which lacked a well-defined melting point and was probably a mixture of 3-acyl and 1,3-diacyl compounds. This mixture was hydrolyzed by brief refluxing with aqueous alcoholic sodium hydroxide as in the preceding example to yield 13.7 g. (38%) of 3-acyl compound (Id), which, after recrystallization from 95% ethanol, had m.p. 256–258°, infrared (μ), 3.13 (N–H) and 6.06 (C=O).

Anal. Calcd. for $C_{17}H_{12}BrNO_3$: C, 57.00; H, 3.38; N, 3.91. Found: C, 57.17; H, 3.59; N, 3.96.

3-(4,5-Dimethoxy-2-nitrophenylacetyl)-5-bromoindole (IIb).—A solution of 2.24 g. (0.006 mole) of Ib in 160 ml. of boiling glacial acetic acid was cooled to 80° and a solution of 0.54 g. (0.006 mole) of concentrated nitric acid (69.6%) in 10 ml. of glacial acetic acid was added. The yellow solution was allowed to cool, whereby the color deepened and a solid began to separate. The mixture was allowed to stand at room temperature for 3 hr., then the solid was collected on a filter, washed several times with glacial acetic acid, and air-dried. Recrystallization from 95% ethanol gave 2.08 g. (83%) of a pale yellow solid, m.p. 250° dec., infrared (μ), 3.05 (N–H) and 6.05 (C=O).

Anal. Calcd. for $C_{18}H_{15}BrN_2O_5$: C, 51.56; H, 3.61; N, 6.68. Found: C, 51.67; H, 3.79; N, 6.41.

3-(4,5-Methylenedioxy-2-nitrophenylacetyl)indole (IIc).—Four grams of Ic was nitrated as in the preceding example (4-hr. reaction time) to yield 2.80 g. (60%) of IIc, which recrystallized from glacial acetic acid as fine yellow needles, m.p. 239–240° dec., infrared (μ), 3.08 (N–H) and 6.20 (C=O).

Anal. Calcd. for $C_{17}H_{12}N_2O_5$: C, 62.96; H, 3.72; N, 8.64. Found: C, 63.21; H, 3.93; N, 8.28.

3-(4,5-Methylenedioxy-2-nitrophenylacetyl)-5-bromoindole (IId).—Nitration of 0.40 g. of Id with 0.11 g. of concentrated nitric acid in 38 ml. of nitromethane for 1 hr. at 60° yielded 0.43 g. (95%) of IId, which crystallized from the reaction mixture. Recrystallization from nitromethane gave pale yellow needles, m.p. 266° dec., infrared (μ), 3.04 (N–H) and 6.18 (C=O).

Anal. Calcd. for $C_{17}H_{11}BrN_2O_5$: C, 50.63; H, 2.75; N, 6.94. Found: C, 50.77; H, 2.88; N, 6.65.

5,6-Dimethoxy-5′-bromo-2,3′-biindolyl (IIIb).—Two grams (0.0048 mole) of IIb was dissolved in 200 ml. of boiling glacial acetic acid, and a solution of 8.0 g. (0.035 mole) of stannous chloride dihydrate in 15 ml. of concentrated hydrochloric acid was added during 5 min. The solution was then boiled for 10 min. and allowed to stand at room temperature overnight. A yellow solid separated; it was collected on a filter, washed several times with acetic acid, followed by several washings with ether, and air-dried. The yield of orange-yellow powder was 2.2 g. This solid (presumably the hexachlorostannic acid complex) was mixed with 8 ml. of 95% ethanol and enough water to make a stirrable paste, and 5% sodium hydroxide solution was added dropwise until the pH of the mixture was about 7. The reaction mixture changed from red-orange to a pale yellow color at completion of the addition. The cream-colored solid was collected by filtration, washed several times with water, air-dried, then extracted with 50 ml. of boiling 95% ethanol divided roughly into three portions. The combined ethanol extracts were allowed to cool and a small amount of granular white solid which separated was removed by filtration and discarded. The ethanol filtrate was heated to boiling, diluted with 20 ml. of water, and allowed to cool. The slightly colored crystalline solid which separated was collected, then recrystallized twice from aqueous ethanol and twice from aqueous methanol to yield 0.40 g. (22%) of IIIb as off-white feathery needles, m.p. 220–221°; ultraviolet spectrum (95% ethanol): λ_{max} mμ (log ε), 247 (4.37), 293 shoulder (4.14), and 323 (4.40). An ethanolic solution of the compound gave a deep blue color with Ehrlich's reagent.

Anal. Calcd. for $C_{18}H_{15}BrN_2O_2$: C, 58.23; H, 4.07; N, 7.55. Found: C, 58.50; H, 4.35; N, 7.52.

5,6-Methylenedioxy-2,3′-biindolyl (IIIc).—A similar reduction of 2.40 g. (0.0074 mole) of IIc with 5.63 g. (0.025 mole) of stannous chloride dihydrate and 8 ml. of concentrated hydrochloric acid in 200 ml. of glacial acetic acid was effected as in the preceding example except that ethyl acetate was used for the extraction. Evaporation of the extracts followed by sublimation of the residue at 200° (0.4 mm.) afforded 0.20 g. (10% yield) of IIIc which, after one recrystallization from aqueous ethanol and a final sublimation, was obtained as fine white needles, m.p. 222–223° dec.; ultraviolet spectrum (95% ethanol): λ_{max} mμ (log ε), 240 (4.44), 279 (4.04), 289 shoulder (4.00), and 335 (4.40). An ethanolic solution of the compound gave a deep blue solution with Ehrlich's reagent.

Anal. Calcd. for $C_{17}H_{12}N_2O_2$: C, 73.89; H, 4.37; N, 10.14. Found: C, 74.09; H, 4.41; N, 10.25.

5,6-Methylenedioxy-5′-bromo-2,3′-biindolyl (IIId).—A similar reduction of 2.00 g. (0.0050 mole) of IId in 250 ml. of acetic acid with 4.00 g. (0.018 mole) of stannous chloride dihydrate in 6 ml. of concentrated hydrochloric acid, followed by a work-up analogous with that of the preceding example, gave 0.84 g. (47% crude yield) of product, m.p. 212–218° dec. Sublimation at 210–215° (0.08 mm.), accompanied by considerable decomposition of the unsublimed residue, yielded white crystals, m.p. 224–226° dec.; ultraviolet spectrum (95% ethanol): λ_{max} mμ (log ε), 248 (4.31), 281 shoulder (4.03), 291 shoulder (4.00), and 333 (4.37); deep blue color with Ehrlich's reagent.

Anal. Calcd. for $C_{17}H_{11}BrN_2O_2$: C, 57.48; H, 3.12; N, 7.89. Found: C, 57.39; H, 3.35; N, 7.91.

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The Photoaddition of Cyclic Ethers to 1-Octene

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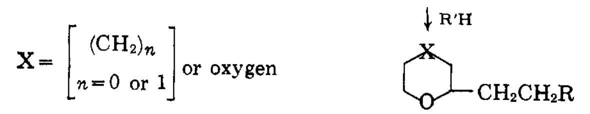
The peroxide-induced reactions of cyclic ethers with 1-octene and maleic anhydride have been reported to produce ketones[1] or α-substituted cyclic ethers[2,3] as the major products. Recent investigations on the light-induced reactions of maleic anhydride,[3] 7,7,8,8-tetracyanoquinodimethane, and tetracyanoethylene[4] with tetrahydrofuran have demonstrated that α-substituted tetrahydrofurans are the main reaction products, while the same reactions of maleic anhydride with tetrahydropyran and 1,4-dioxane have led to nondistillable mixtures.[3]

These studies prompted us to report the results of a similar investigation involving the photoaddition of cyclic ethers to 1-octene at room temperature which have mainly produced α-substituted alkyl ethers. The reaction can be induced directly by light or initiated photochemically by acetone, the latter conditions resulting in higher yields of the alkylated products.

Our results differ from those reported by Wallace and Gritter[1] in that the addition of tetrahydrofuran and tetrahydropyran to 1-octene occurs without ring opening. The formations of 1:1 adducts of tetrahydropyran and 1,4-dioxane with 1-octene are also in contrast to the results obtained by Jacobs and Ecke[3] who have not been able to isolate 1:1 adducts of the same ethers with maleic anhydride.

This addition of cyclic ethers to olefins presumably



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[2] T. J. Wallace, R. J. Gritter, and H. G. Walsh, *Nature*, **198**, 284 (1963), and references cited therein.

[3] R. L. Jacobs and G. G. Ecke, *J. Org. Chem.*, **28**, 3036 (1963).

[4] J. Diekmann and C. J. Pedersen, *ibid.*, **28**, 2879 (1963).

involves a free-radical reaction, as previously suggested,[1,3] for which the preceding mechanism is represented.

Experimental[5]

Experiments with ultraviolet light were conducted in an apparatus similar to the one described by de Mayo[6] with slight modifications. The radiation sources for the acetone-initiated reactions and the direct light-induced reactions were accomplished by Hanau Q81 high pressure mercury vapor lamps fitted into Pyrex or quartz immersion tubes, respectively. The reaction mixtures were cooled externally by running water and were kept under oxygen-free nitrogen. Reactions in sunlight were performed in Pyrex tubes, and the system was flushed with nitrogen after each addition of the olefin.

Reagents were tetrahydrofuran, B.D.H., and tetrahydropyran and dioxane, Fluka. These cyclic ethers were freshly distilled over sodium before use: acetone, absolute, and 1-octene, Fluka. The olefin was shaken with aqueous ferrous sulfate solution and dried (Na_2SO_4); it was freshly distilled and filtered through a short column of Alcoa activated alumina F20 before use.

1-Octene and Tetrahydrofuran with Ultraviolet Light.—A mixture of 1-octene (0.5 g.), tetrahydrofuran (90 ml.), and acetone (5 ml.) was irradiated for 1 hr. A solution of 1-octene (5.1 g.) in acetone (5 ml.) then was added in ten equal portions in 1-hr. intervals and irradiation was continued for another 12 hr. Excess reagents were removed under reduced pressure and then the residue, whose infrared spectrum indicated only traces of carbonylic substances, was distilled. The fraction with b.p. 80–140° (1.5 mm.), 5.4 g., was chromatographed on alumina (270 g.). Elution with pentane gave 2-octyltetrahydrofuran (2.3 g., 25% based on olefin employed) which upon redistillation indicated b.p. 69–71° (0.4 mm.), $n^{26}\mathrm{D}$ 1.4410; lit.[7] b.p. 85–87° (3 mm.), $n^{20}\mathrm{D}$ 1.4412. This substance showed identical boiling point, infrared spectrum, refractive index, and gas chromatographic retention time with those of an authentic sample.[8] The n.m.r. spectrum of this compound exhibited multiplets at τ 6.15 and 8.1, a broad singlet at τ 8.65, and a triplet at τ 9.1 in the ratio 3:3.8:14:3.3.

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 77.90; H, 13.00.

1-Octene and Tetrahydrofuran in Sunlight.—A mixture of 1-octene (0.5 g.), tetrahydrofuran (90 ml.), and acetone (5 ml.) was left in direct sunlight for 1 day. A solution of 1-octene (5.1 g.) in acetone (5 ml.) was then added in ten equal portions in 1-day intervals, and the mixture was left in sunlight for another 7 days. After removal of the solvent, the residue, whose infrared spectrum indicated only traces of carbonylic substances, was filtered through alumina (450 g.) using a 1:1 benzene–ether mixture. The resulting oily residue (8 g.) was distilled *in vacuo*. The fraction with b.p. 70–130° (0.5 mm.), 5.5 g., was chromatographed on alumina (270 g.). Pentane eluted 2-octyltetrahydrofuran (2.7 g., 30%).

1-Octene and Tetrahydropyran with Ultraviolet Light.—The quantities and experimental conditions described above were followed. After removal of the reagents, the residue which contained only traces of carbonylic materials was distilled. The fraction with b.p. 75–150° (1.5 mm.), 4.3 g., was chromatographed on alumina (220 g.). Elution with pentane gave 2-octyltetrahydropyran (1.7 g., 17%), b.p. 84–86° (0.6 mm.), $n^{25}\mathrm{D}$ 1.4458. This substance showed the same physical properties as an authentic sample prepared by the method of Paul.[9] Its n.m.r. spectrum indicated multiplets at τ 6.0 and 6.65, a broad singlet at τ 8.65, and a triplet at τ 9.15 in the ratio 1:2:19.8:3.1.

Anal. Calcd. for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.26; H, 13.12.

1-Octene and Tetrahydropyran in Sunlight.—The procedure described above with the same quantities were followed. After the usual work-up, the remaining residue (7.1 g.) was distilled and the fraction with b.p. 75–150° (1.5 mm.), 3.3 g., was chromatographed on alumina (170 g.). Elution with pentane led to 2-octyltetrahydropyran (2.1 g., 21%).

1-Octene and 1,4-Dioxane with Ultraviolet Light.—Similar procedure and quantities as described above were followed. The residue which contained only traces of carbonylic substances was distilled and the fraction with b.p. 80–180° (0.5 mm.), 5.2 g., was crystallized from petroleum ether (b.p. 60–80°). The precipitate which consisted of the dimers of dioxane[10] was filtered and the mother liquor was chromatographed on alumina (250 g.). The oily substance obtained on elution with pentane was crystallized from pentane to give octyl-1,4-dioxane[2] (2.7 g., 27%), m.p. 37–38°. This substance was further characterized by its n.m.r. spectrum which showed a multiplet at τ 6.2, a broad singlet at τ 8.65, and a triplet at τ 9.1 in the ratio 7:14:2.9, as well as by its mass spectral analysis which indicated a parent ion with $m/e = 200$ and a base peak with $m/e = 87$.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.46; H, 11.82.

1-Octene and 1,4-Dioxane in Sunlight.—The procedure described above, using similar quantities, was followed. After removal of the reagents, the residue was distilled and the fraction with b.p. 80–180° (0.5 mm.), 7.3 g., was collected. Dimers of dioxane were isolated as explained above, and the remaining residue was chromatographed on alumina (350 g.). Elution with pentane led to octyl-1,4-dioxane (3.4 g., 34%).

1-Octene and 1,4-Dioxane with Ultraviolet Light (**without Acetone**).—A solution of 1-octene (1 g.) in 1,4-dioxane (100 ml.) was irradiated for 1 hr. 1-Octene (4.6 g.) then was added in eight equal portions in 1-hr. intervals and the mixture was irradiated for another 12 hr. After work-up, octyl-1,4-dioxane (0.5 g., 5%) was obtained.

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[5] Boiling points and melting points are uncorrected. Merck "acid-washed" alumina was used for chromatography. Gas–liquid chromatography was carried out with a "Pye" argon instrument on a 10% Apiezon M-Celite column at 125°. The n.m.r. spectra were determined on a Varian A-60 spectrometer in deuteriochloroform using tetramethylsilane as internal standard. Analyses were carried out in our microanalytical section directed by Mr. R. Heller.

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[8] 2-Octyltetrahydrofuran was prepared by treating 2-furfuraldehyde with heptylmagnesium bromide followed by catalytic hydrogenation, chrominum trioxide oxidation, and Wolff–Kishner reduction.

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Reactions of Acetylenes. III. Cyclization of Urethanes

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Earlier work[1] in this laboratory and elsewhere has shown that *t*-ethynylcarbinols react with isocyanates to form urethanes (I) which can be readily converted to oxazolidinones (II) by treatment with sodium ethoxide.

α,α-Disubstituted propargylureas (III) when treated with sodium ethoxide in ethanol also gave N-closure products, the imidazolidinones (IV)[1d,2]; treatment of

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[2] N. R. Easton, D. R. Cassady, and R. D. Dillard, *ibid.*, **29**, 1851 (1964).