were obtained during the synthesis, were dissolved in appropriate solvents, and aliquots were oxidized with the modified Lindenbaum mixture. The distribution of activity in the various by-products, as well as the DDT, is shown in the table.

Sample	A	B	C	D	E	F	G.	Н	I	J	K	L	M	DDT
Distri- bution, %	1.13	0.79	1.,51	18.50	9.51	16.66	0.72	9.18	1.09	10.91	22.16	0.43	1.08	4.76

DISTRIBUTION OF C¹⁴ IN THE PRODUCTS OF THE DDT SYNTHESIS

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