physical methods. The ethylene was prepared free of ethane by chemical methods, but at that time, no spectroscopically pure sample of the ethane was available. We have found that the ethylene can be hydrogenated to the ethane, and report herewith the procedure, together with the spectra of the bases. Our previous recommendation of separation by chromatography must be retracted: coincidence of the absorption peaks of benzene and of dipyridylethane invalidate our earlier data.

Hydrogenation.—4.02 g. of dipyridylethane containing about 30% ethylene was dissolved in 100 ml. of ethyl acetate and added to 150 ml. of ethyl acetate containing 0.5 g. of charcoal-supported palladium catalyst (5% Pd) after saturation of the suspension with hydrogen. After 12 hours, 159 ml. of hydrogen had been taken up. The solution was filtered to remove catalyst and concentrated to 35 ml. A first crop of 1.62 g. of product was obtained; working up the mother liquor gave practically quantitative recovery. An ethanol solution of the product was almost completely transparent at 300 mμ, where the ethylene has its strong absorption.

Spectra.—Absorption spectra were measured in ethanol solution at concentrations of the order of 5 to 10 × 10^{-5} molar, using a one-cm. quartz cuvette and a Beckman DU quartz spectrophotometer. The results are shown in Fig. 1, where ϵ is optical density ($D = \log_{10} I_0/I$) divided by molar concentration, for 1,2-di-(γ-pyridyl)-ethane and -ethylene. The spectrum of picoline is also included for comparison.

It will be noted that the conjugation in the ethylene molecule doubles the intensity of the absorption, and shifts the main peak by about 50 mμ toward longer wave length. This shift is similar to that observed in the case of dibenzyl and stilbene. There is apparently little interaction between the two rings in the ethane; its peak coincides with that of picoline and is almost exactly twice as high. In other words, if the absorption coefficient were defined in units of nitrogen concentration, the picoline and ethane curves would coincide. For analytical purposes, the following data are given: 1,2-di-(γ-pyridyl)-ethylene, ϵ 8810 at 299.0 and 289.0 mμ; 1,2-di-(γ-pyridyl)-ethane, ϵ 4410 at 257.0; picoline, ϵ 2200 at 256.0.

Acknowledgment is made to the Office of Naval Research for partial support of this work.

CONTRIBUTION NO. 1160 FROM
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Self-radiolysis of C^{14}-Compounds

BY CHARLES D. WAGNER AND VINCENT P. GUINN

RECEIVED MAY 23, 1953

Tolbert, *et al.*,[1] have reported observations at the University of California and at other laboratories of the decomposition of C^{14}-labeled organic compounds caused by self radiation. In this Laboratory we have observed that a sample of methyl-C^{14} iodide, 0.12 mc./mmole, sealed *in vacuo* in November, 1949, and maintained at room temperature in the absence of light, has become wine red in color due to liberated iodine, whereas samples of methyl-C^{13} iodide treated similarly were colorless. At the present time it is estimated by spectrophotometric comparison with solutions of iodine in methyl iodide of known concentration that 0.135% of the methyl-C^{14} iodide has decomposed to give elemental iodine.

If it is assumed for purposes of approximate calculation that all of the destruction is accomplished solely by ionization induced by electron impact, that ionization is always accompanied by permanent molecular destruction, that all of the energy is absorbed by the labeled compound, and that an ion pair is formed with the average expenditure of 32.5 ev. of energy, it is calculated that the average C^{14} β-particle (51 kev.) destroys 1570 molecules in addition to the molecule originally containing the disintegrating C^{14} atom. On this basis, a preparation containing one millicurie per millimole would destroy itself at the rate of 0.304% per year. Of course recombination of dissociated ions will decrease the extent of radiolysis. On the other hand, radical or ionic chain reactions will enhance the effect by a factor that can be as large as the chain length. The observed methyl-C^{14} iodide degraded to iodine, cited above, 0.135%, happens to be close to the calculated total degradation due to ionization, 0.128%.[2] It would appear that the more serious destruction of choline-C^{14} chloride, calcium glycolate-C^{14} and cholesterol-C^{14} reported[1] must involve chain reactions of some type, even though the compounds were present in the solid state.

We suggest that those concerned with the problem of long-term storage of isotopic compounds of high specific activity consider as a means of meeting this problem the storage of such compounds in appropriate dilute solutions, from which they may be recovered for use. This should have the effect of (1) greatly decreasing the chain length, where chain reactions are a problem, and (2) substituting, to a large degree, radiolysis of the solvent for radiolysis of the labeled compound. There may still be minor problems of (1) attack on the labeled organic material by long-lived or reactive solvent ions, and (2) purification of the labeled compounds from polymeric materials produced in solvent decomposition (*e.g.*, glycols from alcohols or polymeric material from benzene). Choice of a suitable solvent must thus pose a slight problem, but there is already a fairly extensive literature on the radiolysis of organic solvents, from which pertinent information may be obtained.[3] Another possible means of minimizing the extent of self-destruction of labeled compounds is the deposition of the compound as a thin layer, *i.e.*, a layer one or more orders of magnitude thinner than an "infinitely thick" layer, so that most of the electron energy is dissipated in the surroundings rather than in the compound itself.

(1) B. M. Tolbert, *et al.*, THIS JOURNAL, **75**, 1867 (1953).

(2) In the particular case of methyl iodide, the assumptions involved in the calculations appear to be valid. Schuler and Hamill, THIS JOURNAL, **74**, 6171 (1952), found that electrons of energies 0.60 to 1.76 Mev. liberated one iodine atom as elemental iodine for each 37 e.v. of energy absorbed.

(3) See, for example, M. Burton, *J. Phys. Colloid Chem.*, **52**, 564 (1948).

SHELL DEVELOPMENT CO.
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Some New Esters of 2,4-Dichlorophenoxyacetic Acid and their Herbicidal Activity[1]

BY CHARLES R. WAGNER, CHARLES L. HAMNER AND HAROLD M. SELL

RECEIVED JUNE 15, 1953

A number of new esters of 2,4-dichlorophenoxyacetic acid have been prepared by treating 2,4-

(1) Journal article no. 1475 from the Michigan Agricultural Experiment Station, East Lansing.

TABLE I

PROPERTIES AND HERBICIDAL ACTIVITY OF VARIOUS NEW ESTERS OF 2,4-DICHLOROPHENOXYACETIC ACID

Ester	M.p., °C.	Formula	Chlorine, % Calcd.	Chlorine, % Found	Herbicidal activity[a]
Methyl (control)[b]					+++++
4-Acetophenyl	120.5–121.5	$C_{16}H_{12}Cl_2O_4$	20.9	21.0	++
2-Methyl-4,6-dibromophenyl	174.5–175.5	$C_{15}H_{10}Cl_2Br_2O_3$	44.2[c]	44.3[c]	+
Carvacryl	144–146	$C_{18}H_{18}Cl_2O_3$	19.5	19.7	+
4-Nitrophenyl	119–120	$C_{14}H_9NCl_2O_5$	18.7	18.5	+++
Cetyl	41–42	$C_{24}H_{38}Cl_2O_3$	15.4	15.4	+
Guaiacyl	96–98	$C_{15}H_{12}Cl_2O_4$	21.7	21.5	+++
Eugenyl	54–55.5	$C_{18}H_{16}Cl_2O_4$	19.3	19.7	++++
Bornyl	178–180	$C_{18}H_{22}Cl_2O_3$	19.9	20.0	++++
p-Cresyl	94–95	$C_{15}H_{12}Cl_2O_3$	22.3	22.3	+++++
Benzyl	156	$C_{15}H_{12}Cl_2O_3$	24.1	23.6	+
4-Chloro-*o*-cresyl	103–104	$C_{15}H_{11}Cl_3O_3$	30.8	31.1	+++++
3-Methyl-4-chlorophenyl	125–130.5	$C_{15}H_{11}Cl_3O_3$	30.8	31.4	+
3-Methyl-4-chloro-2-nitrophenyl	104–106	$C_{15}H_{10}NCl_3O_5$	27.2	27.6	+++++
4-Methylphenylthio	83–84	$C_{15}H_{11}SCl_2O_2$	21.7	21.6	+++
2-Methylphenylthio	79–80	$C_{15}H_{11}SCl_2O_2$	21.7	21.2	++++
Phenylthio	74.5–75.5	$C_{14}H_{10}SCl_2O_2$	22.6	22.4	+++++

[a] The number of plus signs indicate the relative magnitude of activity of each substance. [b] Previously synthesized, M. S. Newman, Wm. Jones and M. Renoll, THIS JOURNAL, **69**, 718 (1947). The methyl ester has considerable herbicidal action on plants and was used to compare the activity of the other esters. [c] Expressed as total per cent. halide.

dichlorophenoxyacetyl chloride[2] with the appropriate hydroxyl compound.

The herbicidal activity of these substances was determined by preparing solutions of each of the esters having concentrations of 1, 10 and 100 p.p.m. by diluting a 1% stock solution with water. A variety of seeds of field and vegetable crops were soaked in these solutions for 4 and 12 hours, respectively. They were removed, dried on filter to remove excess moisture, planted in flats containing sand and after 2 weeks in the greenhouse were harvested. The herbicidal activity was evaluated by comparing the number of germinated seeds, total fresh weight and height of the treated seedlings with that of the non-treated plants (control) and also with plants treated with methyl 2,4-dichlorophenoxyacetate.

(2) V. H. Freed, THIS JOURNAL, **68**, 2112 (1946).

p-Cresyl 2,4-dichlorophenoxyacetate, 4-chloro-*o*-cresyl 2,4-dichlorophenoxyacetate, 3-methyl-4-chloro-2-nitro 2,4-dichlorophenoxyacetate and phenyl 2,4-dichlorophenoxythioacetate at the same concentrations had herbicidal activity equivalent to methyl 2,4-dichlorophenoxyacetate. Eugenyl 2,4-dichlorophenoxyacetate, bornyl 2,4-dichlorophenoxyacetate and 2-methyl-2,4-dichlorophenoxythioacetic acid had slightly less activity than the former substances. The remainder of the esters were much lower in activity and appear to have little potential value.

The chemical and physical properties and herbicidal activity of the new compounds are summarized in Table I.

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COMMUNICATIONS TO THE EDITOR

PARTIAL SYNTHESIS OF 16α,21-DIACETOXYPROGESTERONE

Sir:

The isolation[1] of a 16-hydroxylated steroid, Δ^5-pregnene-3β,16α,20α-triol from the urine of a boy with an adrenal tumor prompted us to synthesize[2] suitably substituted 16-oxygenated steroids with the object of determining their biological properties and of facilitating a search for their presence in adrenal secretions. The simplest compound of this type which could be expected to possess adrenocortical activity is 16α,21-dihydroxyprogesterone which we have now prepared in the form of its diacetate (I). During the course of this synthesis Simpson and Tait[3] reported on the properties of electrocortin, the most active hormone of the adrenal cortex concerned with

(1) H. Hirschmann and F. B. Hirschmann, *J. Biol. Chem.*, **184**, 259 (1950).

(2) H. Hirschmann, F. B. Hirschmann and M. A. Daus, THIS JOURNAL, **74**, 539 (1952); H. Hirschmann, F. B. Hirschmann and J. W. Corcoran, *Federation Proc.*, **12**, 218 (1953).

(3) A paper presented by S. A. Simpson and J. F. Tait to the Society for Endocrinology, a copy of which was very kindly sent to us by the authors.