analysis.[25] The small amount of hydrogen evolved prior to decomposition contained no hydrocarbon material.

The hydrocarbon fraction isolated from the hydrogenolysis of *N*-cinnamyl-*N*-methylaniline apparently was a mixture of allylbenzene and propylbenzene and did not contain propenylbenzene. Its boiling range was 157–159° (lit.[26] allylbenzene, b.p. 156.3°; propylbenzene, b.p. 159.2°; *trans*-propenylbenzene, b.p. 179°). This fraction readily decolorized solutions of bromine and of permanganate, but it was only partially soluble in concentrated sulfuric acid. The ultraviolet spectra showed a broad maximum about 2625 Å but no absorption at 2830 or 2945 Å. The reported maxima for allylbenzene and propylbenzene are 2620 and 2600 Å respectively, and for propenylbenzene are 2830 and 2945 Å.[27]

In two runs the isolation of the secondary amine was attempted before decomposition of the reaction mixture. The solvent was removed under reduced pressure, and the residual semisolid mass was continuously extracted with hexane. The extract contained no secondary amine and only small amounts of the original tertiary amine.

Analytical methods. The amine mixtures were analyzed by the nonaqueous titration method of Siggia[28] using perchloric acid in glacial acetic acid as the titrant. To perchloric acid (72%) (8.5 ml.) in glacial acetic acid (200 ml.) acetic anhydride (20 ml.) was added as a drying agent. The mixture, after standing 15 hr., was diluted to 1 l. with glacial acetic acid and was standardized several hours later against potassium acid phthalate. A glass-calomel electrode system was used with a Beckman Zeromatic *p*H meter.

On known mixtures of primary, secondary, and tertiary amines the average accuracy of the perchloric acid titration was ±0.25%. The titation method was also used to determine the purity of the tertiary amines from preparative procedures.

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(25) The chromatographic analyses, obtained through the courtesy of L. F. Hatch, The University of Texas, were made on an instrument of proprietary design used regularly for analysis of mixtures of gaseous hydrocarbons. Only qualitative identification of the gases was made because collecting, sampling, and transportation techniques precluded reliable quantitative measurements.

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[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORP.]

Ammonolysis of Vicinal Acetoxy Chlorides

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Ammonolyses of vicinal acetoxy chlorides proceed more readily than the related vicinal dichlorides. Surprisingly, in anhydrous ammonia at 220°, the principal product is vicinal diol; *trans*-2-acetoxycyclohexyl chloride giving a 77% yield of *cis*-1,2-cyclohexanediol. A reversal occurs with aqueous ammonia; an 81% yield of *trans*-2-aminocyclohexanol was isolated. The distribution of products is attributed to a competition between ester ammonolysis and intramolecular chloride displacement by the carbonyl-ammonia intermediate.

The role of neighboring acetoxy groups has been shown in the hydrolysis,[1,2] ethanolysis,[2] and acetolysis[2] of 2-acetoxycyclohexyl arylsulfonates. While the individual steps of ester ammonolysis[3–6] and halide displacement by ammonia and amines[7] are well known, the course of ammonolysis of neighboring acetoxy halide systems has not yet been established. Systems such as these were studied in this work.

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RESULTS

The acetates derived from the chlorohydrins of 2-dodecene, 1-hexene, and cyclohexene, as well as 1,2-dichlorododecane, were subjected to ammonolysis at 220° under autogenous pressure with both aqueous ammonia and anhydrous ammonia in hydrocarbon solvents. Studies in the acyclic series were somewhat complicated by the fact that the starting esters are mixtures of the 1-chloro-2-acetoxy and 1-acetoxy-2-chloro compounds. With the acetoxy chlorides from 1-hexene, for example, vapor phase chromatography indicated a 50/50 mixture of the two isomers. These isomers need not react at the same rate or even by the same mechanism; however, neither the results nor the conclusions appear to be altered by this complication.

The products and yields for the acyclic systems are given in Table I. The acetoxy chlorides from 1-dodecene undergo a 62% conversion to products under conditions where 1,2-dichlorododecane is inert, showing neighboring acetoxy is much more rate enhancing than chloro. The acetoxy group is

TABLE I

AMMONOLYSIS OF ACYCLIC SYSTEMS AT 220°

Substrate	Solvent	Time, Hr.	Mole Ratio NH_3/ Substrate	Reaction, %	Yield, 1,2-Diol, %	Yield, Amino Alcohol, %
1,2-Dichlorododecane	Benzene	4	40	0[a]	0	0
vic-Acetoxy chlorides from 1-dodecene	Benzene	4	50	62	100	0
	o-Xylene	3	25	56	100	0
	Water	3	25	70	82	~18[b]
vic-Acetoxy chlorides from 1-hexene	Water	3	25	93	50	36

[a] Only starting material recovered. [b] Based on 1.24% nitrogen in crude product; 18% as $C_{10}H_{21}CHOHCH_2NH_2$.

also involved in the product-determining step as indicated by the surprising formation of 1,2-diol rather than amino alcohol even under anhydrous conditions. In this anhydrous ammonolysis of an acetoxy chloride, the only source of oxygen is from the acetoxy group. In the presence of water, the extent of reaction appears to be greater and both 1,2-diol and amino alcohols are formed. The yields of amino alcohols appear to increase with decreasing molecular weights of substrate. This suggests that solubility in the aqueous layer may play a role in the distribution of products.

Studies of ammonolysis in the cyclic system, *trans*-2-acetoxycyclohexyl chloride, in both aqueous and anhydrous media are even more revealing. Due to its cyclic structure, there are no positional ambiguities and the stereochemical course of the reaction can be determined. The results are presented in Table II. Once again, ammonolysis in the absence of water leads to 1,2-diol. Even more striking is the complete reversal of product distribution in going from *o*-xylene, *ca.* 80% yield of diol, to aqueous ammonia, *ca.* 80% yield of amino alcohol. Both these products are stereochemically pure; the diol is *cis* and the amino alcohol is *trans*. Further, a control indicated that *cis*-1,2-cyclohexanediol is not converted to *trans*-2-aminocyclohexanol under the aqueous reaction conditions.

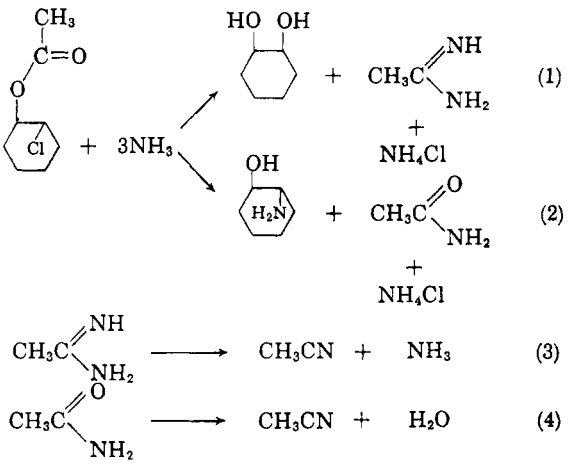
TABLE II

AMMONOLYSIS OF *trans*-2-ACETOXYCYCLOHEXYL CHLORIDE AT 220°

Mole Ratio $NH_3/C_8H_{13}O_2Cl$ = 25

Solvent	*o*-Xylene	Water
Reaction time, hr.	4	3
Reaction, %	100	100
Yield:		
cis-1,2-Cyclohexanediol	77	2
trans-2-Aminocyclohexanol	0	81
Acetamide	14	—
Acetonitrile	55	—

In *o*-xylene-anhydrous ammonia, 77% diol, 55% acetonitrile, and 14% acetamide were isolated. The formation of diol requires that all of the hydroxyl oxygen come from the oxygen of the acetate group. The acetate residue itself appears as acetamidine (Equation 1). Amidines are generally unstable, losing ammonia to form nitriles (Equation 3).[8]



(1) (2) (3) (4)

The 14% yield of acetamide suggests that at least that much amino alcohol may have been formed (Equation 2), even though none of it was detected. There were, however, unresolved higher molecular weight products which might contain secondary or tertiary amino residues formed from the amino alcohol. Some of the acetamide may have been dehydrated to acetonitrile (Equation 4). This is indicated by the presence of some water in the products of the nonaqueous ammonolysis. Equation 4 was also verified as a control carried out under reaction conditions. In any event, the high yield of 1,2-diol makes it clear that with anhydrous ammonia in hydrocarbon media most of the acetonitrile is formed *via* Equations 1 and 3. No efforts were made to isolate the acetate fragment from ammonolysis in aqueous solution. Any acetonitrile, acetamide, or acetamidine would most likely be hydrolyzed to ammonium acetate.

Mechanism. If the reaction were to proceed by simple ionization of the chloride moiety, then the comparably electron-withdrawing chloro or acetoxy groups (Equation 5, X = Cl or OAc) should be

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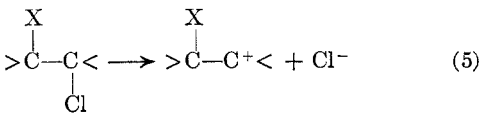
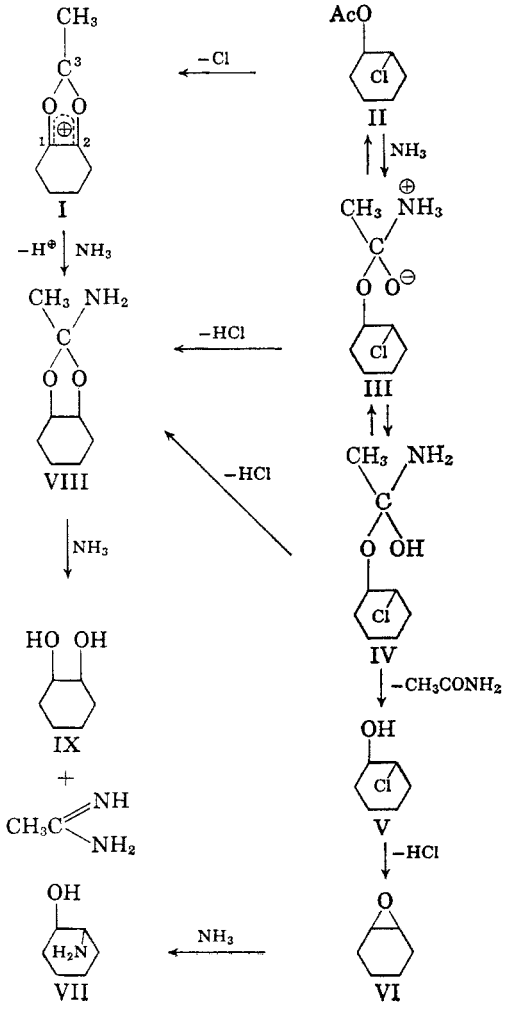


(5)

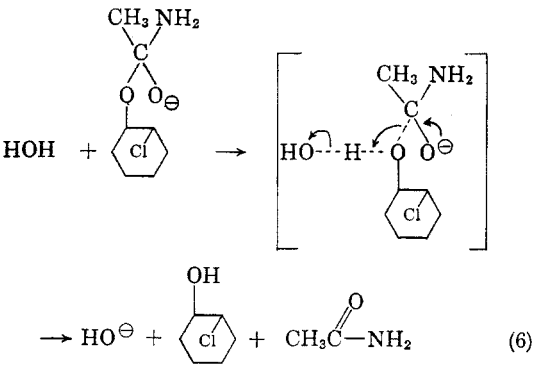
comparably rate retarding. Related work indicates that a neighboring acetoxy group is only 1.4 times less rate retarding at 75° than neighboring chloro for ionization.[9] A similar argument plus the known sluggishness of cyclohexyl systems toward S_N2 reactions[10] may be used as evidence against any direct displacement of chloride by ammonia. The enchanced reactivity of acetoxy chlorides over dichlorides is most certainly due to neighboring group participation,[11] either of the acetate group directly or of an intermediate derivable from it. The hydrolysis,[1,2] ethanolysis,[2] and acetolysis[2] of 2-acetoxycyclohexyl arylsulfonates proceed *via* the cyclic *cis*-cyclohexaneacetoxonium ion (I), which reacts rapidly with ethanol or acetic acid at C-3 to give an ortho ester or an ortho diacetate.[12] These, depending on conditions, give the products of thermodynamic control by reaction at C-1 or C-2 or products of kinetic control by reaction at C-3.

A mechanistic scheme consistent with the observed products and stereochemistry is the following:



trans-2-Acetoxycyclohexyl chloride (II) may react with ammonia at the carbonyl carbon to give intermediate III which then continues normal ester ammonolysis,[3-6] probably *via* intermediates IV and V. The *trans*-chlorohydrin (V) so formed, undergoes intramolecular displacement of chloride ion giving cyclohexene oxide (VI), which is opened by ammonia with inversion to give *trans*-2-aminocyclohexanol (VII).[13] The possibility of IV displacing chloride intramolecularly with the amino group apparently does not occur to any appreciable extent. The resultant cyclic intermediate would give rise to *cis*-amino alcohol, none of which was detected. Winstein and co-workers have shown that, in systems such as neighboring ureido or urethano, participation by oxygen seems favored over nitrogen, at least in neutral solution.[14] On the other hand, III or IV displacing chloride intramolecularly with an alkoxide or hydroxyl group to form VIII is a likely route to *cis*-diol. Alternatively, *cis*-diol may arise by assisted ionization to the *cis*-cyclohexaneacetoxonium ion (I) forming VIII, and ultimately *cis*-diol (IX) by further reaction with ammonia. This route is considered less likely, however, since it requires that generation of an ionic intermediate occurs more readily in anhydrous ammonia-xylene than in aqueous ammonia.

The most consistent scheme involves rapid carbonyl attack by ammonia in either aqueous or anhydrous media to form III and IV. In the presence of proton-donating species, such as water, normal ester ammonolysis proceeds by acid catalyzed facilitation of alcohol loss (Equation 6).



(6)

The role of acid catalysis in the slow step of ester ammonolyses has recently been shown.[5,6] In the absence of proton donors, as in anhydrous ammonia,

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TABLE III

PHYSICAL PROPERTIES OF ACETOXY CHLORIDES

Acetoxy Chloride from	B.P.°/Mm.	n_D^{20}	Calcd., % C	Calcd., % H	Found, % C	Found, % H
1-Dodecene	155–160/4.5	1.4458	63.98	10.36	63.61	10.31
1-Hexene[a]	93–99/12	1.4330	53.78	8.46	54.09	8.49
Cyclohexene[b,c]	100–100.3/12	1.4644				

[a] Vapor phase chromatography indicated two major peaks, 50.2% and 47.5%. [b] Lit.,[18] b.p. 98–98.5°/12 mm., n_D^{25} 1.4630. [c] 98.6% pure by vapor phase chromatography.

ester ammonolysis occurs less readily[4a,15] so that intramolecular displacement of chloride, III, or IV to VIII, can compete to form *cis*-diol. The role of water in facilitating ammonolysis is also borne out by increased yields of amino alcohols with decreasing molecular weight (increasing solubility) in the aqueous ammonolysis of acyclic *vic*-acetoxy chlorides.

The extension of this method of preparing *cis*-glycols to other cyclic systems such as steroids is obvious, supplementing such better known methods as direct hydroxylation by permanganate or osmium tetroxide or by the assisted hydrolysis of acetoxy iodides.[16]

EXPERIMENTAL

1,2-Dichlorododecane. Direct chlorination of 1-dodecene at 20–25° followed by careful fractionation gave 1,2-dichlorododecane, b.p. 134.5–135°/5 mm., n_D^{20} 1.4578.

Anal. Calcd. for $C_{12}H_{24}Cl_2$: Cl, 29.64. Found: Cl, 29.78.

n-Alkylchlorohydrins. 1-Hexene and 1-dodecene chlorohydrins were prepared by chlorination of the pure olefin in aqueous pyridine at 20°. Unchanged olefin and dichlorides were removed by pentane elution of the products on alumina. The chlorohydrins were eluted with ether and fractionated; 1-dodecene chlorohydrin, b.p. 145–147°/7 mm.; n_D^{20} 1.4569; 1-hexene chlorohydrin, b.p. 72–77°/12 mm.; n_D^{20} 1.4475 (lit.[17] b.p. 73–75°/12 mm., n_D^{20} 1.4478).

trans-2-Chlorocyclohexanol. A commercial sample of *trans*-2-chlorocyclohexanol (Aldrich Chemical Co.) was distilled, b.p. 84.5–85°/16 mm., n_D^{20} 1.4910.

vic-Acetoxy chlorides. Equimolar quantities of chlorohydrin and acetic anhydride mixed with 2 drops of concd. sulfuric acid were allowed to react for 2–5 hr. at room temperature. Routine work-up resulted in products with acceptable C and H analyses; physical properties are shown in Table III.

Ammonolyses in anhydrous ammonia. Acetoxy chloride (0.025–0.075 mole) was placed in a 600-ml. stainless steel rocker bomb together with 40–150 g. of distilled hydrocarbon. Sufficient liquid ammonia was added from a sight blowcase to make the mole ratio of ammonia to ester 25 : 1. The bomb was brought up to 220° and autogenous pressure in 30 min. and heated for 3–4 hr. The bomb was cooled quickly (30 min.) and excess ammonia bled off. The contents of the bomb were submitted to distillation through a 30-in. tantalum spiral column. As a typical example, the distillation fractions from the anhydrous ammonolysis of *trans*-2-acetoxycyclohexyl chloride are given.

Cut 1. B.p. 75.5–141°, 1.53 g. Infrared analysis indicated acetonitrile, *o*-xylene, and traces of water. Vapor phase chromatography indicated 1.13 g. acetonitrile, 55 mole % based on input ester.

Cut 2. B.p. 142–145.2°, 114.34 g., mostly *o*-xylene. A white solid which azeotroped over was filtered and dried, 0.60 g., m.p. 72–76°. Infrared spectra indicated it to be mainly acetamide containing small amounts of *cis*-1,2-cyclohexanediol. Recrystallization from carbon tetrachloride gave 0.4 g. (13.6% yield) of pure acetamide, m.p. 77.0–78.4°.

Cut 3. B.p. 145.2–145.5°, 9.24 g., mostly *o*-xylene. Contained a small amount of solid, which was identified as *cis*-1,2-cyclohexanediol, m.p. 97.8–98.6°, 0.06 g.

The filtrates from Cuts 1, 2, and 3 were combined. Vapor phase chromatography indicated 99.9% *o*-xylene.

Bottoms. The brown distillation bottoms, 12.18 g., solidified on cooling. See Separation below.

Ammonolysis in aqueous ammonia. Acetoxy chloride (0.025–0.075 mole) was heated in the stainless steel rocker bomb at 220° and autogenous pressure with a 25-fold molar excess of ammonia as concentrated aqueous ammonia. The bomb was cooled and vented as in the anhydrous ammonia runs.

Separation of diols and amino alcohols. The ammonolysis products, either in their entirety from the aqueous runs or as distillation bottoms from the anhydrous runs, were neutralized with concentrated hydrochloric acid using a 10 volume % excess. The acidic solution was continuously extracted with chloroform for 8 hr. The chloroform extract was dried over magnesium sulfate and the solvent removed. The residues were crystallized from a suitable solvent, pentane for 1,2-dodecanediol, and chloroform for *cis*-1,2-cyclohexanediol. 1,2-Hexanediol was isolated by distillation of the residue. The crystallization mother liquors or distillation bottoms were identified as mixtures of diol containing varying amounts of unchanged acetoxy chlorides.

The acidic aqueous extracts were evaporated to dryness, made basic with 0.3*N* ethanolic sodium hydroxide, and the inorganic salts filtered off. The filtrate was concentrated under vacuum, acidified with 10% aqueous hydrochloric acid, and evaporated to dryness. Trituration with hot 1 : 2 ethanol : benzene followed by filtration and cooling precipitated amino alcohol hydrochlorides, where present. None was detected from the *vic*-acetoxy chlorides from 1-dodecene either aqueous or anhydrous, or anhydrous *trans*-2-acetoxycyclohexyl chloride. However, aqueous runs with the *vic*-acetoxy chlorides from cyclohexene and 1-hexene deposited considerable amine salt as a white solid and as a yellow oil, respectively.

Identification of Products. 1,2-Dodecanediol. 1,2-Dodecanediol, m.p. 59.8–61°, crystallized from *n*-pentane, was isolated from the ammonolysis of the acetoxy chlorides from 1-dodecene with anhydrous ammonia in *o*-xylene. The material had an acceptable elemental analysis and did not depress the melting point of authentic 1,2-dodecanediol, m.p. 60–61°. Diol isolated from ammonolysis in aqueous ammonia melted at 55.8–57.4°. Elemental analysis indicated 1.24% nitrogen, corresponding to 18% yield as dodecanolamine. An infrared spectrum was identical to that of 1,2-dodecanediol, except for bands at 1630 cm.$^{-1}$ and a

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pair at 1590 and 1570 cm.$^{-1}$ These absorptions may be the N-H deformation frequencies for primary and secondary amines, respectively.[19]

1,2-Hexanediol. This material was isolated by distillation, b.p. 112–113°/12 mm., n_D^{20} 1.4400 (lit., b.p., 111°/12 mm).[20] A di-(*p*-nitrobenzoate) was prepared in high yield, m.p. 100.2–100.8°.

Anal. Calcd. for $C_{20}H_{20}N_2O_8$: N, 6.73. Found: N, 6.73.

1-Amino-2-hydroxy- and 1-hydroxy-2-aminohexane. The amino alcohol hydrochloride portion of the products from ammonolysis of the acetoxy chlorides from 1-hexene in aqueous ammonia resisted all attempts at crystallization and was isolated as a partially solid water-soluble oil. Its infrared spectrum was consistent with amino alcohol hydrochloride. A 0.5-g. portion on Schotten-Baumann benzoylation gave 0.7 g. of white plates from benzene, m.p. 105.5–106°.

Anal. Calcd. for $C_{13}H_{19}NO_2$: N, 6.33. Found: N, 6.25.

cis-1,2-Cyclohexanediol. Diol isolated from the ammonolysis of *trans*-2-chlorocyclohexyl acetate in anhydrous ammonia-*o*-xylene, m.p. 95–96.3°, mixed melting point with authentic *cis*-1,2-cyclohexanediol,[21] 98.2–99.2°, mixed melting point with authentic *trans*-1,2-cyclohexanediol,[21] 53–61°. The infrared spectra of all fractions of crystalline diol isolated, as well as the crystallization liquors, indicated the formation of only the *cis* isomers by the absence of bands at 1040, 925, and 855 cm.$^{-1}$ characteristic of the *trans* isomer.

trans-2-Aminocyclohexanol. *trans*-2-Aminocyclohexanol, isolated as its hydrochloride from the ammonolysis of *trans*-2-chlorocyclohexyl acetate in aqueous ammonia melted at 171–172.4° (lit.,[22] m.p., 175°). Schotten-Baumann benzoylation of 0.5 g. of the amino alcohol hydrochloride gave 0.75 g. of *trans*-2-benzoylaminocyclohexanol, white needles from benzene, m.p. 171.8–172° (lit.,[23] m.p. 171–172°).

Acknowledgment. We wish to thank Professor S. Winstein and Dr. Philip S. Magee for many stimulating discussions during the course of this work.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Interaction of an Ivanov and an Ivanov-Like Reagent with γ-Butyrolactone and γ-Valerolactone

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Reactions of the α-chloromagnesium derivative of the chloromagnesium salt of phenylacetic acid with γ-butyrolactone and with γ-valerolactone, and reactions of the α-chloromagnesium derivative of *N,N*-dimethylphenylacetamide with the same two lactones were studied.

Interest in the Ivanov reaction prompted us to study the interaction of a typical Ivanov reagent, the α-chloromagnesium derivative of the chloromagnesium salt of phenylacetic acid, with γ-butyrolactone. Reactions of this lactone had been studied previously with methylmagnesium bromide,[3,4] methylmagnesium iodide,[5,6] and phenylmagnesium bromide.[7,8] In all instances the product obtained showed that one molecular equivalent of the lactone had reacted with two molecular equivalents of the Grignard reagent.

It was found that when γ-butyrolactone was treated with either one or two molecular equivalents of the Ivanov reagent, the reaction products were α-(tetrahydro-2-furylidene)phenylacetic acid (Ia) and 2-benzylidenetetrahydrofuran (IIa).

In order to account for the presence of IIa in the reaction mixture, it may be assumed that the initial reaction product, after acidification, underwent reactions with the formation of the β-keto acid, the hydroxy ketone, and the hydroxybenzyltetrahydrofuran shown in the reaction scheme; the last mentioned product then lost water to form IIa.

Compound Ia dissolved readily in sodium bicarbonate solution and precipitated unchanged after the addition of acid. The unsaturated nature of Ia was proven by the fact that it decolorized bromine and potassium permanganate. When heated to its melting point, Ia lost carbon dioxide and was converted into an oil (IIa) which also gave positive tests for unsaturation.

When Ia was hydrogenated catalytically, a saturated compound, α-(tetrahydro-2-furyl)phenyl-

(1) Abstracted from the Ph.D. dissertation of B. A. Brown, University of Michigan, 1961.

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