[CONTRIBUTION FROM THE DEPT. OF CHEMISTRY, UNIVERSITY OF TORONTO]

REACTIONS OF THE STILBENE-DISODIUM AND -DILITHIUM ADDUCTS

A. G. BROOK, H. L. COHEN, AND GEORGE F WRIGHT

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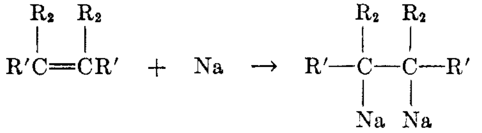
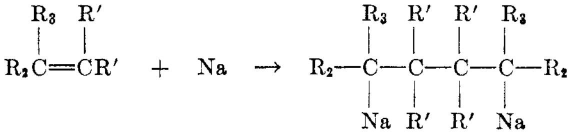
The addition of alkali metals to arylated alkenes was first reported formally by Schlenk and his co-workers in 1914 (1). A comprehensive report and summary was subsequently published by Schlenk and Bergmann in 1928 (2). Typical examples of their addition reactions are shown in equations 1, 2, and 3.



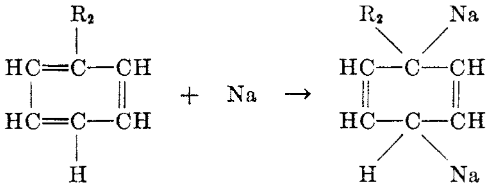
$$R'\overset{R_2}{\overset{|}{C}}{=}\overset{R_2}{\overset{|}{C}}R' + Na \rightarrow R'{-}\underset{\underset{Na}{|}}{\overset{\overset{R_2}{|}}{C}}{-}\underset{\underset{Na}{|}}{\overset{\overset{R_2}{|}}{C}}{-}R'$$

1.



$$R_2\overset{R_3}{\overset{|}{C}}{=}\overset{R'}{\overset{|}{C}}R' + Na \rightarrow R_2{-}\underset{\underset{Na}{|}}{\overset{\overset{R_3}{|}}{C}}{-}\underset{\underset{R'}{|}}{\overset{\overset{R'}{|}}{C}}{-}\underset{\underset{R'}{|}}{\overset{\overset{R'}{|}}{C}}{-}\underset{\underset{Na}{|}}{\overset{\overset{R_3}{|}}{C}}{-}R_2$$

2.



3.

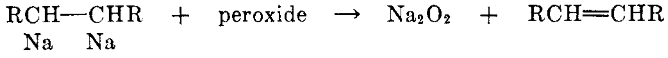
where R′ = CH_3 or H; R_2 = aromatic; R_3 = aromatic or CH_3.

The addition reactions reported by these workers were slow and incomplete in solvents like benzene. Addition was more rapid (although it still required days to weeks) when diethyl ether was used. However this solvent was unstable in presence of the organometallic compound. In most instances the low solubility of the adducts was not conducive to smooth reaction of the type undergone by ordinary organometallic compounds.

These difficulties were subsequently alleviated by the discovery (3) that the adducts are formed rapidly and are soluble and stable in 1,2-dimethoxyethane. As typical examples of the difference in rate of adduct formation in diethyl ether *versus* 1,2-dimethoxyethane, the reaction with 1-phenyl-2-methylpropene and with biphenyl may be cited. Schlenk and Bergmann report (2) that the first of these compounds (equation 2; R′ = CH_3, R_2 = C_6H_5, R_3 = H) does not react with sodium in ether, although Conant and Blatt (4) were able to demonstrate addition to the extent of 55% by reaction for 36 hours with the more reactive and less easily tarnished sodium-potassium alloy. They isolated the carbonation product, 2,2,3,3-tetramethyl-1,4-diphenyladipic acid. We have found that approximately the same yield of this acid may be obtained with sodium alone in the solvent 1,2-dimethoxyethane. Bergmann and Schlenk report that sodium in ether will not react with biphenyl over a 30-day period, although lithium will react to an unstated extent in 14 days. In contrast, we find that reaction of biphenyl with sodium in 1,2-dimethoxyethane is complete in a few hours; the carbonation product corresponds to the 1-phenyl-2,5-cyclohexadiene-1,4-dicarboxylic acid assumed by Schlenk and Bergmann, since dehydrogenation with sulfur yields 4-biphenylcarboxylic acid. It may thus be seen that dimethoxyethane is much more efficient as a medium for the formation of the adduct than is diethyl ether, benzene, or petroleum ether. However we were unable to form an adduct with 1,2-diphenylcyclopropane in 1,2-dimethoxyethane; of course the evidence for π bonding in this cyclic type is not unequivocal.

The reactions of the arylated alkene-alkali metal adducts have not been studied extensively. Despite the demonstrations (5, 6) that dimethoxyethane solutions of the adducts can be carbonated and methylated like typical organometallic compounds, the addition reaction seems to have received little attention or utilization. In this report we have attempted to extend the list of useful reactions. In order to demonstrate their generality, we have chosen the stilbene-dialkali metal adduct, since its preparation and reactions were troublesome for Schlenk and Bergmann.

The relatively high cost and limited availability of 1,2-dimethoxyethane may have discouraged some in the use of this reaction. Undoubtedly the choice of solvent is limited. Thus dimethyldioxolane and dioxane are both unsatisfactory. Actually we have found that tetrahydrofuran, which is cheaper and more readily available than dimethoxyethane, can replace it. However the disadvantages of tetrahydrofuran (hygroscopicity and peroxidation) are not shared by 1,2-dimethoxyethane, so that the latter solvent is still to be preferred for purposes of research. Either solvent must be freed from water by use of sodium and sodium benzophenone ketyl under nitrogen, but this procedure is no more difficult than the proper preparation of diethyl ether for Grignard use. Indeed the presence of ether peroxides is less harmful to the adduct formation than to the preparation of a Grignard reagent, since a trace of peroxide is converted at once to insoluble sodium peroxide. The regenerated arylated alkene may then react with more alkali metal.



$$\underset{\text{Na}}{\text{RCH}}\text{—}\underset{\text{Na}}{\text{CHR}} + \text{peroxide} \longrightarrow Na_2O_2 + \text{RCH=CHR}$$

The preparation of the alkali metal adducts with arylated alkenes is actually easier than the preparation of most Grignard reagents. The sensible heat of reaction is much lower, and coupling reactions are not involved. For these reasons, regulated addition is not required. Since the reaction is complete within a few hours, we originally abandoned the use of the sealed double-arm "Schlenk tube" in favor of a nitrogen-filled stirred reaction flask. More recently we have partially reverted to the Schlenk technique by use of an ordinary cylindrical separatory funnel of which the interchangeable stopper has been replaced by a joint equipped with a stopcock. The funnel is first filled with nitrogen, then with the reagents, and then closed under the nitrogen atmosphere. After the stopcocks are secured by tape, the assembly is shaken mechanically until the reaction is complete. A sample may be withdrawn to check this completeness. Finally the entire darkly-opaque solution of adduct may be drained from the lower stopcock while nitrogen is introduced at the top.

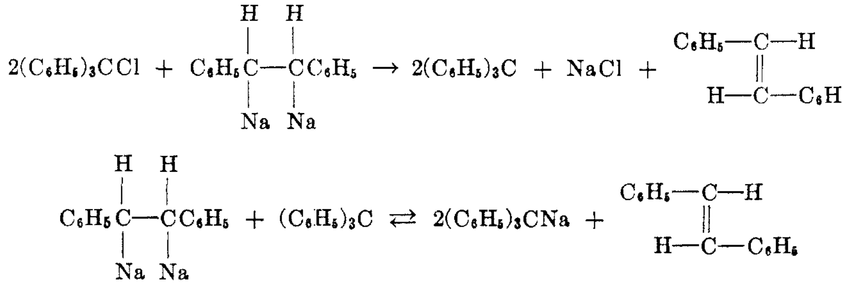
The published literature may be discouraging to some because of the paucity of useful reactions which the adducts have been reported to undergo. This limitation applies mainly to adducts produced according to equation 1 in which the alkali metal atoms are vicinally-linked. Adducts in which the sodium atoms are not adjacent, such as the products shown in equations 2 and 3, behave in diethyl ether solution or suspension much like organomagnesium compounds. On the other hand, the vicinally-linked adducts lose the added sodium and regenerate the alkene when treated with a variety of reagents. The reagents which are reported to regenerate large amounts of alkene from the adducts are listed in Table I. Those items drawn from reference 7 or from the present report involve the stilbene adduct in 1,2-dimethoxyethane. The remainder represent Schlenk's work with tetraphenylethylene in diethyl ether. These latter results might be different if dimethoxyethane were used as the solvent. An investigation is warranted, especially with organic halides, but we have examined only a very reactive halide.

TABLE I

Regeneration of Arylated Alkene from the Metal Adduct

REAGENT	ADDITIONAL PRODUCTS	REFERENCE
Oxygen	Sodium peroxide	1
Sulfur	Sodium sulfide	7
Mercury	Sodium amalgam	2, p. 6
Iodine	Sodium iodide	2
Arsenic trichloride	Sodium chloride	7
Magnesium chloride		This report
Mercuric chloride	Mercury	7
Nitric oxide	Sodium hyponitrite	2, p. 23
Methyl iodide	Sodium iodide	1
Bromobenzene	Biphenyl, sodium bromide	1
Benzaldehyde	Sodium benzoate, benzyl alcohol	2
Formaldehyde	Small amount, probably of $[(C_6H_5)_2COH-]_2$	2
Benzophenone	Benzophenone ketyl	This report
Benzoyl chloride	Benzil, sodium chloride	2, p. 19
Benzonitrile	2,4,6-Triphenyl-s-triazine	This report
Phenyl isocyanate	1,3,5-Triphenyl-s-triazine-2,4,6-trione	This report
Phenyl isothiocyanate	Phenyl isothiocyanate "dimer"	2

Thus we have found that triphenylchloromethane in 1,2-dimethoxyethane reacts much like methyl iodide or bromobenzene in diethyl ether. When the darkly-opaque solution of stilbene-disodium adduct is added slowly to an equivalent solution of triphenylchloromethane, the yellow color of triphenylmethyl appears at first, but is gradually replaced by a deep red-brown color. This color must be characteristic chiefly of the adduct and not of triphenylmethylsodium, because treatment with carbon dioxide produces an 18% yield of *meso*-diphenylsuccinic acid and a 0.4% yield of triphenylacetic acid. Isolation of the disproportionation products of triphenylmethyl, namely triphenylmethane and 1-triphenylmethyl-4-diphenylmethylbenzene, together with stilbene and 1,2-diphenylethane indicates that the following reactions probably are involved.



$$2(C_6H_5)_3CCl + C_6H_5\underset{Na}{\overset{H}{C}}-\underset{Na}{\overset{H}{C}}C_6H_5 \rightarrow 2(C_6H_5)_3C + NaCl + \begin{matrix} C_6H_5-C-H \\ \| \\ H-C-C_6H_5 \end{matrix}$$

$$C_6H_5\underset{Na}{\overset{H}{C}}-\underset{Na}{\overset{H}{C}}C_6H_5 + (C_6H_5)_3C \rightleftarrows 2(C_6H_5)_3CNa + \begin{matrix} C_6H_5-C-H \\ \| \\ H-C-C_6H_5 \end{matrix}$$

Organosodium compounds react with the "active" hydrogen in water, alcohols, and hydrocarbons such as indene and fluorene. The typical disodium adduct is no exception (8). Furthermore organosodium compounds show a strong tendency toward *trans*-metalation with the hydrogen *alpha* to an unsaturation rather than toward addition to that unsaturation. An example of this behavior with the naphthalene-disodium adduct is its reaction with acetonitrile. Dihydronaphthalene and the sodium salt of the nitrile are formed; the latter is amenable to further reactions with organic halides (9). Evidently the same *trans*-metalation takes place when we treat the stilbene-disodium adduct with acetyl chloride or acetic anhydride. The isolable product is 1,2-diphenylethane, admixed with a complex mixture of condensation products.

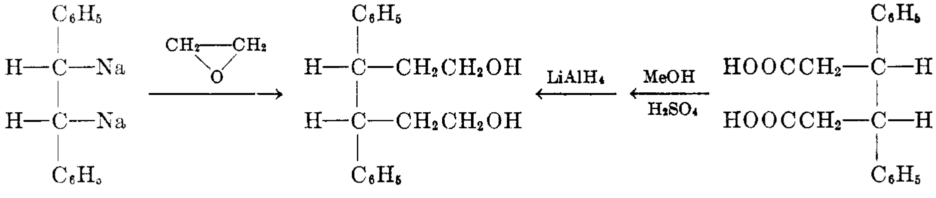
In view of the extreme lability of these alkali metal atoms in the stilbene-disodium adduct, it is surprising that catalytic reduction does not yield 1,2-diphenylethane. However this reduction product is formed, together with sodamide, when the stilbene adduct is dissolved in liquid ammonia (10). On the other hand, Bergmann and Schlenk, and also Wooster, found that the tetraphenylethylene-disodium adduct was inert toward ammonia. It would seem that the lability of the sodium atoms depends on the alkene used as the addend; further, that the stilbene-disodium adduct is an extreme instance of this lability.

The foregoing description does not recommend the arylated alkene-alkali metal adducts for synthetic use. However several useful reactions have been reported (2, 5, 6) and this number has been augmented by our recent investigation. These reactions, all carried out with the stilbene-disodium adduct except for the reaction of the tetraphenyl adduct with sulfur dioxide (2), are summarized in Table II.

The addition with carbon dioxide is most commonly used, and may simply involve transfer of the solution of adduct to an excess of Dry Ice. After recovery of the solvent by vacuum evaporation the carbonation product may be isolated in the usual way. After examination of the diastereomeric diphenylsuccinic acids, Wright (6) confirmed the conclusion of Schlenk and Bergmann that the stereochemical composition of the adduct was independent of the geometric isomer of stilbene used in its preparation. He found furthermore that this stereochemical composition was dependent on the solvent and also, in contradiction to Schlenk and Bergmann, was independent of the choice of lithium or sodium as the metal in the adduct. Insofar as these observations are generalized, the present report confirms the second conclusion but indicates that the third conclusion must be modified when steric effects become important. Actually steric crowding might be expected in view of Schlenk and Bergmann's opinion that the reaction product of sulfur dioxide with the tetraphenylethylene-disodium adduct could not be isolated as the free disulfinic acid because of its instability.

Table II shows that the further observation (6) (that the ratio of diastereomeric addition products is dependent on the reagent to which the adduct is added) may be considered to be a generalization. Not only do different types of reagent (methyl sulfate *versus* carbon dioxide) give different ratios of diastereomeric product, but the difference is apparent with homologs of the same type of reagent. We find that ethyl sulfate does not alkylate the adduct as efficiently as does methyl sulfate (more stilbene is regenerated), but that a mixture comprising a 13% yield of solid *meso-* and a 26% yield of liquid *dd,ll-* 3,4-diphenylhexane can be separated. The configuration of the *dd,ll* isomer has been confirmed by conversion to the hexabromo derivative (11) and that of the *meso* isomer by conversion to dinitrodiphenylhexane (12).

The *dd,ll*-diastereomer also predominates over the *meso-* (35% *versus* 9%) when the adduct (I) is converted partially (30% of stilbene regenerated) to 3,4-diphenyl-1,6-hexanediol (II) by treatment with epoxyethane. The configurations of these diastereomers are established by their alternative syntheses from the known 3,4-diphenyladipic acids (11) (III). These acids have been converted to their methyl esters. Reduction of the esters with lithium aluminum hydride in di-*n*-butyl ether gives the corresponding diols, identical with the products obtained from the stilbene-disodium adduct.



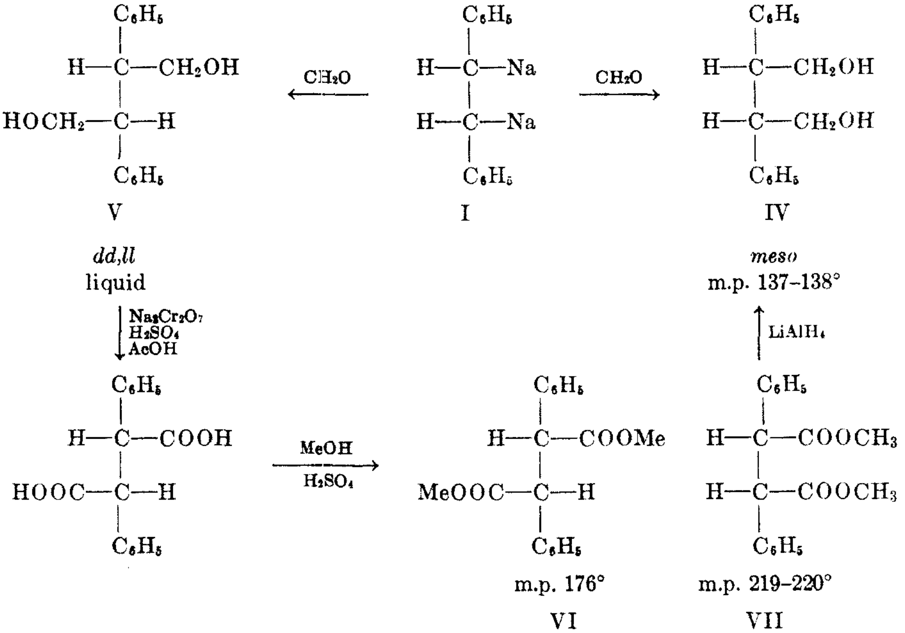
meso, m.p. 159–160°
dd,ll, m.p. 102–103°

meso, m.p. 276°
dd,ll, m.p. 170°

I II III

It was shown in Table I that Schlenk and Bergmann had little success in adding the disodium or dilithium compounds to aldehydes or ketones. However it was suspected that these reactions might proceed differently in 1,2-dimethoxyethane than in diethyl ether. Indeed the stilbene-disodium adduct was found (7) to react with benzaldehyde to give a complex diastereomeric mixture, undoubtedly 1,2,3,4-tetraphenyl-1,4-butandiols. No sodium benzoate or benzyl alcohol, such as Schlenk and Bergmann reported from the reaction of benzaldehyde with the tetraphenylethylene-disodium adduct, was found.

We have confirmed the suspicion that the stilbene-disodium adduct in dimethoxyethane can add to the carbonyl group of some aldehydes and ketones. Our choice has been limited to symmetrical compounds in order to avoid complex diastereomeric mixtures which might be difficult to separate. Formaldehyde in the polymeric form is found to decolorize the adduct within an hour at 25°. In addition to about 35% of stilbene which is regenerated, it is possible to isolate a 5% yield of *meso-* (IV) and a 50% yield of *dd,ll*-2,3-diphenyl-1,4-butanediol (V).



The *dd,ll*-diastereomer has been identified by oxidation to *dd,ll*-diphenylsuccinic acid, which is converted to its methyl ester, m.p. 176°. The *meso*-diastereomer is identical with that glycol obtained by reduction of *meso*-dimethyl diphenylsuccinate (m.p. 219–220°) with lithium aluminum hydride.

The stilbene-disodium adduct differs from magnesium or lithium alkyls since it will not add to benzophenone. Instead, one equivalent of the ketone will appropriate all of the sodium. Subsequent treatment of the purple solution of disodium benzophenone ketyl with carbon dioxide gives 85% yields of benzilic acid and stilbene. Although 5% of benzophenone can be recovered, no diphenylsuccinic acid is found. A blue solution of sodium benzophenone ketyl is formed when two equivalents of ketone are employed, but carbon dioxide converts this solution to a 84% yield of benzilic acid; an equivalent amount of benzophenone is recovered and stilbene is the only other product obtainable from the reaction.

In order to evaluate the reactivity of the adduct in absence of the metal-exchange reaction, the highly-hindered 2,2,6,6-tetramethylcyclohexanone has been treated with both stilbene-dilithium and disodium adducts. No reaction occurs after three hours at 60°, but the adducts are stable. Subsequent treatment with carbon dioxide gives almost quantitative yields of diphenylsuccinic acid.

In view of the inertness of these ketones toward addition with the stilbene-alkali metal adducts, it seemed questionable whether addition to acetone would occur. It might be expected that this reaction would further be complicated by *trans*-metalation with the methylenic hydrogen atoms of acetone. However we have synthesized the diols by other methods in anticipation that they might be found among the reaction products of acetone and the stilbene-alkali metal adducts.

TABLE II

ADDITION REACTIONS OF THE ARYLATED ALKENE-ALKALI METAL ADDUCTS

REAGENT	PRODUCTS	REFERENCE
Carbon dioxide	90% *meso-*, 10% *dd,ll*-Diphenylsuccinic acid	2, 6, 7
Sulfur dioxide	Disodium tetraphenylethanedisulfinate	2
Methyl sulfate	23% *meso-*, 70% *dd,ll*-2,3-Diphenylbutane	6, 7
Ethyl sulfate	13% *meso-* 26% *dd,ll*-3,4-Diphenylhexane + stilbene	
Formaldehyde	5% *meso-*, 50% *dd,ll*-2,3-Diphenyl-1,4-butanediol + stilbene	
Acetone	*dd,ll*-2,5-Dimethyl-3,4-diphenyl-2,5-hexanediol + diphenylethane 2-Methyl-3,4-diphenyl-2-butanol + pinacol + stilbene	
Epoxyethane	9% *meso-*, 35% *dd,ll*-3,4-Diphenyl-1,6-hexanediol + stilbene	
Benzophenone	Sodium benzophenone ketyl	
2,2,6,6-Tetramethylcyclohexanone	No reaction	

The compound which we designate as *dd,ll*-2,5-dimethyl-3,4-diphenyl-2,5-hexanediol (X) has been prepared in 48% yield by boiling under reflux for 6 hours a solution of methyl iodide Grignard reagent and *dd,ll*-dimethyl diphenylsuccinate (VI) in a benzene-ether mixture. However a 2–5% yield of the same diastereomer (X) (in addition to a trace of the other diastereomer, IX) is obtained from *meso*-dimethyl diphenylsuccinate (VII) by similar treatment for 12 hours. This anomalous situation, which would not permit positive specification of diastereomeric configuration, has been resolved to our satisfaction by the use of methyllithium instead of the Grignard reagent with the *meso* ester (VII). Since with methyllithium the forced conditions described above are unnecessary for the formation of the second diastereomer alone, in 30% yield, we are designating it as *meso*-2,5-dimethyl-3,4-diphenyl-2,5-hexanediol (IX). We believe that steric restrictions prevent the addition of Grignard reagent (but not the less-bulky methyllithium) to the *meso* ester. On the other hand isomerization may occur slowly *via* a small amount of the iodomagnesium enolate (VIII). The diastereomer (VI), which will be formed by equilibration of VIII with VII, may then be expected to react slowly with the methyl iodide Grignard reagent to form the glycol (X). The lesser steric restriction in *dd,ll*-2,5-dimethyl-3,4-diphenyl-2,5-hexanediol (X) as compared with the diastereomer (IX) is, perhaps, exemplified by the ease with which X may be converted by hot 50% sulfuric acid to 2,2,5,5-tetramethyl-3,4-diphenyltetrahydrofuran (XI) (13). The diastereomeric IX cannot be cyclized in this manner.

The steric restrictions involved in the *meso* diastereomer (IX) may also account for its absence among the reaction products from the stilbene-alkali metal adducts and acetone. The actual products, listed in Table III, show evidence of a steric effect which is dependent on the metal. The higher yield of diol (X) when the metal (M) has the smaller diameter of lithium contradicts the generalization to be derived from Wright's observation (6) that either lithium or sodium stilbene adduct gives the same diastereomeric ratio of diphenylsuccinic acids upon treatment with carbon dioxide. Finally it may be seen (Exp. 3) that diol X is not formed at all unless acetone is initially present in high excess.

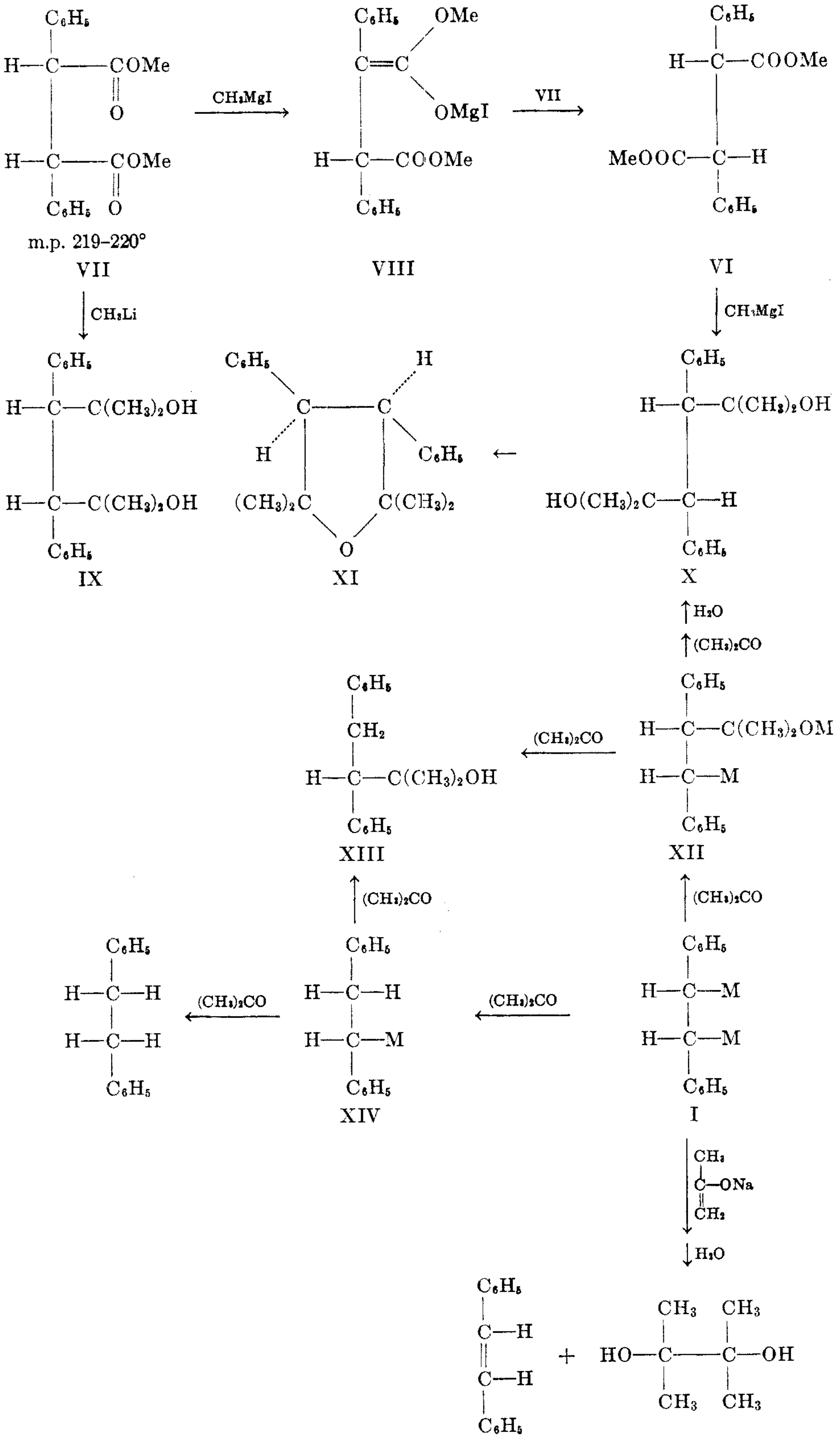
TABLE III

REACTIONS OF ACETONE WITH STILBENE-ALKALI METAL ADDUCTS

EXPT.	METAL	ADDITION SEQUENCE	PRODUCTS, YIELDS, %			
			Diol X	Pentanol	Diphenylethane	Stilbene
1	Li	Adduct → Acetone	23	28	11	10
2	Na	Adduct → Acetone	5	25	30	12
3	Na	Acetone → Adduct	0	20	30	13

The isolation of 2-methyl-3,4-diphenyl-2-butanol (XIII) in a yield (Column 5, Table III) which decreases in the same order as that of the diol X shows for the first time that these adducts (I) react in a stepwise manner. The intermediate XII may then either add acetone to give X or else *trans*-metalate to give XIII. Under the conditions of Experiments 2 and 3, this *trans*-metalation evidently occurs directly with the adduct I (probably *via* intermediate XIV). This opinion is based on the yield of 1,2-diphenylethane which is higher in Experiments 2 and 3 than that found for Experiment 1. *Trans*-metalation is evidently complete, and none of XII or XIV remain at the end of the reaction. Thus carbonation of the reaction mixture yields none of the carboxylic acids expected from these intermediates.

The *trans*-metalation must obviously produce the sodium salt of acetone, yet no condensation products characteristic of this substance have been found. On the other hand a 5% yield of pinacol has been isolated. Its formation has been


m.p. 219-220°
VII
CH_3MgI
VIII
VII
VI
CH_3Li
CH_3MgI
IX
XI
X
H_2O
$(CH_3)_2CO$
XIII
$(CH_3)_2CO$
XII
$(CH_3)_2CO$
$(CH_3)_2CO$
XIV
$(CH_3)_2CO$
$(CH_3)_2CO$
I
$CH_3C(ONa)=CH_2$
H_2O

shown as a reaction between the sodium salt of acetone and the metal atoms of the adduct, stilbene thus being regenerated. If one does not care to account for the sodium salt of acetone in this way, the formation of pinacol may be considered to be a direct reaction of alkali metal (regenerated from the adduct) with acetone.

We do not believe that the addition reactions which we have reported represent the ultimate that can be accomplished with the arylated alkene-alkali metal adducts. However more must be known about the mechanism of reaction before optimum use can be made of it. We have obtained some information concerning the role of the solvent by studies which have been carried out in optically active 2,3-dimethoxybutane. This enantiomer has recently been shown (14) to induce activity in the products of Grignard reactions in which it is the solvent.

The formation of the stilbene-disodium or dilithium adduct in *dextro*-2,3-dimethoxybutane is one-third as rapid as in 1,2-dimethoxyethane. Addition of this solution to an excess of Dry Ice yields a mixture of the diastereomeric diphenylsuccinic acids which are separated by the difference in solubility of their barium salts. The resolvable acid thus obtained melts poorly, as one might expect if it predominated in one of the two enantiomers, since *dd,ll*-diphenylsuccinic acid is a racemic compound. The specific rotation of this product is $[\alpha]_D^{23} = 23.7°$ (4% solution in acetone). Its x-ray diffraction powder pattern shows spacings characteristic of both *dd*- and *dd,ll*-diphenylsuccinic acid. Finally in another experiment the acid has been converted to its dimethyl ester with diazomethane; although this ester has been purified several times by crystallization, it still retains a specific rotation of +5° (in chloroform). It seems evident from these experiments that asymmetric synthesis has occurred to the extent of about 2–8% because of the enantiomeric solvent.

These results would imply that the solvent is involved in the structure of the stilbene-alkali metal adduct, and such may be the case. However the situation is not simple, since either stilbene-disodium or -dilithium adduct, prepared in *dextro*-2,3-dimethoxybutane and treated with methyl sulfate, yields 2,3-diphenylbutane which is inactive. Likewise stilbene-dilithium adduct in *dextro*-2,3-dimethoxybutane reacts with acetone to give a 20% yield of *dd,ll*-2,5-dimethyl-3,4-diphenyl-2,5-hexanediol which is inactive. No significant conclusion can be drawn from these results. However it may be remarked that the only reaction (carbonation) which thus far has been found to give products predominating in *meso*-diastereomer is the one in which the resolvable diastereomer (obtained in small yield) is optically active.

The authors are grateful for a grant in aid from the Banting Research Foundation.

EXPERIMENTAL

Melting points have been corrected against reliable standards. X-ray powder diffraction patterns were determined with Cu K_α (Ni filtered) radiation and are reported in d spacings (Å) at relative intensitives $[I/I_1]$.

Formation of stilbene-alkali metal adducts. The preferred procedure for preparation of the adducts has been described earlier in this report. The formation of the adduct was followed by analysis of 1-ml. samples which were poured into an excess of Dry Ice. After evaporation of the solvent in an air stream, the residue was treated with 10 ml. of water.

The stilbene was filtered off and air-dried. The aqueous filtrate was acidified and the diphenylsuccinic acids were filtered off and vacuum-dried. Both products were weighed; the percent of stilbene which reacted equaled

$$\frac{\dfrac{\text{mg acid}}{270}}{\dfrac{\text{mg stilbene}}{180}+\dfrac{\text{mg acid}}{270}}\times 100$$

Reaction with magnesium chloride. A. With anhydrous magnesium chloride. When a stirred solution of 0.01 mole of stilbene-disodium adduct in 40 ml. of 1,2-dimethoxyethane was treated with 1.0 g. (0.01 mole) of anhydrous magnesium chloride (Aluminum Company of Canada), heat was evolved; within 3 hours after addition, only a slight yellow color remained. The suspension was poured into Dry Ice, allowed to warm to room temperature, and the solvent was then removed under 50 mm. pressure. The residue was extracted with 20 ml. of benzene. This extract yielded 1.7 g. of solid, m.p. 116–120°, which was crystallized from 17 ml. of ethanol. This stilbene, 1.4 g. (78%) melted at 122–124°. No diphenylsuccinic acid was found in the benzene-insoluble residue.

B. With magnesium chloride in presence of a butyl chloride Grignard reagent. When a solution of 0.022 mole of butyl chloride Grignard reagent in 30 ml. of tetrahydrofuran was added dropwise to 0.01 mole of stilbene-disodium adduct in 50 ml. of tetrahydrofuran, a heat effect was observed and decolorization was complete at the end of the addition period (10 minutes). The mixture was poured into an excess of Dry Ice and allowed to warm to room temperature. After removal of the solvent under 50 mm. pressure, the residue was shaken with 10 ml. of water and 20 ml. of benzene. The aqueous extract, after acidification, etherous extraction, and distillation, yielded 1.8 g. (80%) of pentanoic acid, b.p. 184–187°. The benzene solution yielded 1.6 g. (89%) of stilbene, m.p. 118–122°.

Reaction with triphenylchloromethane. A solution of 0.005 mole of stilbene-disodium adduct in 40 ml. of 1,2-dimethoxyethane was added dropwise to a stirred solution of 0.005 mole of triphenylchloromethane in 10 ml. of anhydrous benzene. The color of the cloudy mixture, which was yellow until addition was about half complete, changed gradually through orange into a deep red-brown. When no further color change occurred after 15 minutes, the suspension was poured into Dry Ice. When the mixture had warmed to room temperature and the solvent was removed under 50 mm. pressure, the residue was dissolved in 20 ml. of water and 30 ml. of benzene.

The aqueous solution upon acidification yielded 300 mg. of solid, m.p. 190–223°. This was dissolved in 50 ml. of 10% aqueous ammonia. The excess ammonia was boiled off; then 1.0 g. of barium hydroxide in 7 ml. of water was added, and gaseous carbon dioxide was added. The precipitate was filtered off and treated with 30 ml. of 10% hydrochloric acid. The insoluble portion was crystallized from 1 ml. of acetic acid. The triphenylacetic acid (5 mg., 0.3%, m.p. 268–271°) was identified by mixture melting point. The solution from which the insoluble barium salts were filtered was acidified to yield 250 mg. (18%) of diphenylsuccinic acid, m.p. 224–230°.

The benzene extract contained 1.8 g. of semisolid which was extracted with hot methanol to leave 100 mg. of solid. Crystallization from 1 ml. of carbon tetrachloride yielded 50 mg. of 1-triphenylmethyl-4-diphenylmethylbenzene, m.p. 223–224°. This was characterized by bromination (15). The methanolic extract was evaporated, dissolved in 85 ml. of petroleum ether (b.p. 60–70°), and added to an activated alumina chromatographic column (80–200 mesh, Aluminum Ore Co.). Elution with 265-ml., 765-ml., and 850-ml. portions of petroleum ether, then 850 ml. of benzene, and finally methanol gave the following substances, identified by mixture melting point: (a) 0.51 g. crystallized from 8.5 ml. of methanol, 0.36 g. (39.5%) of diphenylethane, m.p. 51–52°; (b) 0.17 g., m.p. 85–93°, crystallized from 8.5 ml. of methanol, 0.13 g. (10.5%) of triphenylmethane, m.p. 93–94°; (c) and (d), nothing; and (e) 0.34 g. crystallized from 4.5 ml. of methanol, 0.25 g. (28%) of stilbene, m.p. 122–124°.

3,4-Diphenylhexane. A solution of 3.1 g. (0.02 mole) of diethyl sulfate (purified by washing with sodium carbonate and distilling under a vacuum) in 10 ml. of 1,2-dimethoxyethane was added dropwise during 10 minutes to a solution of 0.01 mole of stilbene-disodium adduct in 40 ml. of dimethoxyethane. The decolorized solution was immediately evaporated under 50 mm. pressure and the residue was dissolved in 50 ml. of benzene. This solution was washed with ammonia to decompose excess ethyl sulfate, then dried with magnesium sulfate and evaporated. The residue (2.15 g.) was dissolved in 15 ml. of purified petroleum ether and was then treated with a slight excess of a 5% solution of bromine in carbon tetrachloride; some hydrogen bromide was evolved. Steam-distillation of the mixture with 400 ml. of water left 0.75 g. of residue, which was dissolved in hot petroleum ether (b.p. 80–90°). The 1,2-dibromo-1,2-diphenylethane which crystallized out weighed 0.68 g. (20%), m.p. 235–237°.

The steam-distillate was extracted with benzene. Evaporation of this solution left 1.15 g. of semisolid residue which was dissolved in 6 ml. of hot ethanol and cooled to 4°. The crystals (300 mg., m.p. 86–89°, 13%) were recrystallized from 1 ml. of ethanol; yield 250 mg., m.p. 91–92°. This was identified as the *meso*-diastereomer by nitration (6). The dinitro derivative was crystallized from 1 ml. of acetic acid to give 40 mg. (12%), m.p. 169–170° (12). Evaporation of the ethanolic solution from which the *meso*-diastereomer was filtered left 0.65 g. of oil which was converted to the hexabromo derivative of the *dd,ll*-diastereomer (12). Yield was 0.5 g. (26%), m.p. 213–215°.

3,4-Diphenyl-1,6-hexanediol. Decolorization was complete after the dropwise addition (15 minutes) of 0.9 g. (0.02 mole) of epoxyethane in 10 ml. of dimethoxyethane to a solution of 0.01 mole of stilbene-disodium adduct in 40 ml. of 1,2-dimethoxyethane.

A. meso-Diastereomer. After evaporation of the dimethoxyethane under 50 mm. pressure, the residue was dissolved in water and benzene. The benzene extract was evaporated and extracted with 170 ml. of hot petroleum ether (b.p. 90–100°) to leave 0.35 g., m.p. 145–150°. This was crystallized from 5 ml. of di-*n*-butyl ether yielding 0.25 g. (9%), m.p. 158–160°. After two more crystallizations it melted at 163–163.5°.

Anal. Calc'd for $C_{18}H_{22}O_2$: C, 79.9; H, 8.20.
Found: C, 80.1; H, 8.22.

This diastereomer also was obtained by treatment of dimethyl *meso*-3,4-diphenyladipate (11) (0.32 g., 0.001 mole) in 20 ml. of dimethoxyethane under nitrogen with a solution of 0.00185 mole of lithium aluminum hydride in 10 ml. of di-*n*-butyl ether. The mixture was refluxed for 15 minutes, then cooled while 10 ml. each of wet ether and 30% aqueous sulfuric acid were added. The non-aqueous layer, dried over magnesium sulfate, was evaporated under 50 mm. The residue (0.24 g.) was crystallized twice from 4-ml. portions of di-*n*-butyl ether. The product (0.18 g., 67%) melted at 162.5–163.3°; this melting point was not lowered by admixture with the product obtained from the stilbene-disodium adduct.

B. dd,ll-Diastereomer. The petroleum ether solution from which the *meso*-isomer was originally isolated was evaporated and the residue redissolved in 10 ml. of hot methanol. When cooled to 4°, this solution gradually precipitated 0.74 g. (41%) of solid, which was crystallized from 7.5 ml. of methanol to yield 0.6 g. (33%) of stilbene, m.p. 120–122°. The methanolic mother liquors were evaporated, and the residue crystallized from 30 ml. of petroleum ether (b.p. 90–100°) to give 0.96 g. of *dd,ll*-diastereomer, m.p. 101–103°. This product was thrice crystallized, m.p. 103.6–104.7°.

Anal. Calc'd for $C_{18}H_{22}O_2$: C, 79.9; H, 8.20.
Found: C, 79.8; H, 8.30.

Alternatively this diastereomer was prepared by reduction of 0.32 g. (0.001 mole) of *dd,ll*-dimethyl 3,4-diphenyladipate (10) according to the procedure described above for the *meso*-isomer. The crude product weighed 0.25 g., m.p. 98–101°. This was twice crystallized from 5 ml. of benzene-petroleum ether mixture (1:1), 0.17 g. (63%), m.p. 102–103°. A mixture melting point with the product from the stilbene-disodium adduct was not lowered.

2,3-Diphenyl-1,4-butanediol. Decolorization was complete within 1 hour after 0.01 mole of stilbene-disodium adduct in 40 ml. of 1,2-dimethoxyethane was added to a stirred suspension of 1.0 g. (0.03 mole) of polyoxymethylene (Kahlbaum, sublimation 165°) in 10 ml. of dimethoxyethane. After evaporation of the solvent under 50 mm. pressure, the residue was dissolved in water and benzene. Evaporation of the benzene solution left 2.1 g. of semisolid. This crude product was extracted with 20 ml. of hot petroleum ether (b.p. 90–100°). Evaporation of the extract left 0.8 g. of impure stilbene which was crystallized from 8 ml. of methanol yielding 0.65 g. (35%), m.p. 121–123°.

A. meso-Diastereomer. The dark, oily residue remaining after stilbene was extracted by petroleum ether was dissolved in 2 ml. of acetic acid. After a week at 4° the precipitate (0.11 g., 5%) was collected and crystallized thrice from 20-ml. portions of boiling water; m.p. 137.5–138.5°.

Anal. Calc'd for $C_{16}H_{18}O_2$: C, 79.3; H, 7.49.
Found: C, 79.2; H, 7.65.

This diastereomer also was prepared by reduction of 0.298 g. (0.001 mole) of *meso*-dimethyl diphenylsuccinate in 20 ml. of dimethoxyethane by the procedure described above. The crude product (0.16 g., m.p. 125–133°) was crystallized from 1 ml. of benzene, yield 80 mg. (33%), m.p. 137–138°. A mixture melting point was not depressed.

B. dd,ll-Diastereomer. The acetic acid solution from which the *meso*-isomer was isolated was distilled, finally at 2 mm., to yield 1.2 g. (50%) of an oil, b.p. 150–160°. This diastereomer was not purified rigorously for analysis, but was characterized by oxidation.

A solution of 200 mg. of the oil in 1 ml. of acetic acid was added dropwise to 1 ml. of cold 50 vol.-% aqueous sulfuric acid. To this cooled and stirred emulsion was added 0.5 g. of sodium dichromate in 2 ml. of water. The reaction mixture was then diluted with 15 ml. of ice-water and was extracted with ether. An alkaline extract of the ether solution was washed twice with ether, boiled, cooled, and acidified with dilute hydrochloric acid. The precipitate (65 mg.) was crystallized from 20 ml. of boiling water; 55 mg. (25%) of *dd,ll*-diphenylsuccinic acid, m.p. 170–210°, was obtained. This acid was characterized by 4 hours' reflux in 10 ml. of methanol containing 2 drops of concentrated sulfuric acid. The mixture was poured into cold sodium bicarbonate. The *dd,ll*-dimethyl diphenylsuccinate obtained in this way was crystallized from 2 ml. of benzene, giving 45 mg. (74%) m.p. 175–176°, which was identified by mixture melting point with an authentic sample.

dd,ll-2,5-Dimethyl-3,4-diphenyl-2,5-hexanediol. After addition of 0.143 mole of methyl iodide Grignard reagent in 10 ml. of ether to 4.4 g. (0.0147 mole) of *dd,ll*-dimethyl diphenylsuccinate in 90 ml. of benzene, the mixture was refluxed under nitrogen for 16 hours. Hydrolysis was accomplished with cold aqueous ammonium chloride; the benzene extract was evaporated and the residue crystallized from 75 ml. of benzene, then from 30 ml. of methanol. The *dd,-ll*-diastereomer (2.1 g., 48%) melted at 204–204.5° after recrystallization from methanol.

Anal. Calc'd for $C_{20}H_{26}O_2$: C, 80.5; H, 8.72.
Found: C, 80.4; H, 8.62.

This compound was converted in 40% yield into 2,2,5,5-tetramethyl-3,4-diphenyltetrahydrofuran by stirring for 4 hours in 70% sulfuric acid at 70°. A mixture melting point proved it to be identical with the compound reported previously (13).

meso-2,5-Dimethyl-3,4-diphenyl-2,5-hexanediol. When *meso*-dimethyl diphenylsuccinate in benzene was refluxed with methyl iodide Grignard reagent for 12 hours, the meagre amount of product could be separated into a 5% yield of *dd,ll-* and a 1% yield of material corresponding in melting point to *meso*-dimethyldiphenylhexandiol. Since the Grignard reagent was evidently causing isomerization, we used methyllithium instead.

A solution of 2.4 g. (0.0075 mole) of *meso*-diethyl diphenylsuccinate in 50 ml. of 1,2-dimethoxyethane was added dropwise during 1 hour to a cooled clear solution of methyllithium prepared from 0.84 g. (0.12 atom) of lithium and 8.5 g. (0.06 mole) of methyl iodide in 40 ml. of ether. An oil precipitated which crystallized within 15 minutes. After stirring the red mixture under reflux for 1 hour, it was poured into a cold ammonium chloride solution. The etherous layer was washed and then evaporated in an air stream. Extraction of the oily residue with 30 ml. of hot petroleum ether (b.p. 60–70°) caused it to crystallize.

Recrystallization from 5 ml. of methanol gave 0.72 g. (32%), m.p. 113–114.5°. Two more crystallizations from methanol raised this to 114.2–114.8°.

Anal. Calc'd for $C_{20}H_{26}O_2$: C, 80.5; H, 8.72.
Found: C, 80.3; H, 8.58.

Acetone with stilbene-alkali metal adducts. In a typical reaction, a solution of 0.01 mole of stilbene-disodium or -dilithium adduct in 40 ml. of dimethoxyethane was added dropwise to a cooled, stirred solution of 5 ml. of acetone (0.07 mole) in 10 ml. of dimethoxyethane. Decolorization was immediate, even at −70°. The solvent was evaporated under 50 mm., and the residue was dissolved in water and benzene. Evaporation of the benzene solution left a glassy red residue which was dissolved in 5 ml. of hot methanol. Cooling of the methanolic solution gave a product which was crystallized from 5 ml. of benzene giving 0.15 g. (5%), m.p. 200–202°. After purification, this was found to be identical by mixture melting point with *dd,ll*-2,5-dimethyl-3,4-diphenyl-2,5-hexanediol.

The methanolic solution from which this *dd,ll*-diastereomer was separated was evaporated, and the residue was dissolved in 10 ml. of hot benzene. When this benzene solution was cooled and treated with 2 drops of water, 100 mg. of pinacol hydrate, m.p. 46–47°, separated. It was identified by mixture melting point.

The benzene solution from which the pinacol hydrate was separated was evaporated, then dissolved in 5 ml. of hot petroleum ether (b.p. 60–70°). After 1 week at 4° this solution precipitated 0.7 g., m.p. 56–65°. After 3 crystallizations from 4-ml. portions of petroleum ether, this 2-methyl-3,4-diphenyl-2-butanol (0.61 g., 25%) melted at 70–71°. A mixture melting point with an authentic sample (16) was not lowered.

When the petroleum ether solution from which the methyldiphenylbutanol was separated was seeded with stilbene, 0.22 g. of this substance, m.p. 116–119°, separated out. The petroleum ether was then evaporated, and the residue steam-distilled with 300 ml. of water. An etherous extract of the steam-distillate, evaporated and the residue crystallized from 1 ml. of methanol, yielded 0.55 g. (30%) of 1,2-diphenylethane, m.p. 49–51°.

When this experiment was repeated with *dextro*-2,3-dimethoxybutane, $[\alpha]_D^{20}$ −3.72°, as the solvent, the diol, m.p. 203–204°, was optically inactive in dimethylformamide solution (0.1 g. dil. to 2.0 ml.).

Sodium benzophenone ketyl. A blue color was produced immediately when 0.01 mole of stilbene-disodium adduct in 40 ml. of dimethoxyethane was added slowly to 3.7 g. (0.02 mole) of benzophenone in 10 ml. of dimethoxyethane. After no change occurred in 150 minutes, the solution was poured into an excess of Dry Ice. Processing in the usual manner yielded 2 g., m.p. 145–147°, which was crystallized from water giving 1.9 g. (41%), m.p. 148–149°, identified as benzilic acid by mixture melting point.

The alkali-insoluble reaction products weighed 3.2 g., from which 1.2 g. (66%) of stilbene, m.p. 122–124°, could be separated by cooling a hot methanol solution (17 ml.). The methanolic filtrate was diluted to 40 ml. with ethanol and 2 g. of hydroxylamine hydrochloride and 8 g. of potassium hydroxide were added. After 4 hours' reflux this mixture was poured into water. Filtration removed 0.2 g. (11%) more stilbene, m.p. 117–120°. Neutralization of the filtrate to *p*H 6 precipitated 1.6 g. (40%) of benzophenone oxime, m.p. 142–144°.

Repetition of this procedure with 0.01 mole of benzophenone gave a solution at first blue, then purple. After carbonation the mixture yielded benzilic acid (85%), benzophenone oxime (5%), and stilbene (85%), but no diphenylsuccinic acid.

2,2,6,6-Tetramethylcyclohexanone and stilbene-dilithium adduct. A solution of 0.01 mole of stilbene-dilithium adduct and 3.0 g. (0.02 mole) of tetramethylcyclohexanone in 50 ml. of dimethoxyethane was heated to 60° for 3 hours, then poured into Dry Ice. Processing in the usual manner yielded 2.2 g. (82%) of diphenylsuccinic acid, m.p. 218–223°, and 2.3 g. (77%) of tetramethylcyclohexanone, b.p. 180–184°. This ketone was identified as its oxime, m.p. 148–149° (17).

2,4,6-Triphenyl-s-triazine. A solution of 0.01 mole of stilbene-disodium adduct in 40 ml. of 1,2-dimethoxyethane was added dropwise to a cooled and stirred solution of 2.3 g. (0.022 mole) of benzonitrile in 10 ml. of dimethoxyethane. The first few drops of the adduct were decolorized; further addition caused the mixture to turn deep red. Since no further color change occurred after 30 minutes more, the mixture was poured into excess Dry Ice. When the latter had evaporated, the solvent was removed under 50 mm. pressure and the residue was dissolved in benzene and water. Filtration of this extractant mixture yielded 0.7 g. of crude 2,4,6-triphenyl-*s*-triazine. This was twice crystallized from 5-ml. portions of acetic acid, 0.4 g., m.p. 230–232°, identified by mixture melting point with the substance obtained from sodium metal and benzonitrile (18).

No solid acid precipitated when the aqueous extract was acidified. The benzene extract was evaporated to leave a residue which was dissolved in 10 ml. of hot methanol. This solution precipitated 0.9 g. (50%) of stilbene, m.p. 117–120°, when it was chilled to 4°.

Dilution of the methanolic filtrate with water yielded 0.8 g. of crude triphenyltriazine, which was crystallized from 5 ml. of acetic acid, 0.6 g., m.p. 230–232°. Total yield of triazine was therefore 50% of theoretical.

1,3,5-Triphenyl-s-triazine-2,4,6-trione. When a solution of 2.4 g. (0.02 mole) of phenyl isocyanate was added dropwise to a stirred solution of 0.01 mole of stilbene-disodium adduct in 40 ml. of dimethoxyethane, the mixture turned brown and cloudy. The solvent was evaporated under a vacuum and the residue extracted with 20 ml. of benzene and 10 ml. of water. The solid (1.3 g.) which remained was crystallized from 5 ml. of acetic acid to give 0.9 g. of *sym*-triphenyltriazintrione, m.p. 280–281°. This was identified by mixture melting point (19). The dried benzene extract yielded 1.4 g. (58%) of triphenyltriazinetrione by development in a chromatographic alumina column with benzene.

2,3-Diphenylbutane from reaction in dextro-2,3-dimethoxybutane. The solvent was prepared and purified according to the previous description (14), $[\alpha]_D^{20}$ +3.72°. Decolorization was complete within 5 minutes after the addition of a solution of 0.63 g. (0.005 mole) of pure methyl sulfate in the dimethoxybutane to 0.01 mole of stilbene-disodium adduct in 40 ml. of this solvent. Following distillation of the solvent under 50 mm. pressure, the residue was dissolved in 10 ml. of carbon tetrachloride. This solution was washed with ammonia, dried, and then treated with 5% bromine in carbon tetrachloride until a bromine excess persisted. The solution was steam-distilled, and the non-aqueous phase in the distillate was evaporated. The solid *meso*-diphenylbutane was filtered off; the liquid phase dissolved in toluene showed no optical activity.

This preparation was repeated on a larger scale with addition of 4 times the equivalent amount of methyl sulfate at −50°. The liquid isomer, which was thoroughly separated, b.p. 130–133° (5 mm.), was likewise entirely optically inactive.

sym-Diphenylsuccinic acid from dextro 2,3-dimethoxybutane. A mixture of 18 g. (0.1 mole) of stilbene, 6.94 g. (1 atom) of lithium, and 300 ml. of *dextro*-2,3-dimethoxybutane was stirred for 8 hours under nitrogen, and then decanted into an excess of Dry Ice. This mixture was allowed to warm to room temperature (4 hours), and the solvent was evaporated under 20 mm. pressure. The residue was treated with dilute hydrochloric acid to dissolve the lithium carbonate. The mixture was then made alkaline and extracted with benzene. The evaporated benzene solution yielded 3.41 g., m.p. 95–106°, from which 2.29 g. (12%) of stilbene, m.p. 122°, was obtained by crystallization from ethanol.

The aqueous solution was acidified to yield 23.7 g. (88%) of diphenylsuccinic acids, m.p. 211–237°. This precipitate was dissolved in ammonia, the excess boiled off, and 1060 ml. of saturated aqueous barium hydroxide solution was added. This solution was saturated with carbon dioxide and the cake was filtered off. The filtrate was evaporated to dryness and extracted with acetone. The cake was decomposed with hydrochloric acid and the impure *meso*-diphenylsuccinic acid, m.p. 213–215°, was filtered off, 17.1 g. The filtrate was evaporated to dryness and extracted with acetone. The two acetone solutions were evaporated and the residue was extracted with 5 ml. of boiling benzene. The benzene-insoluble residue weighed 1 g. It was dissolved in 60 ml. of 1% alkali, heated with Darco (charcoal), filtered, and acidified to *p*H 1. This suspension was heated until solution was almost complete, filtered, and cooled to yield 0.4 g. of diphenylsuccinic acid melting at 161–162° with resolidification at 172–178° and remelting at 211–214°. A 5% solution of acetone gave a rotation $[\alpha]_D^{23}$ +23.7°. The x-ray powder diffraction pattern of this product showed lines characteristic of both the enantiomeric acid and the *dd,ll*-racemic compound. The intensities of the spacings for the authentic enantiomer are: [10] 5.06; [8] 5.64, 3.89; [6] 4.29; [3] 8.04; [2] 3.601; [1] 7.25, 5.40, 4.46, 2.386, 3.173, 3.035, 2.540, 2.285. The intensities of the spacings for the authentic racemic compound are: [10] 5.47; [8] 4.62, 3.85; [6] 3.40; [4] 3.17; [3] 2.94, 2.569, 2.492; [2] 4.27, 2.696; [1] 7.62, 6.80, 4.41, 3.98, 2.855, 2.402, 2.313, 2.274, 2.210, 2.111, 2.056, 1.924.

It should be appreciated that the difficulties involved in separation of the *meso-* from the *dd,ll-* and the *dd*-acid bring into question the significance of the observed rotation as a measure of the amount of asymmetric induction which has occurred. In another experiment, which was practically identical except that carbonation was effected with gaseous carbon dioxide, the resolvable diphenylsuccinic acid, 1.2 g., m.p. 165–200°, was converted to the dimethyl ester by reflux in 50 ml. of methanol containing 1 ml. of concentrated sulfuric acid. The ester (1 g., m.p. 165–170°) which was obtained by drowning in aqueous sodium carbonate was twice crystallized from 5 ml. of benzene, 400 mg., melting chiefly at 175–176°. A 10% solution in chloroform gave a *dextro* rotation $[\alpha]_D^{20}$ 5.4° ± 0.5°.

Biphenyl-disodium adduct. Formation of the adduct was complete in several hours when 1.56 g. (0.01 mole) of biphenyl and 1 g. (0.04 atom) of sodium were shaken in 1,2-dimethoxyethane. The solution was poured into Dry Ice; water was added after the carbon dioxide had evaporated. The filtered alkaline solution was acidified and the phenyldicarboxycyclohexadiene was filtered off, 0.75 g. (30%), m.p. 260–262°. This acid after crystallization from acetic acid melted at 270–272° (inserted 10° below m.p.). When 0.3 g. (0.0012 mole) of this acid was heated at 100° with 1 g. (0.025 mole) of potassium ferricyanide in 10 ml. of water for 4 hours, the precipitate (0.1 g.), m.p. 68–70°, was shown by mixture melting point to be biphenyl.

An intimate mixture of 0.1 g. (0.0004 mole) of the dicarboxylic acid with 0.03 g. of sulfur was heated to 220° until evolution of hydrogen sulfide ceased. The cooled mixture was extracted with 10 ml. of boiling xylene. Evaporation of the xylene under 20 mm. pressure left a residue which was crystallized from 2 ml. of acetic acid with Norit; 50 mg. (61%) of *p*-phenylbenzoic acid, m.p. 219–222°, was precipitated. Neut. equiv.: calc'd, 198; found, 190. The acid was converted to its amide, m.p. 221–223°.

2,2,3,3-Tetramethyl-1,4-diphenyladipic acid. A solution of 1.32 g. (0.01 mole) of 1-phenyl-2-methylpropene in 30 ml. of 1,2-dimethoxyethane was shaken with 0.46 g. (0.02 atom) of sodium for 36 hours. The solution was poured into Dry Ice and processed as usual to yield 0.75 g. (42%) of tetramethyldiphenyladipic acid, m.p. 225–232°. This was crystallized from 10 ml. of hot acetic acid, giving 0.6 g., m.p. 238–240°.

1,2-Diphenylcyclopropane with sodium. The diphenylcyclopropane was prepared from 9 g. (0.04 mole) of 2,4-diphenylpyrazoline, 5 g. (0.09 mole) of potassium hydroxide, and 1 g. of 5% platinized asbestos (20). The mixture was heated to 180° (5 mm.) and the distillate was condensed at −80°. This oil was dissolved in ether, washed with dilute hydrochloric acid, dried and distilled over sodium; 4 g. (48%), b.p. 168–170° (18 mm.). This product did not react with sodium in 1,2-dimethoxyethane during 24 hours.

SUMMARY

1. The stilbene-alkali metal adduct in 1,2-dimethoxyethane reacts with diethyl sulfate to give 13% of *meso-* and 26% of *dd,ll*-3,4-diphenylhexane.

2. The adduct in dimethoxyethane reacts with paraformaldehyde to give 5% *meso-* and 50% *dd,ll*-2,3-diphenyl-1,4-butanediol.

3. The adduct in dimethoxyethane reacts with epoxyethane to give 9% of *meso-* and 35% of *dd,ll*-3,4-diphenyl-1,6-hexanediol.

4. The adduct in dimethoxyethane reacts with acetone to give *dd,ll*-2,5-dimethyl-3,4-diphenyl-2,5-hexanediol, also 2-methyl-3,4-diphenyl-2-butanol to-

gether with pinacol, diphenylethane, and stilbene. The absence of the *meso*-diastereomer and the evidence for stepwise reaction indicate strong steric hindrance during this synthesis.

5. No addition occurs when the adduct is treated with 2,2,5,5-tetramethylcyclohexanone or benzophenone. The ketone is recovered in the first instance, and is converted to the ketyl in the second instance.

6. The solvent has been shown to partake in the structure of the adduct, since enantiomeric asymmetry can be induced by use of optically active 2,3-dimethoxybutane as the solvent.

7. It has been shown that the formation of the adducts as well as their ease of reaction is facilitated by the use of dimethoxyethane or tetrahydrofuran as the reaction media.

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