fonic acid was refluxed in a flask to which a Dean–Stark[14] water trap and a condenser were attached. After the maximum amount of water had collected (about 3 hours), the cooled solution was washed with 10% sodium carbonate solution, then with water, and the benzene removed under reduced pressure.

Amination.—The crude bromomethyl compound, 44 g. (0.06 mole) of diethylamine and 100 cc. of dry benzene were heated on a steam-bath in a citrate bottle for 36 hours. After treatment in the described manner, 6.2 g. of the dioxolane was obtained; b.p. 147–151° (0.3 mm.).

2,2-Diphenyl-4-hydroxymethyl-1,3-dioxolane (I).—A mixture of 50 g. (0.21 mole) of diphenyldimethoxymethane[15] and 26.2 g. (0.28 mole) of anhydrous glycerol, in a small distillation flask, was heated at 250–255° (bath temperature) for 8 hours; the distilled methanol weighed 13.4 g. (100%). Upon fractionation, 32.5 g. (60%) of I was obtained; b.p. 133–137° (0.01 mm.). The product slowly solidified; m.p. 51–52° after recrystallization from petroleum ether (90–100°).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.00; H, 6.29. Found: C, 74.91; H, 6.45.

The phenylurethan, after recrystallization from petroleum ether (90–100°), melted at 95–96°.

Anal. Calcd. for $C_{23}H_{21}O_4N$: N, 3.73. Found: N, 3.55.

2,2-Diphenyl-4-benzoyloxymethyl-1,3-dioxolane (IV).—A mixture of 5.8 g. (0.025 mole) of diphenyldimethoxymethane and 5 g. (0.025 mole) of glycerol α-monobenzoate was heated in a small distillation flask for 2 hours at 180–210° (bath temperature); the distilled methanol weighed 1.5 g. (89%). Trituration and then recrystallization of the product by the use of ethanol yielded 3.8 g. (41%) of the benzoate; m.p. 84–85°.

The benzoate was also prepared in 87% yield from I and benzoyl chloride in dry pyridine; m.p. and mixed m.p. 84–85°.

2,2-Diphenyl-4-(β-dimethylaminoethoxymethyl)-1,3-dioxolane Hydrochloride and Methiodide.—Ten grams (0.039 mole) of I, 1.8 g. (0.078 mole) of sodium and 30 cc. of dry toluene were refluxed for 4 hours. The mixture was cooled, decanted from the unreacted sodium, 4.2 g. (0.039 mole) of freshly distilled β-dimethylaminoethyl chloride added, and then refluxed for 4 hours. After the solution had been washed with water until it was neutral, the solvent was removed.

In order to prepare the hydrochloride, the crude amine, dissolved in dry ether, was treated with the calcd. amount of ethereal hydrogen chloride. The precipitated oil turned into a hygroscopic solid after several days in a refrigerator, and frequent triturations with dry ether. It was recrystallized from acetone–ether.

The methiodide was obtained when a mixture of 3.3 g. of the crude amine, 14.3 g. of methyl iodide and 35 cc. of chloroform was heated in a citrate bottle for 5 hours on a steam-bath. The solvent was removed, the residue triturated with dry ether until it became crystalline, the product extracted with hot ethyl acetate, and then recrystallized from acetone–ether.

2,2-Diphenyl-1,3-dioxolane-4-carboxylic Acid (III).—A solution of 13.0 g. (0.08 mole) of potassium permanganate and 2.8 g. (0.05 mole) of potassium hydroxide in 250 cc. of water was stirred and maintained at 50–60° during the portionwise addition of 15.0 g. (0.06 mole) of I. The mixture was then stirred for 1 hour, filtered, and extracted with ether. The aqueous solution was concentrated to a volume of 50 cc., cooled, and covered with 400 cc. of ether. The mixture was stirred vigorously while 10% hydrochloric acid was added, dropwise, until the solution reached a *p*H of 5–6. The ether layer was separated, dried over magnesium sulfate, the solvent removed, and the acid recrystallized from toluene–petroleum ether (90–100°); yield 3.7 g. (23%); m.p. 131–132°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; neut. equiv., 270.3. Found: C, 71.24; H, 5.51; neut. equiv., 270.5.

The β-diethylaminoethyl ester was obtained by the Horenstein and Pählicke procedure.[16]

(14) E. W. Dean and D. D. Stark, *J. Ind. Eng. Chem.*, **12**, 486 (1920).

(15) J. E. MacKenzie, *J. Chem. Soc.*, **69**, 987 (1896).

(16) H. Horenstein and H. Pählicke, *Ber.*, **71**, 1644 (1938).

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Synthetic Application and Mechanism of the Nef Reaction

BY EUGENE E. VAN TAMELEN AND ROBERT J. THIEDE[1]

RECEIVED OCTOBER 15, 1951

A convenient synthesis of apocamphenilone (V) is described. The sequence involves (i) a diene synthesis with cyclopentadiene and 1-nitropropene, (ii) hydrogenation of the double bond and (iii) transformation of the nitro group to carbonyl utilizing the Nef reaction. The stereochemistry of the intermediates and the final product are determined. A rational mechanism for the Nef reaction, along with supporting evidence, is presented.

The observation that aliphatic primary or secondary nitro compounds can be converted to aldehydes or ketones by adding the alkali salts of the former to aqueous mineral acid, was first recorded by Nef.[2] This reaction, which bears the name of its discoverer,[3] has been studied in a few simple cases[4–8]; in addition, it is the key step in a method of extending the aldose chain.[9] It is the purpose of this work to demonstrate further the utility of this remarkably simple transformation and to point out some pertinent features of a reasonable mechanism proposed herein.

The synthetic method we wish to illustrate consisted of the preparation of cyclic ketones *via* a

(1) Abstracted from a research report submitted by Robert J. Thiede in partial fulfillment of the Master of Science degree, University of Wisconsin.

(2) J. U. Nef, *Ann.*, **280**, 263 (1894).

(3) The reaction should be distinguished from that involving the addition of alkali acetylides to aldehydes and ketones, which is also known as the "Nef reaction."

(4) K. Johnson and E. F. Degering, *J. Org. Chem.*, **8**, 10 (1947).

(5) A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).

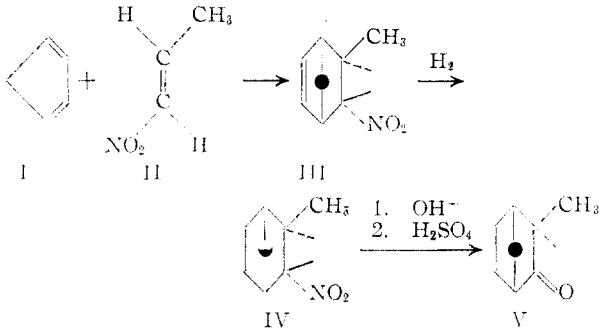
(6) M. C. Kloetzel, THIS JOURNAL, **70**, 3571 (1948).

(7) O. von Schickh, *Angew. Chem.*, **23/24**, 555 (1950).

(8) N. Kornblum and G. E. Graham, THIS JOURNAL, **73**, 4041 (1951).

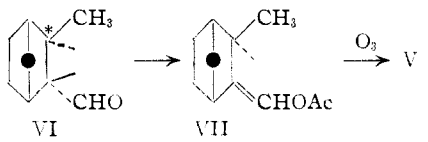
(9) J. C. Sowden and H. O. L. Fischer, *ibid.*, **67**, 1713 (1945); J. C. Sowden, *ibid.*, **72**, 3325 (1950).

Nef reaction on adducts from the diene synthesis utilizing α,β-unsaturated nitroalkenes. Toward this end, cyclopentadiene (I) was condensed with 1-nitropropene (II) in a manner similar to that reported previously by Alder, Rickert and Windemuth[10]; the yield of pure adduct (III) was 59%. All attempts, however, to obtain a pure product from a Nef reaction on III were fruitless. The addition of an aqueous solution of the sodium salt to dilute sulfuric acid was not accompanied by the evolution of nitrous oxide; the oily material which precipitated could not be separated into pure components by crystallization or chromatography. A recent report[11] concerning the reaction of nitrous oxide with olefins implies that the step attempted herein would take an undesired course; in any case, the Nef reaction does not seem to be applicable to nitro compounds containing an olefinic bond. However, the addition of the salt of the the dihydro derivative (IV)[10] to dilute acid was accompanied by a vigorous evolution of nitrous oxide; distillation of the resulting liquid product afforded a 51% yield of apocamphenilone (V), b.p. 59–61° at 10 mm. That V was a single isomer and relatively free from impurity, was indicated by the formation of a single semicarbazone in high yield. Diels and Alder[12] and Komppa[13] have previously ob-



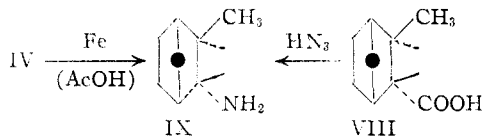
tained apocamphenilone by more circuitous routes.

Although preceding work leaves little doubt about the gross structural features of III, IV and V, the stereochemistry of these substances has not been elucidated. Since the geometry of the dienophile II is not known, no assumptions concerning the structure of the adduct can be made. The configuration of the methyl group[14] in V, however, can be assigned with some assurance by a consideration of a previously published synthesis of that molecule. Diels and Alder[12] converted the aldehyde (VI) to its enol acetate (VII); the latter, upon being ozonized, afforded V in fair yield. It is



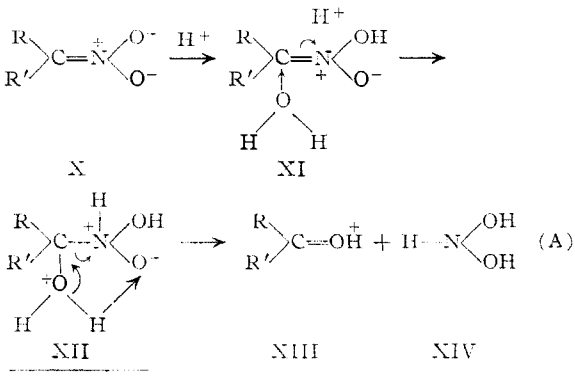
clear that neither of these steps should disturb the asymmetry at C*. Furthermore, air oxidation of VI gives rise to a substance of known stereochemistry, 2-*endo*-carboxy-3-*exo*-methylbicyclo-1.2.2-heptane (VIII).[15] Since, again, the configuration at C* cannot be easily affected in this step, the methyl group in VI—and therefore in V—must be *exo*, as shown above.

In order to determine the configurations of IV and III we turned to a series of steps designed to relate these substances to VIII. Thus, IV was reduced with iron and acetic acid, according to the previously described method of Alder,[10] to the corresponding amine (IX). The Schmidt rearrangement of VIII led to a 52% yield of the same amine



(IX), isolated as the pure hydrochloride. Since the latter reaction has been demonstrated to proceed *with* retention,[16] the configuration of IX must correspond to that of VIII; namely, the methyl substituent must be *exo*, and the amino group, *endo*. This finding, in turn, establishes the configuration of the methyl group in IV as *exo*, because the reduction of IV to IX would not seem to involve asymmetric center 3. The nitro group can be assigned the *endo* configuration with assurance, since Alder has demonstrated[10] that in the cyclopentadiene–nitroethylene case, the reaction takes the stereochemical course characteristic of the diene synthesis, *viz.*, addition resulting in the *endo* configuration of the activating group. If this result is accepted, it is clear that the nitroölefin II must have the *trans* structure; this is apparently the first evidence recorded which bears on the geometry of this molecule. It should be noted further that a consequence of the stereochemical considerations just presented is the conversion of IV to V without participation of the C-methyl asymmetric center; this behavior is in accord with the mechanism for the Nef reaction outlined below.

A compilation of isolated examples in the literature reveals that the course of the Nef reaction is decidedly subject to the structural features of the nitroparaffin molecule. Thus, 2-nitropropane is smoothly converted to acetone in 85% yield,[4]



(10) K. Alder, H. F. Rickert and E. Windemuth, *Ber.*, **71**, 2451 (1938).

(11) F. S. Bridson-Jones, G. D. Buckley, L. H. Cross and A. P. Driver, *J. Chem. Soc.*, 2999 (1951).

(12) O. Diels and K. Alder, *Ann.*, **486**, 202 (1931).

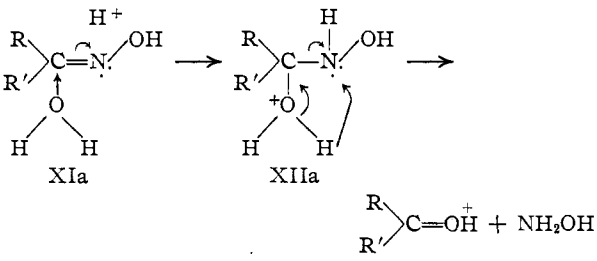
(13) G. Komppa, *Ber.*, **68**, 1127 (1935); G. Komppa and S. Beckmann, *Ann.*, **523**, 68, 83 (1936).

(14) The solid line indicates the *exo* configuration (*cis* to the methylene bridge), while the dotted line denotes the *endo* configuration.

(15) K. Alder and H. Stein, *Ann.*, **514**, 197 (1934).

(16) A. Campbell and J. Kenyon, *J. Chem. Soc.*, 25 (1946).

whereas sodium phenylnitromethane can be converted only to *aci*-phenylnitromethane.[8] We have just shown a mechanism[17] for these characteristics. We wish to direct attention to the similarity of the above mechanism and one that can be written for the well-known hydrolytic cleavage of oximes.[18] The only difference between intermediates XI and XIa and between XII and XIIa is the presence of



XIa XIIa

the nitrogen–oxygen semi-polar bond in the former; this similarity of (A) and (B) strengthens, we feel, the validity of the proposed mechanism for the Nef reaction.

A comparison between the hydrolysis rates of various semicarbazones and the qualitative results in attempted Nef reactions nicely illustrates the mechanistic similarity of the two reactions.[19]

It is apparent from Table I that at least two factors decrease the *rate* of hydrolysis of semicarbazones: (i) steric hindrance of neighboring groups, as in (7); and (ii) resonance stabilization, as in (9). In the latter case, the absence of a significant "plus" charge on the incipient carbonyl carbon,

TABLE I

	Carbonyl compound	Semicarbazone hydrolysis rate constant ($K \times 10^6$)	Yield from corresponding nitro compound, %
(1)	Cyclohexanone	7600	"Very good"[7]
(2)	Acetone	1800	84[4]
(3)	Acetaldehyde	1040	77[4]
(4)	Propionaldehyde	....	80[4]
(5)	4-Ketohexanoic acid	....	65[6]
(6)	Isobutyraldehyde	....	32–36[4]
(7)	Trimethylacetaldehyde	37	...
(8)	2,2-Dimethyl-4-ketovaleraldehyde	....	0[20]
(9)	Benzaldehyde	0.62	0[6]

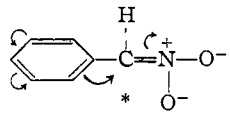
(17) It should be noted that XIV corresponds to the hydrated form of nitroxyl, NOH, which is known to be a precursor of nitrous oxide in aqueous medium. *Cf.* W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1940, p. 196.

(18) Compare L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 333.

(19) Data for both hydrolysis rates and hydrolysis equilibria of ketone and aldehyde derivatives are available (J. B. Conant and P. D. Bartlett, THIS JOURNAL, **54**, 2881 (1932)). The former are used in the present comparison, however, since we believe that hydrolysis in the dynamic sense corresponds more closely to the content of (A). Furthermore, the isolation of a nitroparaffin in an attempted Nef reaction may be safely assumed to indicate a slow, by comparison, rate-determining step in (A). Since the addition of a proton to the nitroalkyl anion should be an essentially instantaneous process, the rate-determining step would most logically be the attack of solvent, as indicated in XI. If this attack is comparatively slow, simple reversion of XI to the free nitroparaffin takes precedent (or XI is isolated as such, *e.g.*, *aci*-phenylnitromethane). Thus, yields of carbonyl compounds in the Nef reactions, and hydrolysis rates of carbonyl derivatives have comparable significance.

(20) Observed by one of the authors. The nitro compound used was 4,4-dimethyl-5-nitropentanone-2.

caused by participation of the benzene ring, presumably moderates attack by solvent at that point. Example (8) is comparable to (7), cited in (i) above; attack by solvent on the carbon bearing the nitro group is prevented by the neopentyl-like system of adjacent substituents. On the other hand, the anion of phenylnitromethane is resistant to solvent attack at C* because of resonance stabilization



the case being similar to that in (ii) above. An obvious prediction based on the foregoing, relates the success of a proposed Nef reaction with the rate of hydrolysis of carbonyl derivatives constituted similarly to the nitroparaffin molecule under consideration.

Experimental[21]

2-*endo*-Nitro-3-*exo*-methylbicyclo[1.2.2.]heptane (IV).—One hundred and sixty grams (2.4 moles) of freshly distilled cyclopentadiene, 115 ml. of glacial acetic acid, 165 g. (1.9 moles) of freshly prepared 1-nitropropene (b.p. 31.0–32.5° at 7 mm.) and 0.1 g. of hydroquinone were added successively to a one-liter, round-bottom flask equipped with a thermometer. A condenser was attached and the reaction mixture gently warmed in an oil-bath until the cyclopentadiene began to reflux (40–45°). The reaction was exothermic, and the temperature rose steadily to approximately 100°. The oil-bath was then removed and the reaction allowed to run as long as refluxing continued. Fractionation gave 171 g. (59%) of the adduct, b.p. 91.5–92.5° at 11–12 mm., $n^{21}D$ 1.4871. The boiling point reported[10] in the literature is 94–95° at 15 mm.

Hydrogenation of the adduct over platinum oxide afforded 84% of the pure saturated nitro compound (IV), b.p. 95–96° at 10 mm., $n^{25}D$ 1.4768. The boiling point recorded[10] is 101–102° at 15 mm.

3-*endo*-Methylbicyclo[1.2.2.]heptan-2-one (Apocamphenilone) (IV).—The dihydro adduct (IV), 35.6 g. (0.23 mole), was added to a solution of 12 g. (0.3 mole) of sodium hydroxide in 150 ml. of water contained in a 200-ml. round-bottom flask. Stirring for two hours effected complete dissolution of the nitro compound. The solution was filtered and extracted with ether to ensure freedom from organic impurities, and then slowly added dropwise to a well-stirred, cooled (0–5°) solution of 25 ml. of concentrated sulfuric acid in 150 ml. of water. The addition was accompanied by the evolution of nitrous oxide and the formation of a blue-green color. The reaction mixture was then extracted with three 50-ml. portions of anhydrous ether; the combined extracts were dried over anhydrous magnesium sulfate and distilled. The yield of apocamphenilone was 14.5 g. (51%), boiling at 59–61.5° at 10 mm. (lit.[12,13] 68–70° at 15 mm.); $n^{25}D$ 1.4677.

Reaction of the ketone with methylmagnesium bromide[12] afforded the *t*-alcohol, "γ-santenol," m.p. 62.5–64.5° (lit.[12] 63–65°). The semicarbazone was obtained in 94% yield (m.p. 175–178°); recrystallization from 10% ethanol yielded material melting at 185–187° (lit. 187–188[13]). The dinitrophenylhydrazone[22] melted at 114–118° (reported 114–115°, 116–117°[23]).

2-*endo*-Amino-3-*exo*-methylbicyclo[1.2.2.]heptane (VIII) (A).—The required acid, 2-*endo*-carboxy-3-methylbicyclo-[1.2.2.]heptane, was prepared according to the method of Alder and Stein.[15] Two grams (0.013 mole) of the acid, 40 ml. of chloroform and 6 ml. of concentrated sulfuric acid were placed in a 100-ml., 3-necked round-bottom flask equipped with a Hershberg stirrer, thermometer and gas

(21) Melting points are corrected; boiling points are uncorrected.

(22) Only the preparation of this derivative in a qualitative test using aqueous DNPH sulfate was successful. Other attempted modifications using, for example, ethanolic DNPH, gave highly impure products.

(23) G. Gratton and J. L. Simonsen, *J. Chem. Soc.*, 1621 (1935).

outlet tube. The mixture was warmed to 35–38°, and 1.7 g. (0.026 mole) of sodium azide was added slowly with vigorous stirring. The reaction was slightly exothermic; and by controlling the rate of addition of the azide, the reaction temperature was maintained at 38–40°. After the addition was complete, the suspension was stirred for one-half hour and allowed to stand for 1.5 hours more. The reaction mixture was then added to 50 ml. of water; after shaking, the aqueous layer, which contains the amine salt, was separated. To this solution was added an excess of aqueous sodium hydroxide; subsequent steam distillation of the free amine into excess 10% hydrochloric acid gave a solution of the amine hydrochloride. The solvent was evaporated under reduced pressure. Recrystallization of the residue from methanol–ethyl acetate afforded a 52% yield of the pure hydrochloride, m.p. 267–270°.

(B).—The amine was also prepared by reduction of the dihydro nitro adduct (IV) with iron and acetic acid.[10] The melting point of the hydrochloride, 268–269°, was undepressed by that of the material described above. The melting point (200–203°) of the urea derivative from (A) also showed no depression upon admixture with the same derivative from (B), m.p. 200–202.5°. The melting point reported for the urea derivative is 203°.[10]

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF BACTERIOLOGY AND IMMUNOLOGY, HARVARD MEDICAL SCHOOL, AND THE DEPARTMENT OF BIOCHEMISTRY, COLLEGE OF PHYSICIANS AND SURGEONS, COLUMBIA UNIVERSITY]

The Stereochemical Specificity of the Oxidation of Cyclitols by Acetobacter Suboxydans[1,2]

BY BORIS MAGASANIK, ROBERT E. FRANZL AND ERWIN CHARGAFF

RECEIVED NOVEMBER 26, 1951

The study of the oxidation of cyclitols by *Acetobacter suboxydans* has been extended to two new desoxyinositols, related to *epi*-inositol (I), one a racemic mixture (VI + VII), the other the corresponding levorotatory isomer (VI). Only the dextrorotatory desoxyinositol (VII) was found to be attacked. The structure of the resulting monoketone (VIII) was determined. These results permit the stricter definition of the rules predicting the type of cyclitol hydroxyls that can be oxidized by the enzyme system. The specific steric requirements for oxidation can be defined by the statement that *only polar hydroxyl groups are oxidized* and that *the carbon atom in meta position to the one carrying the polar hydroxyl group (in counterclockwise direction, if north polar; clockwise, if south polar) must carry an equatorial hydroxyl group.*

In previous communications[3] the oxidative action of *Acetobacter suboxydans* on various polyhydroxy derivatives of cyclohexane, belonging to the inositol and quercitol series, has been described. There exists a considerable body of physical evidence for the chair form of the cyclohexane ring[4]; and when this formulation was extended to its polyhydroxy derivatives, it could be shown[3b,c,d] that only those hydroxyl groups that were located in a polar plane could be oxidized by the biological system, a conclusion borne out by more recent observations[5] on the oxidation of *d*- and *l*-viburnitol by the same organism. It has, however, already been pointed out[3b] that, while none but polar hydroxyl groups were attacked, not all polar hydroxyl groups were so treated. The present paper describes further studies, leading to a more stringent definition of the rules predicting which polar hydroxyl groups can be oxidized.

The compounds discussed here are listed in Table I in two sets of terms based on the numbering systems proposed by us[3b] and by Fletcher, *et al.*,[6] respectively.

(1) This work was supported in part by grants from the American Cancer Society on the recommendation of the Committee on Growth of the National Research Council and from the Nutrition Foundation.

(2) A portion of the material was presented at the American Chemical Society Meeting in Washington, D. C., September, 1948 [B. Magasanik and E. Chargaff, Abstracts, 114th Meeting, American Chemical Society, 35 C (1948)].

(3) (a) E. Chargaff and B. Magasanik, *J. Biol. Chem.*, **165**, 379 (1946); (b) B. Magasanik and E. Chargaff, *ibid.*, **174**, 173 (1948); (c) B. Magasanik and E. Chargaff, *ibid.*, **175**, 929 (1948); (d) B. Magasanik and E. Chargaff, *ibid.*, **175**, 939 (1948).

(4) O. Hassel, *Tids. Kjemi, Bergvesen Met.*, **3**, 32 (1943); *C. A.*, **39**, 2244 (1945); R. S. Rasmussen, *J. Chem. Phys.*, **11**, 249 (1943); C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947); F. D. Rossini and K. S. Pitzer, *Science*, **105**, 647 (1947).

(5) T. Posternak, *Helv. Chim. Acta*, **33**, 350, 1594 (1950).

(6) H. G. Fletcher, Jr., L. Anderson and H. A. Lardy, *J. Org. Chem.*, **16**, 1238 (1951).

TABLE I

POLYHYDROXY DERIVATIVES OF CYCLOHEXANE

No.	Compound Designations previously employed	Numbering system: Present authors[3b]	Numbering system: Fletcher, *et al.*[6]
I	*epi*-Inositol	Cyclohexane-(1,2,3,4,5)-*cis*-hexol	*epi*-Inositol
II	*l-epi*-Inosose	Cyclohexane-(1,3,4,5) *cis*-pentol-2-one	D-2-Keto-*epi*-inositol
III	*d-epi*-Inosose	Cyclohexane-(1,2,3,5) *cis*-pentol-4-one	L-2-Keto-*epi*-inositol
IV	*meso*-Inosose	Cyclohexane-(1,3,5) *cis*-pentol-2-one	2-Keto-*myo*-inositol
V	Desoxycyllitol	Cyclohexane-(1,3,5) *cis*-4,6-pentol	2-Desoxy-*myo*-inositol
VI		Cyclohexane-(1,3,4,5) *cis*-6-pentol	D-2-Desoxy-*epi*-inositol
VII		Cyclohexane-(1,2,3,5) *cis*-6-pentol	L-2-Desoxy-*epi*-inositol
VIII		Cyclohexane-(1,3,5) *cis*-6-pentol-2-one	D-2-Keto-4-desoxy-*epi*-inositol
IX	*meso*-Inositol	Cyclohexane-(1,2,3,5) *cis*-hexol	*myo*-Inositol
X	*d*-Viburnitol	Cyclohexane-(1,2,5) *cis*-4,6-pentol	L-1-Desoxy-*myo*-inositol
XI	*d*-Inositol	Cyclohexane-(1,2,5) *cis*-hexol	D-Inositol
XII	*d*-Inosose	Cyclohexane-(1,2,5) *cis*-pentol-3-one	L-1-Keto-*myo*-inositol
XIII	*l*-Viburnitol	Cyclohexane-(1,4,5) *cis*-2,6-pentol	D-1-Desoxy-*myo*-inositol
XIV	*l*-Inositol	Cyclohexane-(1,2,4) *cis*-hexol	L-Inositol
XV		Cyclohexane-(1,2,4) *cis*-pentol-6-one	D-1-Keto-*myo*-inositol
XVI	*d*-Quercitol	Cyclohexane-(1,2,5) *cis*-3,6-pentol	L-2-Desoxy-*muco*-inositol

For the purposes of the following discussion the spatial constellations of the compounds are of greater significance than their planar projections. The constellations of the substances, numbered as in Table I, will therefore be presented schematically: north polar hydroxyls are indicated by full