Anal. Calcd. for $C_{16}H_{20}O_5N_4$: 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.

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Derivatives of Tetrahydropyran

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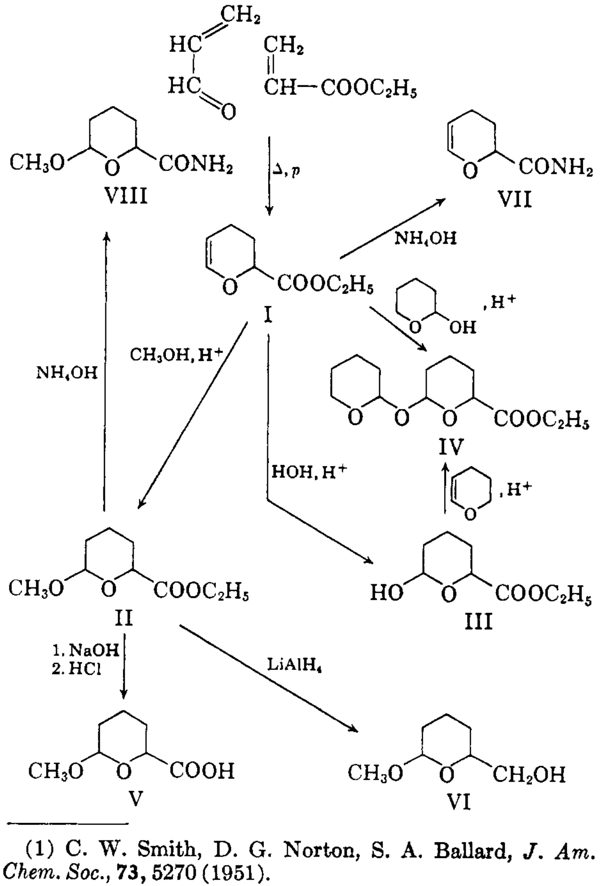
In connection with some kinetic studies, several derivatives of tetrahydropyran were desired. Their preparations are described below.

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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that in II, V, and VI the methoxy group is attached to the C_6. The fact that *IV* was obtained both by the addition of 2,3-dihydro-4*H*-pyran to *III*, as well as by the addition of tetrahydro-2-hydroxypyran to *I*, is additional evidence for the type of link shown in *IV*.

I has been obtained by Whetstone and Ballard[3] by the oxidation of 3,4-dihydro-2*H*-pyran-2-carboxaldehyde with silver oxide followed by treatment of the silver salt with ethyl iodide.

EXPERIMENTAL

Preparation of ethyl 3,4-dihydro-2H-pyran-2-carboxylate (I). Ethyl acrylate (160 ml.), acrolein (92 ml.), and hydroquinone (2.52 g.) were heated in a closed vessel (initial pressure 13.5 atm.) to 189° and kept at this temperature for 78 min. The products were crudely distilled. Fractional redistillation yielded ethyl 3,4-dihydro-2*H*-pyran-2-carboxylate (I) b.p. 73.5–76°/7 mm. (7 ml.). Infrared analysis showed the presence of an ester (doublet) and an isolated double bond (1650 cm.$^{-1}$).

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.54; H, 7.69. Found: C, 61.50; H, 8.21.

The derived 3,4-dihydro-2*H*-pyran-2-carboxamide (VII) had a m.p. of 114–114.5° (hot stage, sublimation).

Preparation of ethyl tetrahydro-6-methoxypyran-2-carboxylate (II). Ice cold *I* (6 ml.) was mixed with ice cold methanol (2.5 ml.) and concd. aqueous hydrochloric acid was added (1 drop). After 5 hr. (3 hr. at room temperature) the mixture was neutralized (sodium bicarbonate), filtered, and distilled. The ethyl tetrahydro-6-methoxypyran-2-carboxylate (II) boiled at 81°–81.5°/2.5 mm., n_D^{25} 1.4422; yield, approximately 6 ml.

The infrared spectrum retained the ester doublet, and showed the absence of the double bond.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.45; H, 8.52. Found: C, 57.25; H, 8.76.

The derived tetrahydro-6-methoxypyran-2-carboxamide (VIII) had a m.p. of 161–162° (hot stage). Profound sublimation started around 130°, the sublimed crystals melting at 159°–160°.

Preparation of ethyl tetrahydro-6-hydroxypyran-2-carboxylate (III). Compound *I* (8 ml.) was mixed with water (14 ml.), acetone (10 ml.), tetrahydrofuran (30 ml.), and concd. aqueous hydrochloric acid (1.7 ml.). It was stirred for 1 hr. and deionized by Dowex 1X-4 anion exchange resin (bicarbonate form). Concentration *in vacuo* gave an oil. Distillation yielded ethyl tetrahydro-6-hydroxypyran-2-carboxylate (III) b.p. 114–115.7°/1 mm. (1.3 ml.), n_D^{24} 1.4586. The infrared spectrum showed hydroxyl, no water, no double bond.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.20; H, 8.05. Found: C, 54.89; H, 8.17% H.

Preparation of ethyl tetrahydro-6-[tetrahydropyran-2-oxy]-pyran-2-carboxylate (IV). Compound *III* (1.1 ml.) was mixed with 2,3 dihydro-4*H*-pyran (1.3 ml.) and concd. aqueous hydrochloric acid was added (1 drop). The mixture was left at room temperature for 3 hr., neutralized with aqueous sodium bicarbonate, and distilled to yield ethyl tetrahydro-6-[tetrahydropyran-2-oxy]pyran-2-carboxylate (IV) b.p. 142–144°/1 mm., n_D^{25} 1.4650; yield: approximately 1 ml.

Anal. Calcd. for $C_{13}H_{22}O_5$: C, 60.48; H, 8.53. Found: C, 60.25; H, 8.32% H.

The infrared spectrum showed no hydroxyl, no double bond, and an ester (doublet). When *I* was allowed to react with tetrahydro-2-hydroxypyran (acid catalysis), a product was obtained with boiling point 145–148°/2 mm., which had an infrared spectrum identical with that of *IV*, n_D^{25} 1.4648.

Preparation of tetrahydro-6-methoxypyran-2-carboxylic acid (V). Saponification of *II* (1 ml.) with sodium hydroxide (0.25 g.) in ethanol water (3 ml., 50/50 v./v.) for 1 hr., followed by acidification (6*N* hydrochloric acid), dilution with water (25 ml.), extraction by ether, and concentration of the dried (with sodium sulfate) ether layer, yielded an oil. Paper chromatography of the product, tetrahydro-6-methoxypyran-2-carboxylic acid, in ethyl acetate–acetic acid–formic acid–water (18:3:1:4) followed by spraying with an aqueous solution of Chlorophenol Red (0.8%), showed a bright yellow spot, R_f = 0.80.

Preparation of tetrahydro-6-methoxypyran-2-methanol (VI). Compound *II* (6 ml.) dissolved in absolute tetrahydrofuran (10 ml.) was added dropwise to a solution-suspension of lithium aluminum hydride (10 g.) in absolute tetrahydrofuran (160 ml.) while stirring. Stirring was continued overnight, and the mixture was refluxed for 6 hr. The hydride was decomposed by the dropwise addition of ethyl acetate followed by aqueous tetrahydrofuran to the reaction mixture at room temperature. Water was added (total of 450 ml.) and the slurry was filtered. Tetrahydrofuran was removed *in vacuo* and the aqueous solution was adjusted to 2*N* with sodium hydroxide, left for 2 hr. and continuously extracted with ether (4 days). The dried extract was concentrated *in vacuo* and the residual oil was distilled to yield tetrahydro-6-methoxypyran-2-methanol (VI). b.p. 70–75°/1.8 mm. (1.25 ml.), n_D^{25} 1.4535.

Anal. Calcd. for $C_7H_{14}O_3$: C, 56.55; H, 9.58. Found: C, 56.53; H, 9.53.

The infrared spectrum showed a hydroxyl peak, no water and no carbonyl.

When VI was heated on the steambath with aqueous sulfuric acid (1*N*) for 2 hr., the resulting hydrolysate had a positive Fehling reaction.

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Cyclization of 1,5-Diphenyl-1,3,5-pentanetrione with Ethyl Oxalate. 3,5-Dibenzoyl-1,2,4-cyclopentanetrione and Its Quinoxaline[1]

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Recently,[3,4] the terminal methyl group of benzoylacetone was benzoylated to form triketone I. This triketone has now been cyclized with ethyl oxalate by sodium ethoxide in refluxing ethanol to

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[2] National Science Foundation Predoctoral Fellow, 1958–60.

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