TABLE II

GLYCOL DICARBAMATES

Glycol	M.P. (°C.)	Yield (%)	Solvent[a]	Analysis Nitrogen Calcd.	Found
Cyclohexane-1,4-diol	265	50	N	13.86	13.81
Cyclopentane-1,1-dimethanol	155	33	CP	12.96	12.99
Norcamphane-2,3-dimethanol	157	54	CP	11.56	11.36
Norcamphane-2,5-dimethanol	223	45	WM	11.56	11.22
2,2′-(1,5-Naphthylenedioxy)diethanol	265	54	N	8.38	8.29
2,2′-(2,5-Dichloro-*p*-phenylenedioxy)diethanol	236	94	H	7.93	7.67
2,2′-(2,5-Di-*t*-butyl-*p*-phenylenedioxy)diethanol	178	25	CP	7.07	6.80
2,2′-(4,4′-Sulfonyldiphenoxy)diethanol	227	25	N	6.60	6.89
5-Hydroxymethyl-β,β,5-trimethyl-2-*m*-dioxane-ethanol	196	33	AW	9.69	9.33
β,β,β′,β′-Tetramethyl-2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diethanol	241	82	AW	7.18	7.02
2,2-Dimethyl-1,5-pentanediol	155	97	WM	12.84	12.69

[a] Solvent for recrystallization: H, acetic acid; N, nitromethane; A, acetone; W, water; C, chloroform; P, petroleum ether M, methanol.

reaction mixture was then warmed to room temperature and poured onto ice to precipitate the product. Recrystallization from nitromethane gave 2.0 g. (50%) of the dicarbamate, m.p. 265°.

Cyclopentane-1,1-dimethanol dicarbamate. This compound was prepared by an adaptation of the method previously described.[6] A solution of 2.6 g. (0.02 mole) of cyclopentane-1,1-dimethanol in 25 ml. of chloroform and 5 ml. of pyridine was added to a solution of 5 g. (0.05 mole) of phosgene in 40 ml. of toluene at 0–5°. After warming to room temperature for about 10 hr. the solution was cooled to −78° and treated with liquid ammonia. The mixture was warmed to room temperature. The precipitate was collected and recrystallized from chloroform-petroleum ether to give 1.1 g. (33%) of the dicarbamate, m.p. 154–155°.

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(3) C. C. Stock in J. P. Greenstein and A. Haddow, *Advances in Cancer Chemotherapy,* Vol. II, pp. 446, 459, Academic Press, New York, 1954.

(4) The authors are indebted to Drs. C. C. Stock and D. A. Clarke of the Sloan-Kettering Institute for conducting these tests.

(5) Analyses by Micro Tech Laboratories, Skokie, Ill. All melting points are corrected.

(6) B. Ludwig and E. Piech, *J. Am. Chem. Soc.,* **73,** 5779 (1951).

Preparation and Polymerization of Vinyl Azide

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Vinyl azide, which has been previously described,[1] has been prepared by an improved process. This process is suited for the laboratory preparation of vinyl azide if proper precautions for handling this highly sensitive material are observed. On one occasion a sample in a distilling flask with a ground glass joint detonated when the joint was rotated. Vinyl azide should be handled as a highly sensitive material which is easily detonated. Statements in the literature[1a,2a] that this material is "surprisingly stable" should be regarded as misleading and erroneous.

Some preliminary polymerization studies with vinyl azide have established that a white, apparently infusible solid polymeric product can be obtained by bulk polymerization with peroxide or azo bis initiators. The polymer is highly combustible. Above 70° the azide decomposes with the formation of hydrazoic acid. It has been established that no triazole is present in the higher boiling liquids during the polymerization.

EXPERIMENTAL

β-Chloroethyl azide. One hundred grams of β-chloroethyl *p*-toluenesulfonate was refluxed with a slight excess of sodium azide in the minimum amount of methanol-water mixture necessary to give a homogeneous solution. This solution was prepared by adding methanol to the ester and a half-saturated aqueous solution of sodium azide until a homogeneous solution was obtained. After 24 hr. refluxing the reaction mixture was diluted with water and extracted with ether. The washed and dried ether solution was distilled to give 57–65% yields of β-chloroethyl azide, b.p. *ca.* 45°/25 mm.

Vinyl azide. To a hot solution of 100 g. potassium hydroxide in 400 ml. of water and 500 ml. of ethylene glycol was added 52.5 g. of β-chloroethyl azide dropwise. The vinyl azide distilled from the reaction mixture as formed. A short period of reflux after the completion of the addition completed the reaction. The water-vinyl azide mixture in the receiver was freed of water by freezing and decantation. The vinyl azide, b.p. 30°, does not freeze even at −80°. It is obtained in yield of about 20 g. (*ca.* 60%). This amount is probably larger than should be handled by ordinary laboratory procedures, since this amount can cause very severe damage on detonation. Ethanol may be used instead of ethylene glycol, but the separation of pure vinyl azide from the aqueous-alcohol distillate is then much more difficult.

Vinyl azide polymerization. All polymerizations were run in nitrogen-filled screw cap vials.

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(1) M. O. Forster and S. H. Newman, *J. Chem. Soc.* (*a*) **97,** 2570 (1910); (*b*) **99,** 1278 (1911).

(2) C. E. Schildknecht, *Vinyl and Related Polymers,* John Wiley and Sons, 1952, (*a*) p. 80, (*b*) p. 397.

Solution: Solutions of vinyl azide in methanol (about 1 ml. in 3 ml.) containing *ca.* 3 mg. of azobisisobutyronitrile were heated for from 1 to 24 hr. at temperatures of from 50–75° in screw cap vials. The vials were cooled, opened, and the solution evaporated to dryness. The white flakes of polymer were soluble in methanol but insoluble in water. The yields of polymer were under 5%.

Suspension: Exploratory attempts to polymerize vinyl azide by suspension techniques in water by the usual techniques gave no polymer.

Emulsion: Emulsion polymerizations with a standard recipe[2b] of ammonium persulfate 0.5%, sodium lauryl sulfate 10%, and sodium bisulfite 0.2% in water acidified to *p*H 2 with acetic acid, gave only small yields of polymer at temperatures of from 50 to 75° and times of 1 to 24 hr. The amount of polymer in all cases was very small and did not seem to increase in quantity after the first few hours. The vinyl azide was never completely reacted.

Bulk: Bulk polymerizations were run using benzoyl peroxide or azobisisobutyronitrile as initiators in concentrations of 0.1 to 1%. At temperatures of 50–70° yields of less than 5% were obtained. Temperatures over 70° caused decomposition of the vinyl azide as evidenced by brown coloration. This decomposition was very rapid at 100°.

The polymer obtained in the polymerizations listed above was a white, flaky, apparently infusible solid. It burned furiously when held to a flame and decomposed violently when touched with a hot wire. Such combustibility makes carbon-hydrogen analysis impossible. Nitrogen analyses, which are notoriously untrustworthy for polymers, were also not attempted. As a result, no ultimate analytical data are available to characterize the polymer. It is to be noted that polymers obtained in such low yield may very well include fragments from the initiator as a significant portion of their composition.

In all polymerizations a large part of the vinyl azide was converted into higher boiling liquids which were always completely water soluble. No 1,2,3-triazole was ever detected although sensitive methods were used to detect it.

In polymerizations run at temperatures over about 70° ammonium azide crystals formed on the upper wall of the vials. This is a known decomposition product[3] of hydrazoic acid. If vinyl azide cleaves above 70° into hydrazoic acid, the other product would probably be acetylene but that has not been detected.

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(3) L. F. Audrieth, *Chem. Revs.*, **15**, 169 (1934).

Radioactive Estrogens[1a]

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The recent publication of Hartman *et al.*[1b] prompts us to report a very similar synthesis with radioactive carbon, as well as with tritium.

Ozonolysis of 19-nortestosterone 17-acetate[2] (III) followed by decomposition of the ozonide with hydrogen peroxide gave, in 50% yield, 17β-acetoxy-5-keto-3,5-seco-4-norestrane-3-oic acid.

Lactonization by treatment with acetic anhydride and sodium acetate furnished, in 54% yield, the desired 17β-acetoxy-5-hydroxy-3,5-seco-4-nor-5(10)-estrene-3-oic acid 3,5-lactone.

This enol lactone acetate was added to the equimolar amount of methyl magnesium iodide-C^{14} in ether. The reaction mixture was decomposed with dilute hydrochloric acid and after being worked up as usual, the obtained crude product cyclized with hydrochloric acid in acetic acid.[3] The reaction product furnished after purification, in 47% yield, 19-nortestosterone acetate-4-C^{14} (III).

Attempts to aromatize that compound directly by dehydrogenation[4] with selenium dioxide gave, consistently, a yield below 35%. Dehydrogenation of estra-3,5-diene-3,17β-diole diacetate (I)[2] with selenium dioxide gave however, in very good yield, the desired 17-dihydroequilenin-17β 3,17-diacetate-4-C^{14} (IIb).

Bromination[5] of 19-nortestosterone 17-acetate-4-C^{14} (III) in dry ether with bromine and a few drops of hydrogen bromide in acetic acid gave crude 2,6-dibromo-19-nortestosterone 17-acetate-4-C^{14}, which was dehydrobrominated[6] with lithium chloride in dimethylformamide, giving in 75% yield (calculated on 19-nortestosterone 17-acetate-4-C^{14}) the desired estra-1,3,5(10),6-tetraene-3,17β-diol 17-monoacetate-4-C^{14} (IVa), m.p. 247–250°. This tetraene, obtained from a nonradioactive model run, was reacted with tritium and prereduced palladium-on-charcoal to give estradiol 17β-acetate-6,7-*t*.

Estra-1,3,5(10),6-tetraene-3,17β-diol 17-acetate-4-C^{14} (IVa) gave, after reduction[5] with 30% palladium-on-charcoal in ethyl acetate under hydrogen for 3 hr., estradiol 17β-acetate-4-C^{14} (V), in 95% yield. The specific radioactivity of this product and of its starting material (4-C^{14}-19-nortestosterone 17-acetate) was identical.

Estra-1,3,5(10),6-tetraene-3,17β-diol 17-acetate-4-C^{14} (IVa) was acetylated[5] with acetic anhydride in pyridine and the resulting 3,17-diacetate (IVb) was dehydrogenated[5] with selenium

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(1a) Since this note was submitted S. Kushinsky, Abstracts of 131st Meeting, AMERICAN CHEMICAL SOCIETY, p. 36-O, reported a very similar synthesis.

(1) (b) J. A. Hartman, A. J. Tomasewski, and A. S. Dreiding, *J. Am. Chem. Soc.*, **78**, 5662 (1956).

(2) J. A. Hartman, *J. Am. Chem. Soc.*, **77**, 5151 (1955).

(3) Compare L. M. Thompson, C. H. Yates, and A. D. Odell, *J. Am. Chem. Soc.*, **76**, 1194 (1954).

(4) Compare H. J. Ringold, G. Rosenkranz, and F. Sondheimer, *J. Org. Chem.*, **21**, 239 (1956); C. Meystre, H. Frey, W. Voser, and A. Wettstein, *Helv. Chim. Acta*, **39**, 734 (1956).

(5) Compare C. Djerassi, G. Rosenkranz, J. Romo, S. Kaufmann, and J. Pataki, *J. Am. Chem. Soc.*, **72**, 4534 (1950).

(6) Compare R. P. Holysz, *J. Am. Chem. Soc.*, **75**, 4432 (1953).