water, dried over sodium sulfate, decanted, and acidified with ethereal hydrogen chloride. The solid products were recrystallized until constant melting points were obtained and they were identified by mixture melting points with authentic samples of the hydrochlorides of the known dialcohols.

The following amino ketones were successfully reduced, and the yields of identified products (corresponding to IV–V) were: α-[*N*-ethyl-*N*-(β-hydroxyethyl)amino]desoxybenzoin[3a] (IId) (51%); α-[*N*-benzyl-*N*-(β-hydroxyethyl)amino]-desoxybenzoin[3d] (IIg) (43%); α-[*N*-ethyl-*N*-(β-hydroxyethyl)amino]acetophenone[3c] (IIh), product isolated as the picrate (61%); α-[*N*-ethyl-*N*-(β-hydroxyethyl)amino]-*p,p'*-dichlorodesoxybenzoin[3b] (IIi) (58%); α-[*N*-(1-hydroxy-2-butyl)amino]-*p,p'*-dichlorodesoxybenzoin[4] (IIb) (64%); α-[*N*-2(3-phenyl-1-hydroxypropyl)amino]desoxybenzoin[4] (IIj) (49%); the recrystallization solvents and physical characteristics of the dialcohols prepared, are those given in the references.

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[CONTRIBUTION FROM THE BIOCHEMICAL RESEARCH LABORATORY, THE DOW CHEMICAL COMPANY]

Adducts of *tert*-Alcohols Containing an Ethynyl Group with Dihydropyran. Potentially Useful Intermediates

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Acetylenic alcohols of the type RR'C(OH)C≡CH have been found to add smoothly and in high yield to dihydropyran to form tetrahydropyranyl compounds of the general structure RR'C(C≡CH)O—(C_5H_9O). The tetrahydropyranyl grouping is stable to alkali but easily removed by aqueous acid or exchangeable with lower alcohols by acid catalysis. Organometallic intermediates are easily formed by reaction at the acetylenic hydrogen and compounds such as the γ-hydroxy-α,β-acetylenic acids, esters, and ketones thus are readily available.

Woods and Kramer[1] introduced dihydropyran for the protection of hydroxyl groups. Alcohols and phenols were added to dihydropyran by acid catalysis and the resulting adducts were found to be stable to alkali.

Later (1948), Parham and Anderson[2] extended this work to include adducts of other monohydric phenols and some dihydric phenols. The adducts were found to be stable to lithium alkyls. For example, the *p*-bromophenol–dihydropyran adduct was treated with butyllithium and carbonated. Removal of the tetrahydropyranyl group was then accomplished with aqueous acid.

In 1950, Henbest, Jones, and Walls[3] prepared an adduct with propargyl alcohol and in 1953, Jones and Mann[4] used the same adduct in the preparation of 4,4-diethoxy-2-butyn-1-ol.

On hydrolysis, the tetrahydropyranyl group is converted to γ-hydroxyvaleraldehyde.[2] Alcoholysis gives 2-alkoxytetrahydropyrans.[1] Both are easily separated from the desired products.

A British patent (698,736) claims the addition of primary and secondary alcohols to selected dihydropyrans but gives no examples with secondary alcohols.

Crombie and Jocklin[5] have reported the addition of a secondary alcohol to dihydropyran.

In each of the above cases, either concentrated hydrochloric acid or phosphorus oxychloride was employed as catalyst and the products worked up with ether. We have extended this work to include a number of tertiary ethynyl alcohols of the general formula RR'C(OH)C≡CH, where R is alkyl or phenyl and R' is methyl and where R and R' make up a cycloalkyl ring. Although tertiary alcohols are known to present steric problems in some reactions, we have found that each of the alcohols employed here gave pure products in good yield (see Table I).

In order to avoid volatile catalysts and to simplify work-up of the reaction mixture, *p*-toluenesulfonic acid was used as catalyst. Anhydrous potassium carbonate was added to the cooled reaction mixture to neutralize the acid and the product could then be distilled after a simple filtration.

If ether or other solvents are used in the work-up it should be noted that a basic or neutral drying agent *must* be employed. *Magnesium sulfate* is sufficiently *acid* to reverse the addition in only a few hours.

The tetrahydropyranyl compound thus formed provides protection for the hydroxyl group and, even where the hydroxyl group may not need protection, provides a degree of solubility which can be useful. For example, in the carbonation

(1) G. F. Woods and D. N. Kramer, *J. Am. Chem. Soc.* **69**, 2246 (1947).

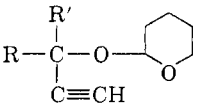
(2) W. E. Parham and E. L. Anderson, *J. Am. Chem. Soc.* **70**, 4187 (1948).

(3) H. B. Henbest, E. R. H. Jones, and I. M. S. Walls, *J. Chem. Soc.*, 3646 (1950).

(4) R. G. Jones and M. J. Mann, *J. Am. Chem. Soc.* **75**, 4048 (1953).

(5) L. Crombie and A. G. Jocklin, *Chem. & Ind. (London)*, **1954**, 1197.

TABLE I

TETRAHYDROPYRANS:[a] 

R	R′	B.P.°	Press., mm.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3	CH_3	64.5–65.5	8	$C_{10}H_{16}O_2$	71.39	71.16	9.59	9.45
CH_3CH_2	CH_3	62.5–64.5	3.3	$C_{11}H_{18}O_2$	72.49	72.62	9.95	9.67
$(CH_3)_2CHCH_2$	CH_3	47–50	0.6–0.2	$C_{13}H_{22}O_2$	74.24	73.94	10.55	10.24
$CH_3(CH_2)_5$	CH_3	76–77	0.12	$C_{15}H_{26}O_2$	75.58	75.08	10.99	10.45
	CH_3	99–100.5	0.02	$C_{15}H_{18}O_2$	78.22	78.37	7.88	7.85
R,R′= 		101.5–102.5	3.6–3.7	$C_{13}H_{20}O_2$	74.96	74.67	9.68	9.52

[a] Yields ranged from 60.4 to 84.4%.

of the Grignard derivative of the ethynyl alcohols, the magnesium derivatives of the free alcohols are so insoluble, even in tetrahydropyran, as to present contact problems and thus inordinate reaction times. The dihydropyran adducts, however, are quite soluble, even at −70°.

EXPERIMENTAL

General procedure. The appropriate alcohol (1 mole) and dihydropyran (1.2–2 moles) are mixed in a round-bottomed flask fitted with a thermometer or thermocouple well and a reflux condenser with drying tube. A few crystals of *p*-toluenesulfonic acid are added and dissolved by swirling. With the lower molecular weight alcohols, the exothermic addition begins almost at once and the reaction is usually complete within 0.5–1 hr. With higher molecular weight alcohols, the mixture may be heated on the steam bath for 0.5–1 hr. to ensure complete addition.

A gram or two of anhydrous potassium carbonate is added to the cooled mixture and stirred well for 0.5 hr. or allowed to stand overnight. A magnetic stirrer is most convenient for stirring. The salts are removed by filtration, excess dihydropyran recovered by distillation at atmospheric pressure and the product by distillation at reduced pressure (Table I).

The products are colorless, slightly to very viscous and indefinitely stable in the absence of acid.

It should be mentioned that, in a test tube experiment, evidence was obtained that even *tert*-butyl alcohol adds readily to dihydropyran, though no attempt was made to isolate the product.

Since an equimolar mixture of the two reactants would contain the same carbon and hydrogen values as the products, the infrared spectrum of each product was obtained. The spectra were consistent with their formulation as adducts; no hydroxy groups were detected and the acetylenic linkage and its reactive hydrogen were undisturbed.

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[CONTRIBUTION FROM THE INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE]

Synthesis of 3-Methyl-5,6,7,8-tetrahydro-1-naphthol

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Cyclization of the dienic acid obtained by dehydration followed by hydrolysis of ethyl γ-(Δ′-cyclohexenyl)-β-methyl-β-hydroxybutyrate with phosphorus pentoxide leads to the formation of 3-methyl-5,6,7,8-tetrahydro-1-naphthol whose structure was proved by dehydrogenation to 3-methyl-1-naphthol and also by an unambiguous synthesis.

A case of cyclization reaction involving an oxocarbonium ion belonging to an unsaturated side chain forming the part of a ring system and an ethylenic double bond was first studied by Bagchi, Bergmann, and Banerjee[1] in connection with the synthesis of 9-hydroxy-*sym*-octahydrophenanthrene. This observation has now been extended to the study of a case involving the cyclization of an ethylenic double bond present in a six-membered ring and a carboxyl group in a linear unsaturated side chain resulting in the formation of 3-methyl-5,6,7,8-tetrahydro-1-naphthol.[2]

As a suitable system, the dienic acid (III, R = H) obtained by the dehydration and hydrolysis of ethyl γ-(Δ′-cyclohexenyl)-β-methyl-β-hydroxybutyrate (I) was prepared for this work. Cyclohexenyl acetone required as the starting material was prepared according to the method of

(1) P. Bagchi, F. Bergmann, and D. K. Banerjee, *J. Am. Chem. Soc.*, 71, 989 (1949).

(2) D. K. Datta and P. Bagchi, *Sci. and Culture (Calcutta)*, 17, 525 (1952).