to boiling for 10 min. The solid precipitate was filtered with suction, redissolved in 1.5 l. of boiling water, filtered again hot, and dried. The yield of the crude product was 10 g. (92%). Several recrystallizations from 1:1 absolute ethanol-benzene gave a white crystalline solid,[6] m.p. 221–222.5°.

Anal. Calcd. for $C_{20}H_9O_5NCl_2$: C, 58.0; H, 2.2; N, 3.4; Cl, 17.1. Found: C, 58.2; H, 2.6; N, 3.1; Cl, 17.3.

3,6-Dichloronitrofluorane II. This material was prepared from nitrofluorescein II, using a procedure analogous to that described above. The yield of the crude product was 9 g. (82%), and the recrystallized material[6, 7] melted at 215–216°.

Anal. Calcd. for $C_{20}H_9O_5NCl_2$: C, 58.0; H, 2.2; N, 3.4; Cl, 17.1. Found: C, 58.1; H, 2.4; N, 3.1; Cl, 17.0.

3,6-Dihydroxy-9-(m-nitrophenyl)-xanthene (MNX) and its diacetate. A mixture of 3.8 g. (0.025 mole) of *m*-nitrobenzaldehyde and 5.5 g. (0.050 mole) of resorcinol was fused at 195–200° and maintained at that temperature for 3 hr. during which the mixture hardened into a dark mass. The melt was ground in the mortar and heated on a steam bath with 15 ml. of 6*N* hydrochloric acid for 1 hr. The solid was filtered, dissolved in *N* sodium hydroxide, and reprecipitated with *N* hydrochloric acid. The product, m.p. 185–188° dec., showed blue fluorescence in alkaline solution which was quenched on acidification.

One gram of the product was dissolved in 5 ml. of pyridine and treated with 5 ml. of acetic anhydride. The solution was heated on a steam bath for 0.5 hr., left at room temperature overnight, and then poured into iced water. The resulting precipitate was filtered and dried. After the diacetate had been recrystallized several times from acetone-ethanol, it melted at 185–190° dec. It was found to be hygroscopic.

Anal. Calcd. for $C_{23}H_{17}O_7N.1^1/_2H_2O$: C, 61.89; H, 4.51. Found: C, 62.30; H, 4.05.

3,6-Dihydroxy-9-(p-nitrophenyl)-xanthene (PNX) and its diacetate. These compounds were prepared, using *p*-nitrobenzaldehyde and resorcinol as starting materials, by the procedures described above. Both products did not melt below 300° and were hygroscopic.

Anal. (diacetate) Calcd. for $C_{23}H_{17}O_7N.H_2O$: C, 63.16; H, 4.38; N, 3.20. Found: C, 63.68; H, 3.97; N, 3.21.

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(6) A γ-lactone form was indicated by the strong infrared absorption band at 1760 cm.$^{-1}$ (*cf.* ref. 7), lack of color and fluorescence, and low solubility in water and alkalis.

(7) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, Inc., New York, 1954, p. 159.

The Preparation of Oxetanones

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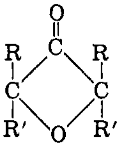
Within recent years several oxetanones have been synthesized.[4] We wish to report that we have completed the synthesis of 2,4-dimethyl-2,4-diethyl-3-oxetanone[5] (Ia) and 2,2,4,4-tetraphenyl-3-oxetanone[4b] (Ib) by the method used to synthesize 2,2,4,4-tetramethyl-3-oxetanone[4c,f] (Ic).



Ia. R = CH_3; R′ = C_2H_5
Ib. R,R′ = C_6H_5
Ic. R,R′ = CH_3

Included in this report are descriptions of the synthesis of 2,2,4,4-tetramethyl-3-oxetanol (II) and 2,2,3,4,4-pentamethyl-3-oxetanol (III). Both of these have been prepared from Ic.

EXPERIMENTAL[6]

The preparation of 2,5-dimethyl-2,5-diethyltetrahydro-3-furanone (IV). The procedure of Richet[7] gave 145 g. (70%) of ketone, b.p. 190–196°, from 209 g. of 3,6-dimethyl-4-octyne-3,6-diol.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.59. Found: C, 70.65; H, 10.75.

The preparation of 2,5-dimethyl-2,5-diethyltetrahydro-furan-3,4-dione (V). Thirty-one grams of IV was added dropwise to a suspension of 24 g. of selenium dioxide in 400 ml. of dioxane and 20 ml. of water. The mixture was stirred and heated to reflux temperature during the addition of IV and for 12 hr. thereafter. The selenium was removed by filtration and the dioxane evaporated under reduced pressure. The residue was dissolved in ether and the solution stored over Drierite. After filtration and evaporation of the solvent, the residue was purified by distillation, yielding 27 g. (68%) of V, b.p., 56–63° at 1 mm.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.31; H, 8.82. Several attempts to prepare V by way of the dibromo derivative[4c] of IV were unsuccessful.

The preparation of 2,4-dimethyl-2,4-diethyl-3-oxetanol-3-carboxylic acid. (VI). A procedure previously described for rearranging a diketone[4c] was followed. This produced 5.7 g. (30%) of VI from 17.7 g. of V. After several crystallizations from carbon tetrachloride, the acid melted at 127–128°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 59.46; H, 8.92; neut. equiv., 202. Found: C, 59.69; H, 8.77; neut. equiv., 200.4.

The preparation of Ia. The lead tetraacetate oxidation of VI was employed as in the preparation of Ic.[4c] A yield of 4.2 g. (60%) of Ia, b.p., 133–134° resulted from the oxidation of 10 g. of VI. Ia solidified on cooling; m.p. of resublimed product, 56–57°.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.87; H, 10.26. Found: C, 70.46; H, 9.90. The oxetanone readily formed a 2,4-dinitrophenylhydrazone derivative,[8] m.p., 135–136°.

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(1) Taken from the Ph.D. Dissertation of James L. Harper, Emory University, 1957.

(2) Tennessee Eastman Fellow, 1956–57.

(3) To whom inquiries should be sent.

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(5) No effort has been made to resolve this or any related compounds into the various stereoisomers.

(6) All melting and boiling points are uncorrected. Microanalyses were done by Drs. G. Weiler and F. B. Strauss, Oxford, England.

(7)(a) H. Richet, R. Dulon, and G. Dupont, *Bull. Soc. Chim., France*, 693 (1947). (b) H. Richet, *Ann. chim.*, [12] **3**, 317 (1948).

Anal. Calcd. for $C_{15}H_{20}O_5N_4$: N, 16.66. Found: N, 16.33. The infrared spectrogram of Ia showed a strong carbonyl absorption at 5.5 μ. This is characteristic of the spectrograms of the other oxetanones.[4b,c]

Preparation of Ib. Ib has been prepared by the oxidation of tetraphenylallene[9] and tetraphenylacetone.[4b] The synthesis reported here started with the preparation of 128 g. (50% yield) of 1,1,4,4-tetraphenyl-2-butyne-1,4-diol from 225 g. of benzophenone and acetylene by the procedure of Dupont.[10] The procedure of Tichamolow and Druchinin[11] was used to convert 5 g. of the diol into 2.5 g. (50% yield) of 2,2,5,5-tetraphenylfurandione. The procedure described above for the preparation of VI was used to convert 2 g. of the dione into 1.9 g. (93% yield) of 2,2,4,4-tetraphenyl-3-hydroxyoxetane-3-carboxylic acid, m.p., 189–90°.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found: C, 79.52; H, 5.61. Ib was prepared as indicated above for Ia, 1.1 g. (63% yield) from 2 g. of the hydroxy acid. The purified tetraphenyloxetanone melted at 199–200° and did not depress the melting point of a sample prepared by the oxidation of tetraphenylacetone.[4b]

The preparation of II. (a) A solution of 4 g. of Ic in 50 ml. of anhydrous ether was added dropwise with stirring to a suspension of 1 g. of lithium aluminum hydride in 100 ml. of dry ether. After heating at reflux temperature for 1 hr. the excess lithium aluminum hydride was decomposed with water and the two phase system placed in a continuous ether extractor for 8 hr. The ether layer was separated and the ether evaporated at reduced pressure. The crude residue was crystallized from petroleum ether (b.p. 00–00°) to yield 2.3 g., 58% of II, m.p., 101–102°.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.61; H, 10.78. Found: C, 64.49; H, 10.89.

(b) A solution of 4 g. of Ic in 50 ml. of dry ether was added dropwise to a solution of isopropylmagnesium bromide made from 3.9 g. of isopropyl bromide and 1 g. of magnesium in 100 ml. of dry ether. The addition was accompanied by a steady evolution of gas. After the addition was plete, the solution was stirred for 15 min. and then 50 ml. of a saturated aqueous solution of ammonium chloride was added. The two phase mixture was placed in a continuous ether extractor for 8 hr. Separation of the ether layer, evaporation of the ether under reduced pressure, and crystallization of the residue from petroleum ether gave 0.8 g. (20%) of II, m.p. and mixture m.p. with sample prepared as described in (a) above, 101–102°.

The preparation of III. In a manner identical with the procedure described in (b) above 4 g. of Ic and an excess of methylmagnesium iodide were used to prepare 1.1 g., (25% yield) of III, m.p., 129–130°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.66; H, 11.11. Found: C, 66.66; H, 11.17.

Acknowledgment. We wish to thank the Tennessee Eastman Company and the Richard K. Whitehead Foundation for their generous support of this research. We also thank the Air Reduction Chemical Company for generously supplying us with the dimethylhexynediol and dimethyloctynediol used in the synthesis of the oxetanones.

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Derivatives of Tetrahydropyran

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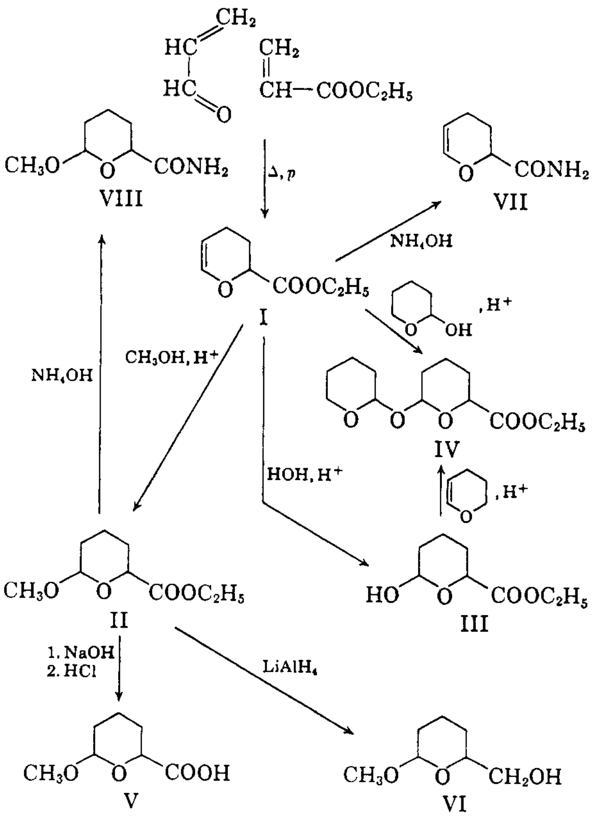
In connection with some kinetic studies, several derivatives of tetrahydropyran were desired. Their preparations are described below.

All derivatives were prepared from ethyl 3,4-dihydro-2*H*-pyran-2-carboxylate which was obtained in poor yield, similarly to the method of Smith *et al.*,[1] from the Diels-Alder addition of ethyl acrylate to acrolein. The structure of the addition product was established by 1) carbon-hydrogen analysis, and by 2) conversion to the known amide.[1]

In the 3,4-dihydro-2*H*-pyran series, it is known that addition of ROH to the $\Delta^{5,6}$-double bond yields a product having the alkoxy radical attached to the C_6, the hydrogen radical attached to the C_5.[2] No structure proof of the herein described derivatives was undertaken, but when VI was hydrolyzed with aqueous sulfuric acid (1*N*), the resulting product had a positive Fehling reaction, indicating



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