The residue in the reaction flask was diluted with ether and extracted with sodium bicarbonate solution. On boiling the bicarbonate extract with α-chlorotoluene there was obtained 25.5 g. of methyl benzyl sulfone (68% yield), indicating that the aqueous extract had contained sodium methanesulfinate.

The acid found in the hydrogen chloride trap corresponded to only 7% of the original chlorine.

Reaction of methanesulfinyl chloride with benzene. One-half mole of methanesulfinyl chloride (49.25 g.) and 300 ml. dry benzene were placed in a three-neck flask fitted with sealed stirrer and reflux condenser. To the third neck was attached, by means of a large-diameter rubber tubing, a 125-ml. Erlenmeyer flask containing 135 g. (1.00 mole) of powdered anhydrous aluminum chloride. While maintaining the liquid reactants at 0° the aluminum chloride was added in small portions over a period of 30 min. and the reactants were then refluxed on the steam bath overnight. After working up the reaction mixture in the usual manner there was obtained 21 g. of colorless methyl phenyl sulfoxide boiling at 115° (2 mm.), having n_D^{25} 1.5880 and showing strong infrared absorption in the vicinity of 1040 cm.$^{-1}$ This liquid solidified when placed in the refrigerator overnight but melted on warming to room temperature. Oxidation of the product gave a solid melting 86–88° and unchanged when mixed with an authentic sample of methyl phenyl sulfone. Methyl phenyl sulfoxide is reported to have n_D^{20} 1.5885, to melt at 30.0–30.5°, to boil at 104° (0.7 mm.)[8] or 140–142° (13 mm.)[9] when absolutely dry and to show infrared absorption, when a liquid, at 1044 cm.$^{-1}$ [10] The yield corresponded to 26%, based on the sulfinyl chloride used.

The method described, of adding anhydrous aluminum chloride to the mixture of sulfinyl chloride and benzene, proved superior to the usual method of adding the chloride to a mixture of benzene and aluminum chloride. Numerous attempts to follow the latter procedure, using a variety of reactants, yielded only tars.

Reaction of methanesulfinyl chloride with aromatic amines. Nine and three-tenths grams of redistilled aniline (0.10 mole), dissolved in 100 ml. of anhydrous ether, was added dropwise with constant stirring to a solution of 4.95 g. methanesulfinyl chloride (0.05 mole) in 100 ml. ether cooled to −40 or −50°. After the reaction mixture had stood overnight, aniline hydrochloride was filtered out in quantitative yield. The ethereal solution was washed repeatedly with water and sodium bicarbonate solution, dried over calcium chloride, and evaporated either under vacuum or by blowing through it a stream of cold air. Decomposition always occurred when the ether solutions were evaporated by heating.

As the solvent was removed, crude methanesulfinanilide crystallized. Repeated recrystallization from anhydrous ether, washing with petroleum ether and with carbon tetrachloride gave a 71% yield of pure methanesulfinanilide melting at 86.88°.

Anal. Calcd. for C_7H_9ONS: N, 9.02. Found: N, 8.87.

Methanesulfin-p-toluidide, obtained in the same manner, melted at 96–98°, with decomposition occurring 103–106°.

Anal. Calcd. for $C_8H_{11}ONS$: N, 8.28. Found: N, 8.05.

ORONO, ME.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DE PAUL UNIVERSITY]

Acetylenic Reactions of 2-(Phenylethynyl)tetrahydropyran[1]

ROBERT ZELINSKI[2] AND JAMES LOUVAR

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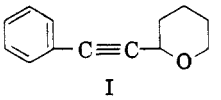
2-(Phenylethynyl)tetrahydropyran (I) was hydrogenated to 2-(2-phenylethyl)- and 2-(2-cyclohexylethyl)-tetrahydropyran. Addition of bromine and iodine to I yielded crystalline dihalides, hydration gave α-(2-tetrahydropyranyl)acetophenone, and addition of methanol formed α-(2-tetrahydropyranyl) acetophenone dimethylacetal.

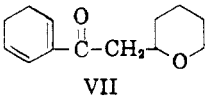
In parallel with the glucosylation of acetylene and phenylacetylene by coupling of alkynylmetal compounds with tetraacetyl-α-D-glucopyrannosyl bromide,[3] racemic 2-(phenylethynyl)tetrahydropyran (I) was prepared as a model compound and examined in some reactions intended for its carbohydrate counterpart.

Like the glycosyl halides, 2-halotetrahydropyrans show the characteristic reactivity of alpha halogen ethers toward organometallic compounds. For example, a series of 2-alkynyl-3-chlorotetrahydropyrans[4] has been prepared from 1-alkynylmagnesium halides and 2,3-dichlorotetrahydropyran. It is not unlikely that organolithium would yield similar products.[5]

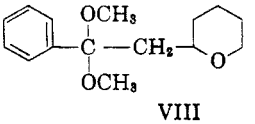
The racemic 2-(phenylethynyl)tetrahydropyran (I) was obtained in 66% yield from 2-chlorotetrahydropyran and phenylethynylmagnesium bromide. It very easily formed peroxides upon exposure to air.



I



VII



VIII

(1) The financial assistance of the Research Corp. is gratefully acknowledged.

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(3) R. Zelinski and R. Meyer, *J. Org. Chem.*, **23**, 810 (1958).

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Low pressure hydrogenation of the phenylethynyl compound I over platinum oxide removed both the aromatic and the alkyne unsaturation, forming 2-(2-cyclohexylethyl)tetrahydropyran (II). However, by using palladium on charcoal it was possible to reduce I to 2-(2-phenylethyl)tetrahydropyran (III). Both II and III were also prepared by alkylation of 2-chlorotetrahydropyran with the appropriate Grignard reagent.

A considerable number of attempts were made to reduce the acetylenic bond to the olefin. A combination of zinc, copper, and acetic acid[6] was without effect, lithium aluminum hydride[7] caused only a minor amount of reduction, and sodium and ammonia[8] gave an unidentified product which did not appear to be the desired *trans*-2-(2-phenylethenyl)tetrahydropyran.

Experiments to accomplish this by partial hydrogenation were unsatisfactory because the reaction could not be sufficiently controlled and because it proved impossible to separate the resultant mixtures by fractional distillation at the necessary reduced pressure. Thus both Raney nickel[8] and palladium on calcium carbonate[9] gave inseparable mixtures even when with the latter catalyst the amount of hydrogen absorbed was limited to the stoichiometric quantity for olefin formation.

2-(Phenylethynyl)tetrahydropyran (I) showed the expected reactivity of the acetylenic bond. It readily formed a 1 : 1 crystalline adduct (IV) with 2,4-dinitrobenzenesulfenyl chloride. Like diphenylacetylene,[10,11] I added molar equivalents of bromine and of iodine to form a crystalline dibromide (V) and diiodide (VI). However, attempts to obtain the dichloride were unsuccessful.

Hydration of I to α-(2-tetrahydropyranyl)-acetophenone (VII) was catalyzed by mercuric oxide in aqueous alcohol.[12] It was identical to the ketone prepared from 2-tetrahydropyranylacetyl chloride[13] and diphenylcadmium. The 2,4-dinitrophenylhydrazones were also identical. That VII was not the alternate hydration product, 2-(phenylacetyl)tetrahydropyran,[14] was clearly evident from comparison of physical properties and melting points of the dinitrophenylhydrazones.

Lithium aluminum hydride easily reduced the racemic ketone VII to a mixture of the four stereoisomeric alcohols. However, attempts to prepare crystalline urethans or dinitrobenzoates gave only oily products.

α-(2-Tetrahydropyranyl)acetophenone dimethylacetal (VIII) was obtained by methanolysis of I catalyzed by mercuric oxide and boron trifluoride etherate.[15] The structure was substantiated by hydrolysis to the ketone VII, which was characterized through its 2,4-dinitrophenylhydrazone. Attempts to add only an equimolar amount of methanol to I and so to obtain the enol ether of VII were unsuccessful.

In an analogous way,[15] reaction of 2-(phenylethynyl)tetrahydropyran (I) with acetic acid was attempted. The addition product was formed, but fractionation was erratic and accompanied by decomposition since the odor of acetic anhydride was present in all fractions. The presence of the *gem* diacetate or the enol acetate of VII or of VII itself was demonstrated by the rapid formation of the 2,4-dinitrophenylhydrazone of VII upon addition of 2,4-dinitrophenylhydrazine to one of these fractions.

EXPERIMENTAL[16,17]

2-(Phenylethynyl)tetrahydropyran. 2-Chlorotetrahydropyran was freshly prepared by addition of the calculated amount of anhydrous hydrogen chloride to anhydrous dihydropyran cooled in an ice bath. The solution was then diluted with dry ether and used directly. Phenylethynylmagnesium bromide was prepared by refluxing for 1 hr. a solution of 20.0 g. (0.20 mole) of phenylacetylene in 50 ml. of ethyl ether with the ethylmagnesium bromide obtained from 32.7 g. (0.30 mole) of ethyl bromide and 7.3 g. (0.30 g.-atom) of magnesium in 150 ml. of ether. The crude 2-chlorotetrahydropyran (0.30 mole) was added in one portion to form a pasty mass in a few minutes. This was hydrolyzed after 10–15 min. by a cold solution of ammonium chloride. The ether extract was distilled through an 18-in. Vigreux column to give 24.6 g. (65%) of colorless 2-(phenylethynyl)-tetrahydropyran (I), b.p. 149° (8 mm.), n_D^{25} 1.5600, d_{25} 1.020.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.59. Found: C, 83.51; H, 7.64.

The 2,4-dinitrobenzenesulfenyl chloride adduct (IV) of 2-(phenylethynyl)tetrahydropyran (I) was obtained by warming 0.19 g. of I and an equimolar amount of 2,4-dinitrobenzenesulfenyl chloride in 2.0 ml. of glacial acetic acid. The crude solid which formed on standing at room temperature was crystallized from benzene to give 83% of the adduct (IV), m.p. 203–204°.

Anal. Calcd. for $C_{18}H_{17}N_2O_5SCl$: Cl, 8.67; N, 6.85. Found: Cl, 8.52; N, 6.74.

A sample of I which was stored in a corked container at room temperature for a week was found[18] to contain 84 m. equiv. of peroxide per 1000 g. of sample. If a molecular weight of 218 is assumed for the hydroperoxide, its concentration was 2%.

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(16) Elemental analyses by Micro Tech Laboratories, Skokie, Ill.

(17) Unless otherwise specified, fractional distillations were conducted in a Piros-Glover spinning band column.

(18) I. M. Kolthoff and A. I. Medalia, *Anal. Chem.*, **23**, 595 (1951).

2-(2-Cyclohexylethyl)tetrahydropyran (II). A mixture of 7.5 g. (0.04 mole) of 2-(phenylethynyl)tetrahydropyran (I), 0.1 g. of platinum oxide, and 20 ml. of absolute methanol was hydrogenated at 60 p.s.i.g. and room temperature for 8 hr. Fractional distillation[17] gave 5.5 g. (66%) of 2-(2-cyclohexylethyl)tetrahydropyran (II), b.p. 155–160° (12–15 mm.), n_D^{25} 1.4712, d_{25} 0.921.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.52; H, 12.32. Found: C, 79.45; H, 12.42.

Compound II was also prepared by dropwise addition of 37 g. (0.30 mole) of crude 2-chlorotetrahydropyran in 50 ml. of dry ether to the Grignard reagent prepared from 38.6 g. (0.20 mole) of 2-cyclohexylethyl bromide, 7.3 g. (0.30 g.-atom) of magnesium, and 100 ml. of dry ether. Fifteen minutes after addition of the halopyran, the reaction mixture was hydrolyzed with cold water and a little hydrochloric acid. The ether layer was separated, neutralized, dried over sodium sulfate, and distilled through the Vigreux column to give 24 g. (59%) of 2-(2-cyclohexylethyl)tetrahydropyran, n_D^{25} 1.4707.

2-(2-Phenylethyl)tetrahydropyran (III). A mixture of 5.6 g. (0.03 mole) of 2-(phenylethynyl)tetrahydropyran (I), 1.0 g. of palladium on charcoal[19] and 50 ml. of alcohol was hydrogenated for 2.5 hr. at room temperature and 60 p.s.i.g. Fractional distillation gave 4.0 g. (70%) of 2-(2-phenylethyl)tetrahydropyran (III), b.p. 125° (5 mm.), n_D^{25} 1.5122, d_{25} 0.976.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.73; H, 9.50.

By the procedure described for the preparation of II, the Grignard reagent from 0.3 mole of 2-phenylethyl bromide reacted with 0.30 mole of 2-chlorotetrahydropyran to give after fractional distillation 30 g. (52%) of colorless III, b.p. 142° (10 mm.), n_D^{25} 1.5121, d_{25} 0.979.

Other attempts to reduce 2-(phenylethynyl)tetrahydropyran. The first three methods were attempts to cause reduction to a *cis* olefin. Following the general procedure described in the literature for reduction of diphenylacetylene to *cis*-stilbene,[6] an attempt to reduce 2-(phenylethynyl)tetrahydropyran (I) with acetic acid and a zinc-copper couple caused essentially no reduction.

Catalytic hydrogenation of I occurred with Raney nickel[8] or palladium on calcium carbonate,[9,19] but a pure product could not be separated.

Two methods were tested to reduce the ethyne (I) to a *trans*-olefin. Lithium aluminum hydride[7] had no effect. On the other hand, sodium and liquid ammonia[8] caused reduction, but the product did not have an elemental analysis corresponding to *trans* 2-(2-phenylethynyl)tetrahydropyran.

Addition of halogen to 2-(phenylethynyl)tetrahydropyran. A solution of 10.8 g. (0.0600 mole) of bromine in 25 ml. of carbon tetrachloride was slowly added to an ice cold solution of 11.2 g. (0.0600 mole) of 2-(phenylethynyl)tetrahydropyran (I) in 25 ml. of the same solvent. The whole was stirred in the cold for 15 min. and then the solvent was evaporated on a steam bath. The semisolid residue was crystallized from petroleum ether to yield 4.8 g. (33%) of 2-(phenylethynyl)tetrahydropyran dibromide (V), m.p. 118–119°.

Anal. Calcd. for $C_{13}H_{14}OBr_2$: C, 45.30; H, 4.16; Br, 46.32. Found: C, 45.24; H, 3.80; Br, 46.55.

When 1.86 g. (0.0100 mole) of I and 2.54 g. (0.0100 mole) of iodine were allowed to stand in 25 ml. of carbon tetrachloride for two days, evaporation of the solvent and recrystallization from petroleum ether gave 3.8 g. (86%) of the diiodide (VI), m.p. 137–138°.

Anal. Calcd. for $C_{13}H_{14}OI_2$: C, 35.48; H, 3.21; I, 57.68. Found: C, 35.77; H, 3.37; I, 57.80.

Bubbling chlorine through a solution of I in carbon tetrachloride at 0° left an oily product which could not be crystallized. The increase in weight suggested that substitution might have occurred as well as addition.

(19) Baker and Co., Newark, N. J.

α-(2-Tetrahydropyranyl)acetophenone (VII). A mixture of 9.3 g. (0.050 mole) of 2-(phenylethynyl)tetrahydropyran (I), 0.5 g. of sulfuric acid, 0.5 g. of mercuric oxide, and 100 ml. of 70% alcohol was heated in a magnesium citrate bottle on a steam bath for 6 hr. After having been cooled to room temperature, the contents were poured into a saturated sodium bicarbonate solution. This mixture was then extracted with petroleum ether and the extract was filtered and fractionally distilled to give 8.6 g. (84%) of α-(2-tetrahydropyranyl)acetophenone (VII), b.p. 123–124° (0.8 mm.), n_D^{25} 1.5373, d_{25} 1.062.

Anal. Calcd. for $C_{13}H_{16}O$: C, 76.44; H, 7.90. Found: C, 76.40; H, 7.99.

The *2,4-dinitrophenylhydrazone* of VII, m.p. 188–189°, was obtained[20] in 81% yield after one recrystallization from alcohol and ethyl acetate.

Anal. Calcd. for $C_{19}H_{20}O_5N_4$: C, 59.36; H, 5.24; N, 14.58. Found: C, 59.33; H, 5.55; N, 14.33.

The *semicarbazone* of VII, m.p. 133–135°, was obtained[20] in 31% yield after recrystallization from aqueous alcohol.

Anal. Calcd. for $C_{14}H_{19}O_3N_2$: C, 64.34; H, 7.33; N, 16.08. Found: C, 64.63; H, 7.24; N, 15.82.

Compound VII was also made another way. The undistilled 2-tetrahydropyranylacetyl chloride[13] from 0.20 mole of the corresponding acid was dissolved in 100 ml. of dry benzene and added as rapidly as possible to the diphenylcadmium prepared from 0.30 g.-atom of magnesium, 0.30 mole of bromobenzene, and 0.16 mole of cadmium chloride. After 15 min. of reflux, the mixture was poured into cold aqueous ammonium chloride and extracted with ether which was then dried and distilled to give a 9% yield of α-(2-tetrahydropyranyl)acetophenone (VII), b.p. 161–163° (10 mm.), n_D^{25} 1.5362. A mixture of its 2,4-dinitrophenylhydrazone, m.p. 187.5–188.5°, with the 2,4-dinitrophenylhydrazone of VII prepared by hydration of I showed no melting point depression.

Reduction of α-(2-tetrahydropyranyl)acetophenone (VII). A solution of 6.1 g. (0.030 mole) of VII with 25 ml. of a saturated ether solution of lithium aluminum hydride was shaken at room temperature for 2 hr. and then was cautiously poured into cold 5% sulfuric acid. The petroleum ether extract of this was dried and fractionally distilled to give 5.5 g. (89%) of a colorless mixture of stereoisomers of 1-phenyl-2-(2-tetrahydropyranyl)ethanol, b.p. 125–128° (1 mm.), n_D^{25} 1.5285.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.35; H, 8.66.

Attempts to prepare the 3,5-dinitrobenzoate and the phenylurethan gave oils.

α-(2-Tetrahydropyranyl)acetophenone dimethylacetal (VIII). A solution of 5.6 g. (0.03 mole) of 2-(phenylethynyl)tetrahydropyran (I) in 9.6 g. of anhydrous methanol was slowly added with stirring and occasional cooling to a warm mixture of 0.5 g. of red mercuric oxide, 0.2 ml. of boron trifluoride etherate, and 0.5 ml. of methanol. The mixture was cooled, the flask was stoppered tightly, and the whole was heated on a steam bath for 1 hr. with occasional shaking. It was then cooled, 0.5 g. of potassium carbonate was added, and the mixture was filtered. The filtrate was fractionally distilled to give 4.0 g. (53%) of α-(2-tetrahydropyranyl)-acetophenone dimethylacetal (VIII), b.p. 109–114° (2–3 mm.), n_D^{25} 1.5075, d_{25} 1.068.

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.96; H, 8.81.

To prepare a solid derivative, VIII was treated[20] with 2,4-dinitrophenylhydrazine. The immediate yellow precipitate was recrystallized from alcohol and ethyl acetate to give the 2,4-dinitrophenylhydrazone of VII, m.p. 189–190°,

(20) R. L. Shriner and R. C. Fuson, *Systematic Identification of Organic Compounds*, third edition, John Wiley and Sons, Inc., New York, 1948, p. 171–172.

which showed no melting point depression with an authentic sample.

Acetolysis of 2-(phenylethynyl)tetrahydropyran (I). A tightly stoppered flask containing 5.6 g. (0.30 mole) of I, 0.5 g. of mercuric oxide, 0.2 ml. of boron trifluoride etherate, and 18 g. of glacial acetic acid was heated on a steam bath for 1 hr. The mixture was poured into cold water which was then extracted with ether. The ether solution was washed with aqueous sodium bicarbonate, dried, and fractionally distilled at 107–148° (1 mm.). Separation was unsatisfactory, but refractive indices varied from 1.5285 to 1.5380 at 20°. Decomposition seemed to occur and the odor of acetic acid or anhydride was noticeable in many fractions.

The 2,4-dinitrophenylhydrazone of VII was obtained from one of the fractions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DEPAUL UNIVERSITY]

Glucosylation of Acetylenes[1]

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The first example of a glucosylated acetylene has been prepared by reaction of tetraacetyl-α-D-glucopyranosyl bromide with phenylethynylmagnesium bromide. The hydrate (II) of this compound, 1-phenyl-2-(tetraacetyl-β-D-glucopyranosyl)-ethyne (I), was catalytically reduced to 1-phenyl-2-(tetraacetyl-β-D-glucopyranosyl)ethane (IV) which was also prepared by the analogous glucosylation of 2-phenylethylmagnesium bromide. Glucosylation of sodium acetylide gave a small yield of a crystalline carbohydrate derivative of undetermined structure.

The glucosylation of hydrocarbons with a carbohydrate moiety in which the pyranose ring is preserved has been accomplished by using glycosyl halides in two familiar organic reactions. Thus the Friedel-Crafts reaction has led to the glycosylation of aromatic hydrocarbons. The second and more general way is the coupling of organometallic compounds with α-halo ethers, as extended to include glycosyl halides, a procedure of obviously greater scope. Both approaches were originated by Hurd and Bonner[3] and extended by them in work which has been largely reviewed by Bonner.[4] Since then the glycosylation of organometallics has been applied to a variety of carbohydrates[5] and Grignard reagents[5–9] as well as to organocadmium[10] and organoalkali[11] compounds. It was our purpose to extend the scope of this synthesis still further by employing organometal derivatives of 1-alkynes.

The only report in the literature concerning attempted glycosylation of acetylenes is that of unsuccessful efforts[5] to couple tetraacetyl-α-D-glucopyranosyl bromide with ethynebis(magnesium bromide) and with sodium or lithium acetylide. Since the application of common reactions of acetylenes to glycosylated acetylenes would obviously provide a starting point for the preparation of many novel carbohydrates and derivatives, the problem of glycosylating acetylenes was attempted again. However, in view of the reported lack of success with metal derivatives of acetylene itself,[5] phenylacetylene was selected first.

The procedures developed by Hurd and Bonner were applied to the coupling of one mole of tetraacetyl-α-D-glucopyranosyl bromide with twelve of phenylethynylmagnesium bromide. From the ether phase of the usual hydrolysis mixture methylbisphenylethynylcarbinol was recovered in good yield. Acetylation of the dehydrated aqueous phase and crystallization of the crude material from anhydrous alcohol or hydrocarbon solvent gave a levorotatory, crystalline compound, m.p. 134–135°, which we describe as anhydrous 1-phenyl-2-(tetraacetyl-β-D-glucopyranosyl)ethyne (I). Evaporation of the mother liquor left a dextrorotatory sirup which could not be crystallized.

Recrystallization of I or the crude product from wet isopropyl or 95% ethyl alcohol gave a different crystalline species (II), m.p. 125–126°. The specific rotations of I and II were identical, the two compounds were interconvertible by crystallization from suitable solvents such as benzene and even ethanol, and II was readily dried to yield I. All the analytical evidence supports designation of

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(1) This work was made possible by grant from the Research Corp.

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(10) C. D. Hurd and R. P. Holysz, *J. Am. Chem. Soc.*, **72**, 2005 (1950).

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