ALKYLATION OF THE MONO- AND DI-SODIUM ADDUCTS OF STILBENE

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This report is a continuation of the investigation into the reactions of the adducts obtained when alkali metals are treated with aryl-substituted alkenes (1). The alkene used in the present study is stilbene, the sodium adduct of which has been treated with triethyl phosphate and with alkyl halides in several reaction media.

Although tetrahydrofuran has been used successfully, the most common solvent employed in formation and reaction of the adduct has been 2,5-dioxahexane (1,2-dimethoxyethane) (1). Now it has been found that the rate of adduct formation in the latter solvent is closely comparable with the rate in 3,6-dioxaöctane. Thus a 50% yield of adduct is obtained in 20 minutes in the first of these diethers and in 23 minutes in the second, but 35 minutes is required when the stilbene-disodium adduct is prepared in 3,6,9-trioxaündecane. These yields are determined by carbonation.

Previously it has been assumed that these adducts were stable in the glycol ether solvents, but we now have found that slow ether-fission does occur. In order to accentuate this tendency the stilbene-disodium adduct is prepared at 100° in 3,6-dioxaöctane. Carbonation of an aliquot gives a 50% yield of *meso*-diphenyl-succinic acid after three minutes, while five minutes after the introduction of the sodium the yield is 74 mole-per cent. However this yield decreases to 37% after 15 minutes. After three hours at 100° there is no evidence of stilbene-disodium adduct, but 90% can be isolated as 1,2-diphenylethane (II). One may presume that this fission of the ether proceeds *via* an adduct-ether coördination compound such as I, although the possible participation of the R group must be

I   II
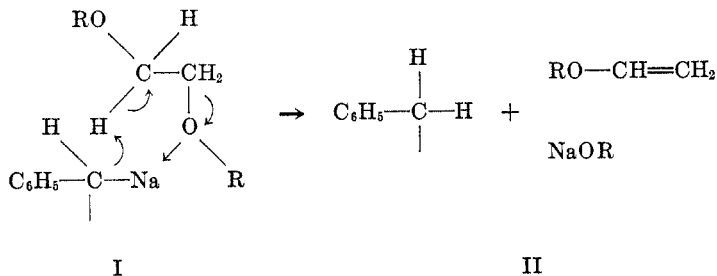
considered in all of these ethers except 2,5-dioxahexane. It is evident that useful reactions with the stilbene-disodium adduct must proceed at a rate that is somewhat faster than this ether-fission.

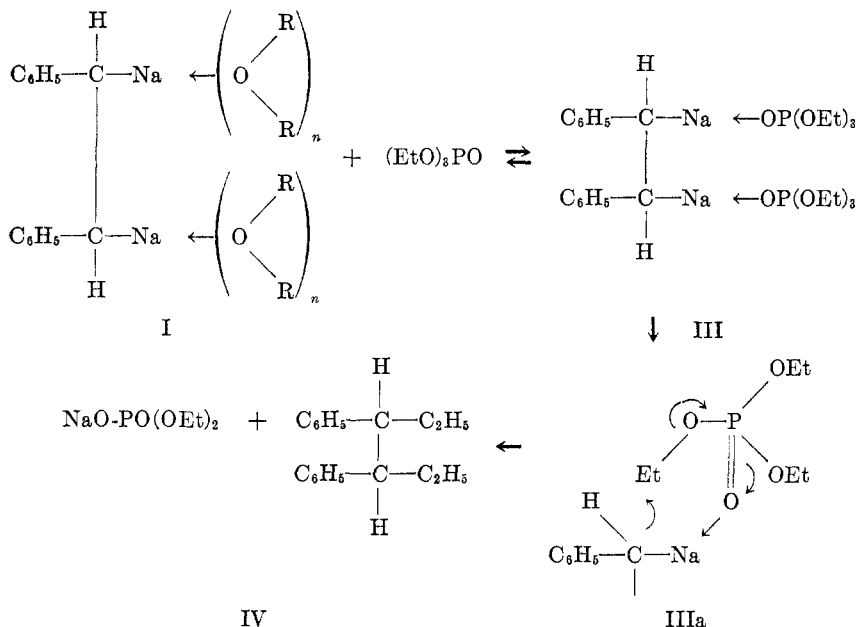The rate of useful reaction with the adduct in the several ethers has been

tested in terms of a new method of alkylation, alternative to that with dialkyl sulfates (1). Yields of 97, 93, and 81 mole-per cent, comprising the *meso* and *dd*, *ll* diastereomers of 3,4-diphenylhexane, can be obtained by treatment of the adduct with triethyl phosphate in 2,5-dioxahexane, 3,6-dioxaöctane, or 3,6,9-trioxaündecane respectively. The ratios of diastereomers (determined by separation in 80–90% recovery through activated alumina) from reactions in these ethers in the order named are *dd*, *ll* to *meso* of 1.5, 1.4, and 1.9. This effect of solvent on the diastereomeric ratios has been observed previously (2). Probably it is significant that the third of these media exerts an effect that is somewhat different from that of the two diethers.

Indeed this distinction among the media is found during examination of the reaction rates. When reaction of the adduct with triethyl phosphate in dioxahexane or dioxaöctane is allowed to proceed for three hours before the system is treated with carbon dioxide, the product contains no diphenylsuccinic acid. However the 4% yield of this acid, which is isolated from the reaction in trioxaündecane, shows firstly that addition of carbon dioxide to the adduct is more rapid than that of triethyl phosphate, and secondly that reaction in trioxaündecane is slower than that which occurs in the diethers. This sluggishness of reaction in the most complex ether, together with its greater tendency to be split by the adduct, is reflected in the yield of 90% which is obtained when the adduct in trioxaündecane is carbonated directly after an initial time of seven hours during which it is formed. Under comparable conditions the yields of diphenylsuccinic acid in the other two solvents are virtually quantitative.

We suggest that this difference may be attributed to the coördinative strength of the several ethers, since it has been shown (3) that the hydrogen-bonding capacity of trioxaündecane is greater than that of dioxahexane or dioxaöctane. We believe also that the difference in rate involves the coördinative strenth of triethyl phosphate which has been shown to have a hydrogen-bonding capacity that is comparable with the ethers (4). When this ester is added to the solution of stilbene-disodium adduct an appreciable evolution of heat is observed; the medium becomes more viscous and a colored precipitate is formed immediately. However carbonation of aliquots shows that the actual alkylation reaction is much slower and can, indeed, be followed by the gradual loss of color in the reaction system.

These phenomena may be explained as a displacement of the ether coördinated with the stilbene-disodium adduct by the phosphate, most easily with dioxahexane and dioxaöctane and more slowly with the more basic trioxaündecane. The conversion of the stilbene-disodium-phosphate complex (III) to 3,4-diphenylhexane (IV) is depicted as dependent on proximity of an alkyl group to the carbon at which it will eventually be attached (IIIa). In this sense the alkylation and the ether-fission are presumed to follow the same mechanism of reaction.

Since alkyl halides are less electron-donating than are esters, the absence of precipitation or increased viscosity when halides are added to the adduct solu-

$$C_6H_5\!-\!\overset{\overset{\displaystyle H}{|}}{C}\!-\!Na \quad \longleftarrow \left(O\!\!\begin{smallmatrix} \nearrow R \\ \\ \searrow R \end{smallmatrix}\right)_n$$

$$C_6H_5\!-\!\underset{\underset{\displaystyle H}{|}}{C}\!-\!Na \quad \longleftarrow \left(O\!\!\begin{smallmatrix} \nearrow R \\ \\ \searrow R \end{smallmatrix}\right)_n$$

$$+ \ (EtO)_3PO \ \rightleftarrows$$

$$C_6H_5\!-\!\overset{\overset{\displaystyle H}{|}}{C}\!-\!Na \quad \longleftarrow OP(OEt)_3$$

$$C_6H_5\!-\!\underset{\underset{\displaystyle H}{|}}{C}\!-\!Na \quad \longleftarrow OP(OEt)_3$$

I $\downarrow$ III

$$NaO\text{-}PO(OEt)_2 \ + \ C_6H_5\!-\!\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\underset{\displaystyle C_6H_5\!-\!C\!-\!C_2H_5}{C\!-\!C_2H_5}}} \quad \longleftarrow$$

IV   IIIa

tion is not surprizing. Nevertheless a variety of halides react with the stilbene-disodium adduct. These reactions are listed in Table I.

It may be seen in the Table that 1-chloropropane reacts smoothly with the adduct to give a good yield of the hitherto-unknown 4,5-diphenyloctanes. In view of the subsequent tabulated experiments the preparative method is considered to be presumptive evidence for these structures. The diastereomeric configuration is assigned on the basis of melting point, by analogy with the 2,3-diphenylbutanes and the 3,4-diphenylhexanes. All reactions with saturated halides give brilliant blue or red intermediate colors but few react so cleanly as does this normal halide.

Thus reaction of the stilbene-disodium adduct in dioxahexane with 2-chloropropane occurs with intermediate blue color and yields not only the diastereomeric 2,5-dimethyl-3,4-diphenylhexanes (VI, R = H), but also some stilbene as well as the monoalkylated product, 3-methyl-1,2-diphenylbutane (VII, R = H). The occurrence of the latter product indicates that the secondary alkyl group exerts a steric effect not observed with the primary halide. Since decolorization of the reaction system is relatively rapid (three to four hours), only slight ether-fission should have occurred. Consequently the appearance of the mono-alkylated product must be attributed to hydrogen transfer from the secondary alkyl group of the complex V, R = H.

We have in structure V (R = H) attributed the formation of the mono-alkylated derivative to obstruction of the alkylating group. Undoubtedly this factor is of primary importance. Thus when the tetraphenylethylene-disodium adduct is treated with 2-chloropropane the only isolable product conforms by analysis with the composition of 3-methyl-1,1,2,2-tetraphenylbutane. Furthermore the

TABLE I*

STILBENE-DISODIUM ADDUCT IN 2,5-DIOXAHEXANE WITH ORGANIC HALIDES AT −80°C.

HALIDE	REACTION TIME, min.	YIELD, DIALKYL-DIPHENYL-ETHANE, %		YIELD, MONO-ALKYLDI-PHENYL-ETHANE, %	RECOVERED STILBENE, %	YIELD, DIPHENYL-ETHANE, %
		meso	dd, ll			
1-Chloropropane	90	31	49			
2-Chloropropane	210	30	45	14	6	
2-Chloropropane[a]	210	29	34	14	15	
2-Chloropropane[b]	480	4	0	10		
2-Chloropropane[f]	—	19	26	38	18	
2-Bromopropane	240	17	24	5		
2-Chloro-2-methylpropane	1800	0	0	21	6	2
	720	0	0.25	25	10	5
2-Chloropropene	600	0	0		82	
1-Chloro-2-propene[c]	15	0	0		50	
Benzyl chloride	1	0	0		95	39
Dichloromethane[d]	90				55	
1,2-Dichloroethane	60				95	
1,3-Dichloropropane	150	86				
	150[e]	7	44		4	
1,4-Dichlorobutane	90	0	77		6	

[a] Stilbene-dilithium adduct; [b] Diethyl ether as reaction medium, unidentified oils; [c] Yielded 5% of $(C_{17}H_{17})_2$; [d] Unidentified oils; [e] 2 moles of adduct per mole of halide, then carbonated, yielded 32% diphenylsuccinic acid; [f] Carried out at +25°.

* The yields reported here take no account of oils found in the reaction products which thus far have been incapable of separation.

ratio of products obtained from stilbene-dilithium and 2-chloropropane are not widely different from those obtained from the disodium adduct. However the regeneration of stilbene from both adducts probably involves a polar influence of the secondary halide. The deleterious effect of the bromine atom in alkylation yield using 2-bromopropane may be interpreted similarly, though a search for
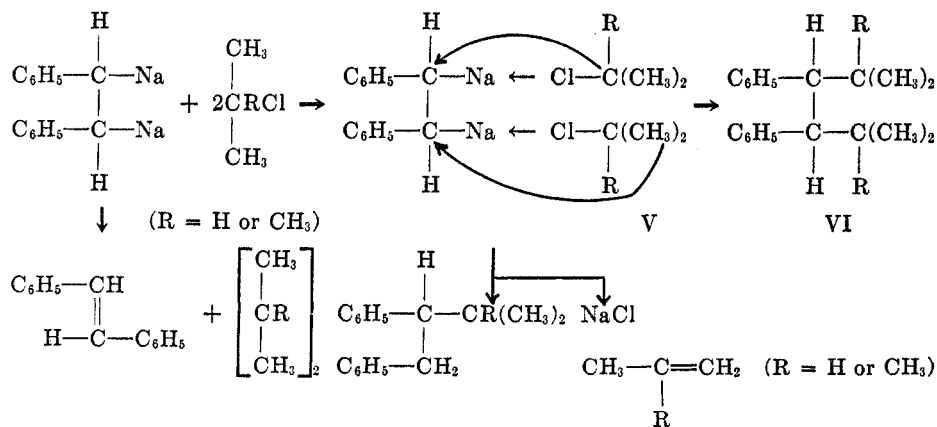

VII

stilbene was not made. Furthermore the very low yields obtained when diethyl ether rather than dioxahexane is used as the reaction medium point to the benefit of polarization in reactions of the adduct. Of course the reaction in diethyl ether suffers further from its heterogeneous nature. Parenthetically, it is quite obvious from our results that Schlenk's failure to alkylate the adduct with methyl iodide in diethyl ether may be attributed to an unfortunate choice of halide and reaction medium.

The effect of temperature on the reaction is notable. Most of the experiments with halides were effected at $-80°$. When 2-chloropropane is added to the adduct at $+25°$ the yield of the mono-alkylated product VII (R = H) is increased to 38 % at the expense of the yield of dialkylation products (VI, R = H). In one experiment at 25° wherein the adduct has been added to the halide during three days the low yield of diastereomers VI (R = H) is augmented by a 54% yield of VII, together with much 1,2-diphenylethane indicative of ether-fission.

The higher-melting form of our 2,5-dimethyl-3,4-diphenylhexane had previously been prepared by Conant and Blatt (5) by coupling of 2-methyl-1-phenylpropyl chloride Grignard reagent with cupric chloride. We consider this compound to be the *meso*-form and thus our lower-melting diastereomer is designated as the *dd, ll* form on the basis of its elemental analysis. We have established the identity of our mono-alkylation product by synthesizing this 3-methyl-1,2-diphenylethane (VII R = H) from 3-methyl-1,2-diphenylbutanol-2 (VIII) (6) and then reducing the mixture of alkenes (IXa and b) obtained by dehydration of this alcohol. The 3-methyl-1,2-diphenylethane thus formed has been compared with the product of adduct alkylation by conversion to the dinitro derivative (X).
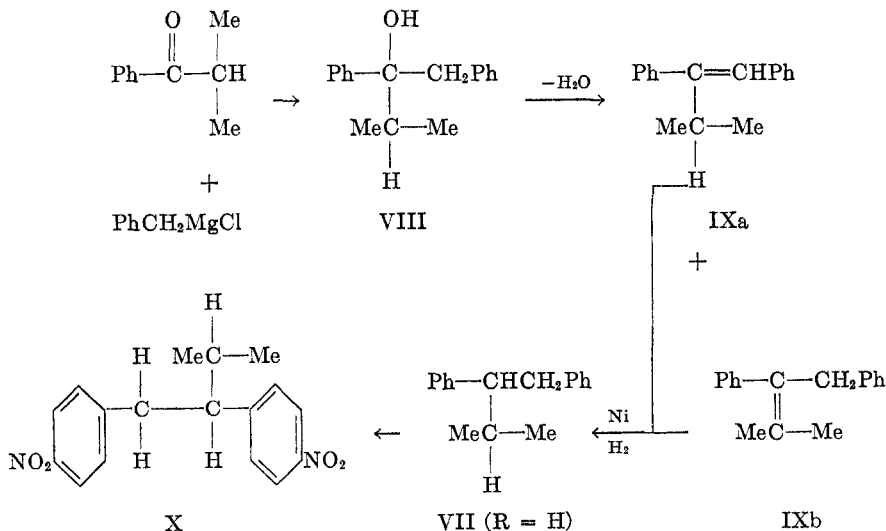
The behavior observed for the isopropyl halides is accentuated when 2-chloro-2-methylpropane is treated with the stilbene-disodium adduct. None of the expected dialkylated product, 2,2,5,5-tetramethyl-3,4-diphenylhexane (VI,
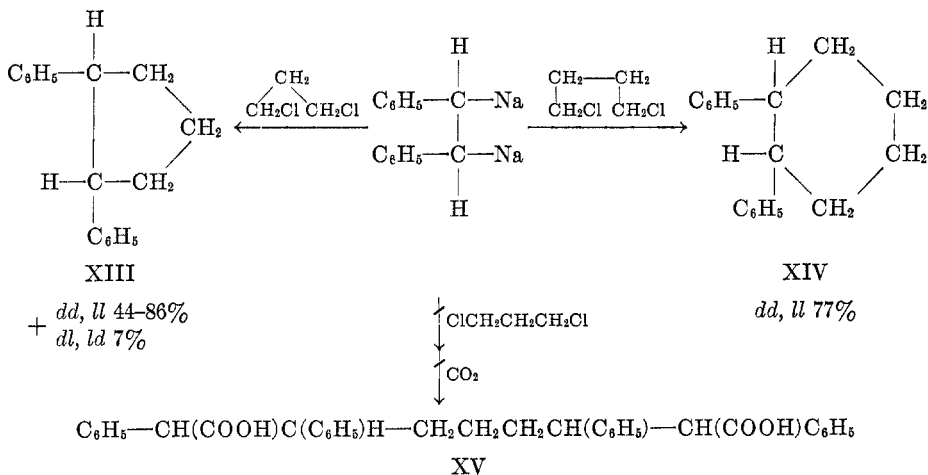
R = CH₃), is produced when equivalent amounts of reagents are used, and only a trace of a product of the empirical formula, $C_{22}H_{30}$, is isolable when a ten-fold excess of the halide is employed. If this substance is the dialkylated product, then it must be the *dd*, *ll* isomer since the known compound (5) possessing this structure has the higher melting point expected for the *meso* diastereomer.

The chief product from the adduct and 2-chloro-2-methylpropane is the mono-alkylation analog (VII, R = CH₃), the yield being essentially the same (20–25 %) whether two or 20 equivalents of the halide are used, and is appreciably greater than the yield of VII (R = H). This may be expected since the use of 2-chloro-propane involves less steric hindrance. The construction of scale models shows that considerable hindrance occurs between two *tert*-butyl groups attached to adjacent carbon atoms, although it is known that compounds containing such groups may be prepared (5, 7). Such preparations undoubtedly involve radical reactions. One might first presume that radicals are not involved significantly in the reaction between adduct and 2-chloro-2-methylpropane because almost none of the vicinal di-*tert*-butyl-substituted diphenylethane is formed. However this slow reaction does yield 2–5 % of diphenylethane (probably in consequence of ether-fission) and also stilbene. The abstraction of sodium from the adduct to form stilbene indicates that coupling of the radicals of two halide molecules has occurred. However the following information shows that the mechanism of such coupling may be intricate.
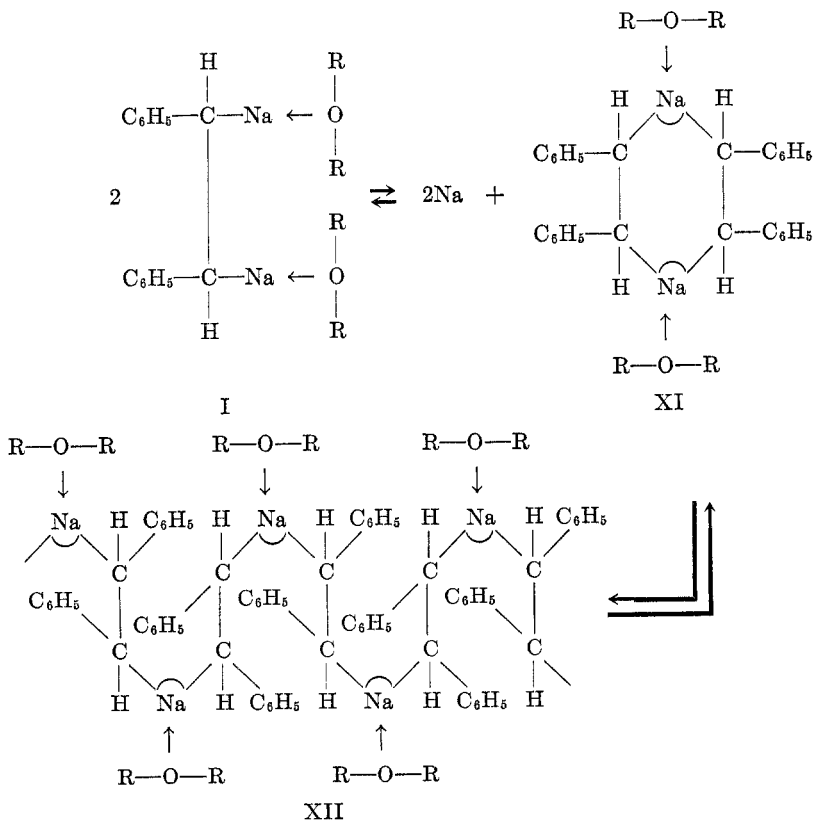
This coupling reaction with halides and the adduct to form stilbene was first reported by Bergmann and Schlenk (8), ethane being produced from methyl iodide and biphenyl from bromobenzene. The wide difference in reactivity of these halides cannot be correlated with a simple mechanism describing their reaction. The tendency for 2-chloro-2-methylpropane to undergo the coupling reaction (10 % as recovered stilbene) is accentuated in the case of the highly-polar benzyl chloride, which reacts almost instantaneously and quantitatively in this sense. Likewise 50 % of the stilbene in the adduct is regenerated by reaction with 1-chloro-2-propene. In this instance the remaining oils may represent alkylation, since we have been able to isolate but not identify a small fraction with an empirical formula corresponding with that of 4,5-diphenyl-1,7-octadiene.

Not only do these reactive halides couple by abstraction of sodium from the adduct, but this reaction occurs also with relatively unreactive halides. However this coupling reaction is much slower. Thus 2-chloropropene requires 600 minutes to decolorize a dioxahexane solution of the adduct, but the only isolable product comprises 82 % of the stilbene in the adduct. Less definite is the reaction of dichloromethane, which regenerates 55 % of the stilbene from the adduct, the remainder of the reaction being an oil in which 1,2-diphenylcyclopropane could not be found. At present we can explain these reactions of unreactive halides only on the basis that they do not coördinate with the adducts but, instead, react with free atomic sodium in the reaction medium. The source of this free sodium will be discussed later in this report.

We have considered 1,2-dichloroethane in a separate category, since vicinal dihalides usually act as coupling reagents for organometallic compounds. Indeed

$$\text{XIII} \quad\xleftarrow{\underset{CH_2Cl\ CH_2Cl}{CH_2}}\quad \underset{\substack{C_6H_5-C-Na \\ | \\ C_6H_5-C-Na \\ |}}{\overset{\substack{H \\ |}}{}} \quad\xrightarrow{\underset{CH_2Cl\ CH_2Cl}{CH_2-CH_2}}\quad \text{XIV}$$

XIII

+ dd, ll 44–86%
+ dl, ld 7%

XIV dd, ll 77%

$$\downarrow \text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$$
$$\downarrow \text{CO}_2$$

$$C_6H_5-CH(COOH)C(C_6H_5)H-CH_2CH_2CH_2CH(C_6H_5)-CH(COOH)C_6H_5$$

XV

a 95 % regeneration of stilbene from the adduct is observed, and no 1,2-diphenyl-cyclobutane is detected. On the other hand 1,3-dichloropropane reacts smoothly with the adduct to give an 86% yield of the known dd, ll-1,2-diphenylcyclo-pentane (XIII) (9). The tendency toward this cyclization is so great that 1,2-

$$2 \quad\underset{\substack{C_6H_5-C-Na \\ | \\ H}}{\overset{\substack{H \\ |}}{}} \leftarrow \underset{\substack{R \\ | \\ O \\ | \\ R}}{\overset{\substack{R \\ | \\ O \\ | \\ R}}{}} \quad\rightleftarrows\quad 2Na \;+\; \text{XI}$$

I

XII

diphenylsuccinic acid and not 1,2,6,7-tetraphenylheptane-1,7-dicarboxylic acid (XV) is the product of carbonation when two equivalents of the adduct are treated with one of the dichloropropane. The yield of dd, ll-1,2-diphenylcyclopentane is only 44 % in this instance; however under these conditions a 7 % yield, probably the dl, ld diastereomer (10), can also be isolated.

A similar cycloalkylation occurs when the adduct is treated with 1,4-dichlorobutane. The 1,2-diphenylcyclohexane melts higher than that diastereomer reported by Parmerter (11), and therefore is probably the dd, ll diastereomer, whereas Parmerter's compound is the less symmetrical dl, ld isomer. Our yield of diphenylcyclohexane is slightly lower than that of the diphenylcyclopentane, and the regeneration of stilbene is slightly higher.

Early in this report a reasonable mechanism of ether-fission has been presented to explain monoalkylation, but it is not the only reaction by which the etherous medium is cleaved. This is evident if the stilbene-disodium adduct is allowed to age in 2,5-dioxahexane for eight days before treatment with carbon dioxide. The yield of diphenylsuccinic acid is thus reduced from quantitative to 42 % while 47 % of the adduct is converted to stilbene and diphenylethane. This result may be explained by the assumption that the stilbene-disodium adduct may lose atomic sodium to an acceptor, leaving a stilbene-monosodium adduct. The latter may be represented either as the dimer XI or the polymer XII. This monosodium

adduct is conceived as an internally stabilized radical wherein the linkage C   C represents 3-electron binding $(C:Na\cdot C \leftrightarrow C\cdot Na:C)$. The reaction of XI with 2,5-dioxahexane may then be represented as follows:
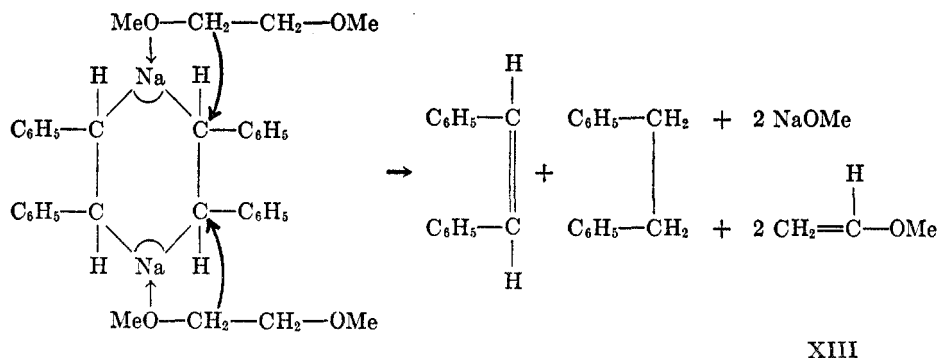

XIII

The sodium which is regenerated by conversion of di- to mono-sodium adduct must then react partially with regenerated stilbene, and partially with ethers such as methyl vinyl ether (XIII).

The concept of an alkene-monosodium adduct is not new. It has been shown by Scott, Walker, and Hansley (12) that naphthalene forms a 1:1 adduct with sodium which reacts with carbon dioxide to give equivalent amounts of naphthalene and dihydronaphthalene-dicarboxylic acids. Furthermore this adduct is stable only in the presence of a medium such as 2,5-dioxahexane. We believe that this adduct is similar to that depicted as (2 I ⇌ 2 Na + XI) except that the

equilibrium is well to the right of the equation expressing the naphthalene-sodium adduct and well to the left for the stilbene-sodium system.

It is a consequence of this hypothesis that addition of stilbene to the system comprising (2 I $\leftrightarrows$ 2 Na + XI) should shift the equilibrium to larger concentrations of the monosodium adduct XI. Such a change is exhibited in the color of the system. When stilbene-disodium in dioxahexane or, especially, in 3,6-dioxaöctane is viewed in thin layers its color is red, but addition of one equivalent of stilbene changes this color to green. Indeed this phenomenon is observed during the formation of the adduct, since the color of the sodium metal is initially red
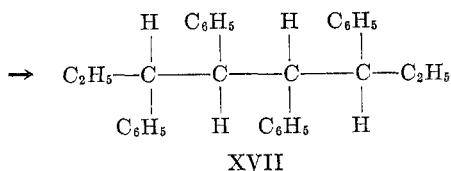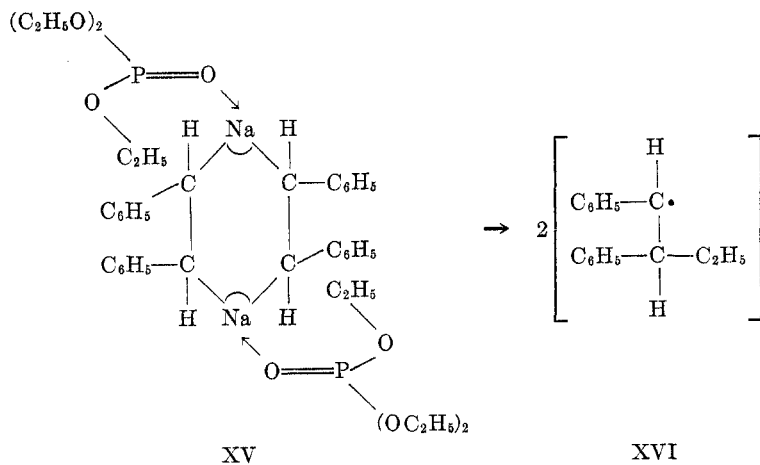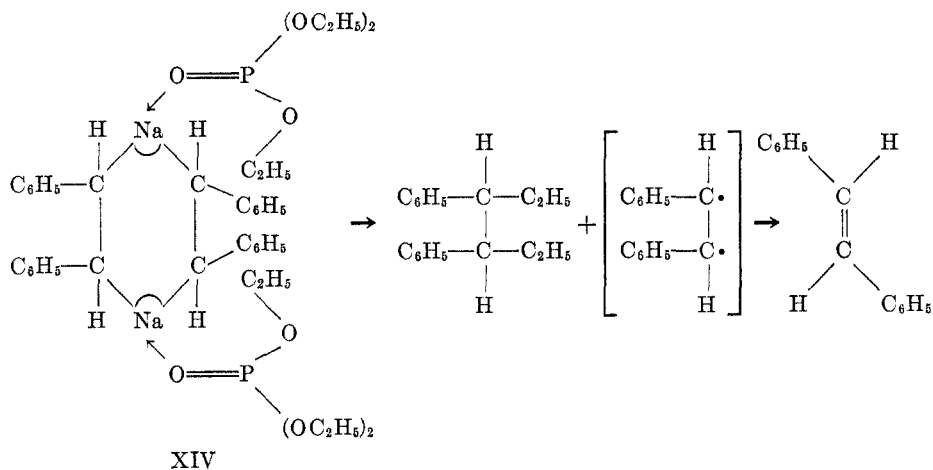
while the medium around it (containing excess stilbene) is initially green. Subsequently, after 50–55 % of the stilbene has reacted (according to yields obtained by carbonation of aliquots), the color of the medium becomes red. Dependence of the equilibrium on temperature is also observed qualitatively when sodium is heated with 2 mg. of stilbene in 4 ml. of didecyl ether under nitrogen. In this instance the medium never becomes colored, but the sodium surface is red at 120–140° and blue at 165–185°; this color change is entirely reversible during at least 20 cycles.

The reality of structures like XI or XII has been tested with substances like triethyl phosphate which we have shown to react normally with the stilbene-disodium adduct (I → IV). When the green solution from one mole of stilbene and one mole of stilbene-disodium adduct in 2,5-dioxahexane is treated with the ester it becomes blue and a precipitate forms. Subsequent processing gives low but equal yields of the two 3,4-diphenylhexanes as well as about the same yield of oil, half of which is a crystalline compound with molecular weight and analysis conforming with that of 3,4,5,6-tetraphenyloctane (XVII). The remainder of the oil is not amenable to separation into any of the other five diastereomers of XVII. The occurrence of these products may be explained in terms of the coördinative complexes, XIV and XV, resulting when dioxahexane is replaced by triethyl phosphate.

The formation of XVII implies a homolytic reaction involving a radical such as XVI. More definite evidence for intermediate radical formation is provided by treatment of the stilbene-monosodium adduct with 2-chloropropane. This halide, which alkylates the stilbene-disodium adduct to form dimethyldiphenyl-hexanes (VI, R = H) in 75 % yield and methyldiphenylbutane (VII, R = H) in
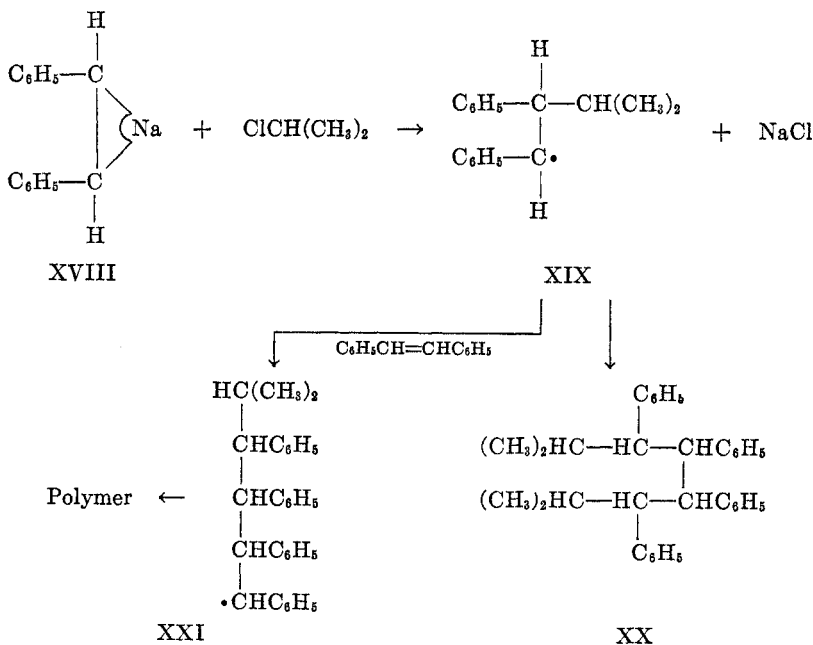
14% yield, gives only traces of these products when treated with the stilbene-monosodium adduct. Instead a complex product is obtained from which is obtained stilbene, a polymer probably containing isopropyl groups, and two compounds conforming in analysis and molecular weight with two diastereomers of the hitherto-unknown 2,7-dimethyl-3,4,5,6-tetraphenyloctane (XX).

The mode of formation of these products is expressed in the formulation. For convenience the stilbene-monosodium adduct is expressed as the monomer, XVIII, to which the sodium atom has contributed the odd electron. Reaction with 2-chloropropane leading to elimination of sodium chloride leaves the radical XIX, which undergoes dimerization to at least two diastereomers of XX. Alternatively the radical XIX may combine with stilbene to give a new, free, radical, XXI, which continues in this way toward formation of a polymer of a type reported previously (13).

Not expressed in the formulation is the meagre yield of the 2,5-dimethyl-3,4-diphenylhexanes. These may arise either from the mono- or from the small amount of stilbene-disodium adduct which is assumed to be in equilibrium with sodium and the stilbene-monosodium adduct. Assumption of this equilibrium provides an explanation for the tendency toward coupling which occurs with very reactive and also very inert organic halides. It is reasonable to postulate that active halides couple because of the atomic sodium which is involved in this equilibrium, rather than that these halides react directly with the adduct. The unreactive halides like 2-chloropropene may be presumed also to react with the atomic sodium, reluctantly but completely because they are too inert to coördinate with either the mono- or di-sodium adduct. Between these extremes is to be found the useful reaction which may be carried out with either of the two adducts.

EXPERIMENTAL

All melting points have been corrected against reliable standards. The X-ray diffraction patterns (Cu K_α Ni-filtered radiation) are recorded as spacings in A at relative intensities $[I/I_1]$.

The stilbene-disodium adduct. A. *Preparation for synthesis.* The stilbene (1.80 g., 0.01 mole) was placed in a dry nitrogen-filled modified Schlenk tube (Figure 1). A rapid stream of nitrogen was passed through "a" and out the mouth of the tube while 40 ml. of 2,5-dioxahexane, 3,6-dioxaöctane, or 3,6,9-trioxaündecane and 0.92 g. (0.04 atom) of sodium were added through the mouth of the tube. It was then stoppered and all closures (lubricated with silicone grease) were taped into place. After mechanically shaking for five to ten hours the deeply-colored solution was drained through "b" from excess sodium either into the appropriate reagent or into a nitrogen-filled flask to which the reagent was then added. Yields of adduct were obtained by removal of an aliquot into excess Dry Ice under conditions by which air and moisture were excluded.

B. *Rate of formation.* A flame-dried 100-ml. three-necked flask was equipped with a gas-tight glass-chain constant-speed stirrer, thermometer, nitrogen inlet, and wide-bore stop-cock which acted as a sampling port through which a nitrogen-filled pipette could be inserted. *trans*-Stilbene (1.8 g., 0.01 mole) was introduced, the flask was swept with nitrogen, and 40 ml. of a diether was added and stirred. When solution was complete, a single block 6 × 6 × 20 mm. of sodium was added. Reaction commenced at once and no temperature increase was observed. Aliquots (2 ml.) were withdrawn into 20 g. of water-free Dry Ice.
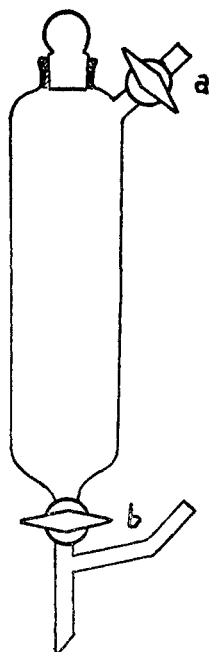
FIGURE 1

TABLE II

COLOR CHANGES AND YIELDS *versus* TIME

ETHER	COLOR CHANGE, min.	PERCENT YIELD AFTER REACTION TIMES, MIN.										
		15	25	30	45	50	60	65	90	100	120	345
Dioxahexane..................	20		56			84					98	
Dioxaöctane..................	25	36		59	76		85			97		
Trioxaündecane..............	35	26		42	60			72	80		86	89

Water (20 ml.) was added when the aliquot system reached 20°. The precipitated stilbene was filtered off, vacuum-dried, and weighed. The filtrate was acidified with 2 ml. of concentrated hydrochloric acid, digested at 90–100° for 30 minutes, then cooled, filtered, dried one hour at 85°, and weighed. Balanced yields and color change from green to red are recorded in Table II with respect to time. In all cases the diphenylsuccinic acid (upon which the yield was chiefly based) melted at 243–252°, but the melting point of the recovered stilbene decreased from 117–122° to 83–101° with increasing time of reaction.

Reaction of stilbene-disodium adduct with ethers. A. *With 2,5-dioxahexane.* A solution of 0.01 mole of adduct in 40 ml. of this ether was aged eight days at 25°, then treated with gaseous carbon dioxide. After evaporation of solvent and addition of 30 ml. each of water and diethyl ether, the aqueous layer was separated and acidified to yield 42% of the possible 2,3-diphenylsuccinic acid. The etherous phase was evaporated and steam-distilled. The first 100 ml. of distillate contained 0.40 g. (22%) of pure 1,2-diphenylethane. The residue, crystallized from ethanol, yielded 25% of impure stilbene, m.p. 113–118°.

B. *With 3,6-dioxaöctane.* A solution of 0.005 mole of adduct in 40 ml. of the ether was heated under pure nitrogen for three hours at 100°. The color changed from red to yellow-

TABLE III

Yields from Ethylation of Stilbene-Disodium with Triethyl Phosphate

| PRODUCT | YIELDS FROM THE REACTION MEDIUM: | | | | | |
| | Dioxahexane | | Dioxaöctane | | Trioxaundecane | |
	mg.	%	mg.	%	mg.	%
meso-3,4-Diphenylhexane............	721	30	825	35	545	23
dd,ll-3,4-Diphenylhexane............	1100	46	1174	49	1065	45
1,2-Diphenylethane................	46	2	122	7	165	9
Diphenylsuccinic acid..............	0	0	0	0	120	5
Total recovery....................		78		91		82

brown. Carbonation yielded no trace of diphenylsuccinic acid. Separation by methanol crystallization, followed by chromatographic elution of a petroleum ether (b.p. 60–70°) solution of the evaporated mother liquor on 20-mesh alumina (activated at 185° for two days), yielded 0.82 g. (90%) of 1,2-diphenylethane, m.p. 51–52°, identified as before by mixture melting point.

Reactions of triethyl phosphate. A. With stilbene-disodium adduct. A solution of 0.01 mole of adduct in 40 ml. of a diether was stirred under nitrogen while 2 g. (0.011 mole) of freshly-fractionated (b.p. 98° at 14 mm.) triethyl phosphate in 5 ml. of the ether was added during 25 minutes at 0 to +5°. The exothermic reaction was accompanied by increase in viscosity and the appearance of a precipitate. Thirty minutes later the reaction temperature was increased to 25° and maintained for three hours unless the color disappeared sooner. Dry gaseous carbon dioxide was then added, and the colorless system was diluted with water and extracted with diethyl ether. The aqueous phase was acidified to precipitate diphenyl-succinic acid.

The etherous phase was water-washed to remove poly-ethers (which would have been vacuum-evaporated originally in a purely preparative procedure) and the diethyl ether was evaporated. The residue, dissolved in the minimum of petroleum ether (b.p. 60–70°) was eluted by the same solvent from a column of Alcoa Activated Alumina, Grade F.20 (reactivated at 185° for two days). After fractional removal of the 3,4-diphenylhexanes the diphenylethane and stilbene were eluted in that order by use of 95:5 petroleum ether-methanol. The products were identified as described previously (1), but no stilbene was detected. The yields of these products are shown in Table III.

B. *With stilbene-monosodium adduct.* A solution of 0.005 mole of stilbene-disodium adduct in 40 ml. of dioxaöctane was treated with 0.005 mole (0.9 g.) of stilbene and then chilled and stirred while 2 g. (0.011 mole) of triethyl phosphate was added during 20 minutes at 0 to +5°. After 30 minutes more the temperature was raised to 25°. Seventy minutes later the system, now colorless, was processed as described in procedure A. Elution from the alumina column yielded 0.326 g. (14%) each of *meso-* and *dd,ll*-diphenylhexane, then 0.039 g. of the diphenylethane fraction. Further elution gave 0.481 g. of a fraction which yielded 0.274 g. (13%), m.p. 101–102°, after crystallization from methanol.

Anal. Calc'd for $C_{32}H_{34}$: C, 91.9; H, 8.14; Mol. wt. (Rast), 418.

Found: C, 91.7; H, 8.40; Mol. wt. (Rast), 419.

The final elution from the column (95:5 petroleum ether-methanol) yielded 0.904 g., from which was isolated 0.72 g. (40%) of stilbene, m.p. 122–123° (identified by mixture melting point), after crystallization from petroleum ether (b.p. 60–70°).

The eluted *meso*-diphenylhexane melted at 87–90°. A single crystallization raised this to 91–92° and its identity was proven by mixture melting point. The *dd,ll*-diphenylhexane was identified by its conversion to the hexabromo derivative (1).

The 4,5-diphenyloctanes. A solution of 1-chloropropane (1.73 g., 0.022 mole) in 5 ml. of dioxahexane was added during ten minutes to a solution of 0.01 mole of stilbene-disodium

adduct in 40 ml. of dioxahexane stirred under nitrogen at −80°. The system became deep blue in color, then after one hour it was colorless. The system was filtered and the filtrate was vacuum-evaporated. The residue (2.61 g., m.p. 85–90°) was crystallized from 15 ml. of absolute ethanol, 0.59 g. of *meso*-4,5-diphenyloctane, m.p. 95–97°. Distillation of the ethanolic filtrate, finally at 165–175° (10 mm.), gave an oil which deposited 0.21 g., m.p. 94.5–95.5°. Total yield of the *meso* diastereomer is thus 30% of theoretical. Two crystallizations from ethanol (20 ml./g.) gave a sample, m.p. 97.5–98°.

Anal. Calc'd for $C_{20}H_{26}$: C, 90.2; H, 9.84.

Found: C, 89.8; H, 10.0.

The oil remaining after separation of the *meso* diastereomer was redistilled, b.p. 160–165° (7 mm.), 1.09 g. (41%), n_D^{20} 1.5406. This *dd,ll*-4,5-diphenyloctane melted at about 0°.

Anal. Calc'd for $C_{20}H_{26}$: C, 90.2; H, 9.84.

Found: C, 90.0; H, 10.0.

3,3-Dimethyl-1,2-diphenylbutane. A solution of 2.04 g. (0.022 mole) of 2-chloro-2-methyl-propane in 3 ml. of 2,5-dioxahexane was added rapidly with stirring to 0.01 mole of stilbene-disodium adduct in 40 ml. of dioxahexane at −80°. After 15 minutes the temperature was increased to 25° and maintained until the intermediate blue color had entirely faded (30 hours). The system was then filtered and the solvent evaporated. The residue (2.56 g.) was adsorbed on a 1.5 × 20 cm. column of Alcoa activated alumina. Elution with petroleum ether (b.p. 40–60°) gave 50 ml. yielding 0.4 g. of unidentified oil, then 100 ml. yielding 0.49 g. (20.6%) of dimethyldiphenylbutane, m.p. 30–35°. After 50 ml. of further eluate (yielding 0.09 g. of unidentified oil), the next 75 ml. yielded 0.04 g. (2%) of 1,2-diphenylethane. Finally the column was stripped with 400 ml. of 98:2 petroleum ether-methanol to remove 0.11 g. (6.1%) of impure stilbene, m.p. 90–110°. The crude dimethyldiphenylbutane was purified by two low-temperature crystallizations with absolute ethanol (4 ml./g.), m.p. 36–37.5°.

Anal. Calc'd for $C_{18}H_{22}$: C, 90.7; H, 9.3.

Found: C, 90.6; H, 9.5.

When a ten-fold excess of the halide was added in an otherwise identical experiment the decolorization was complete in 12 hours. Identical processing gave 0.6 g. (25%) of dimethyldiphenylbutane (VII, R = CH₃), m.p. 34–37°, and 0.09 g. (5%) of 1,2-diphenylethane. When the crude VII was dissolved in 3 ml. of methanol a solid, m.p. 138–140°, wt. 0.008 g., separated. When crystallized from 1 ml. of ethanol it melted at 141–141.5°.

Anal. Calc'd for $C_{22}H_{30}$: C, 89.7; H, 10.3.

Found: C, 89.6; H, 10.3.

3-Methyl-1,1,2,2-tetraphenylbutane. A mixture of 0.005 mole (1.86 g.) of tetraphenyl-ethylene, m.p. 222–224°, and 0.46 g. (0.02 atom) of sodium in 40 ml. of 2,5-dioxahexane was shaken for 31 hours before aliquots added to Dry Ice showed by the amount of water-insoluble material that reaction was 87% complete. The dense slurry in the deep red solution was cooled to 0° and 1.57 g. (0.02 mole) of 2-chloropropane was added. After one day the system (faded to a permanent pale bluish-purple color) was filtered and evaporated. The residue (2.21 g.) was crystallized from 7 ml. of absolute ethanol, 0.29 g. (15.4%), m.p. 151–156°. Crystallization from acetic acid (6 ml./g.) raised this m.p. to 155.5–157.5°.

Anal. Calc'd for $C_{29}H_{28}$: C, 92.5; H, 7.5.

Found: C, 92.6; H, 7.6.

The evaporated filtrate from the ethanolic crystallization was crystallized from 10 ml. of petroleum ether, b.p. 40–60°, yielding 0.02 g. of crude 1,1,2,2-tetraphenylethane, m.p. 203–205°. A mixture melting point with an authentic sample (m.p. 209–211°) was not lowered.

The 1,2-diphenylcyclopentanes. The stilbene-disodium adduct (0.01 mole) was treated with 1,3-dichloropropane (0.022 mole) at −80°. The system assumed a distinct reddish color which faded in three hours. The system was then filtered and evaporated. The residue (2.60 g., m.p. 58–63°) was crystallized from 6 ml. of absolute ethanol (chilled to 0°), 1.90 g., m.p. 63–65° (86%) of *dd,ll*-1,2-diphenylcyclopentane.

In a second otherwise identical experiment, 0.56 g. (0.005 mole) of 1,3-dichloropropane

was added. After 15 minutes at −80° and five hours at +25° the system had not yet decolorized but was then treated with gaseous carbon dioxide. The bleached system was filtered to remove salts which, dissolved in water, ether-extracted, and acidified, yielded 0.85 g. (31%) of diphenylsuccinic acid.

The filtrate from the salts was vacuum-evaporated (30 mm.) and the residue, 1.28 g., m.p. 48–58°, was dissolved in 6.5 ml. of hot methanol. Upon cooling, 0.80 g. of dd,ll-1,2-diphenylcyclopentane, m.p. 63–65°, separated. The filtrate, evaporated, left a residue, m.p. 40–58°, which was adsorbed on a 1.5 × 34 cm. activated alumina column and eluted with petroleum ether (b.p. 40–60°). The first 50 ml. of eluate was evaporated, leaving 0.18 g. of dd,ll-1,2-diphenylcyclopentane (total, 44%), m.p. 61–62°. The next 75 ml. of eluate yielded 0.16 g. (7.2%) of meso-1,2-diphenylcyclopentane, m.p. 31–35°. The column, eluted with 300 ml. of 97:3 petroleum ether-methanol, finally yielded 0.07 g. (4%) of impure stilbene, m.p. 95–120°.

dd,ll-1,2-Diphenylcyclohexane. The stilbene-disodium adduct (0.01 mole) in 40 ml. of dioxahexane was treated with 0.022 mole of 1,4-dichlorobutane at −80°. The system became purple, then decolorized in 90 minutes. After filtration it was evaporated (30 mm.) and the oil was distilled, 2.01 g., b.p. 155–170° (7 mm.). This distillate, dissolved in 5 ml. of methanol and chilled to 0°, yielded 1.53 g., m.p. 49–52°. The filtrate was evaporated leaving 0.49 g. which was adsorbed on alumina. Elution of the 1.5 × 37 cm. column with 150 ml. of petroleum ether (b.p. 40–60°) removed 0.29 g., m.p. 49–51°, or a total of 77% of dd,ll-diphenylcyclohexane. The next 150 ml. of eluant removed 0.1 g. of unidentified oil. Finally petroleum ether-methanol removed 0.1 g. (6%) of stilbene.

The dd,ll-diastereomer was crystallized from methanol (3 ml./g.), m.p. 54.5–55.5°. The six strongest x-ray diffraction lines are [10] 4.187; [9] 4.480, 4.371; [7] 6.411; [4] 5.535, 3.880.

Anal. Calc'd for $C_{18}H_{20}$: C, 91.7; H, 8.53.

Found: C, 91.4; H, 8.76.

Regeneration of stilbene from the adduct. Several halides regenerated all or most of the stilbene. Thus a color change at −80° from red to purple to colorless occurred with one equivalent of dichloromethane during one hour. Only 45% of stilbene could be recovered; the remainder was an unidentified oily mixture. On the other hand decolorization under the same conditions with 1,2-dichloroethane occurred during 30 minutes with intermediate purple color; the recovery of stilbene was 95%. The same recovery was observed after the almost instantaneous reaction with two equivalents of benzyl chloride at −80° and no intermediate color was observed. These reactions were rapid. On the other hand no rapid change was observed when two equivalents of 2-chloropropene were added to the adduct at −80°. Even at +25° it required 17 hours for the intermediate blue color to be replaced by a colorless precipitate. However the only isolable product was an 82% yield of stilbene.

While 1-chloro-2-propene also regenerated 50% of the stilbene in the adduct, it is discussed separately because of a second product. The color of the system at −80° faded during 15 minutes from purple to pink when two equivalents of halide were added to the adduct. When the temperature was increased to +25° the pink color faded away. Evaporation of the solvent after filtration left 1.88 g. which, crystallized from absolute ethanol (at 0°), yielded 0.91 g. (50%) of pure stilbene. The evaporated mother liquors left an oil which crystallized, m.p. 75–110°. Crystallization from 3 ml. of absolute ethanol yielded 0.115 g., m.p. 146.5–149°. Two recrystallizations from ethanol and one from acetic acid raised this m.p. to 150–152°. The x-ray diffraction pattern (nine strongest lines) is [10] 5.55; [9] 5.79, 4.17; [8] 3.95; [3] 3.74, 3.65; [0.5] 11.18, 9.76, 8.38.

Anal. Calc'd for $C_{17}H_{17}$: C, 92.2; H, 7.74.

Found: C, 92.5; H, 7.75.

Reactions of 2-chloropropane. A. *With stilbene-disodium or -dilithium adduct.* A solution of 0.025 mole (1.96 g.) of 2-chloropropane in 5 ml. of 2,5-dioxahexane was added during ten minutes to stirred adduct (0.01 mole) in 40 ml. of dioxahexane at −80°. After 15 minutes the system was maintained at +25° for three to four hours. The color, at first dark blue, faded to colorless. The diether was then vacuum-evaporated and the residue was taken up

in water and benzene. The benzene phase, twice water-washed, was dried and evaporated. The residue (2.58 g.) was crystallized from absolute ethanol (10 ml./g.). This *meso*-2,5-dimethyl-3,4-diphenylhexane, m.p. 150–151°, 0.75 g., when augmented by 0.05 g. more by elution from alumina, constituted a 30% yield. The six strongest x-ray diffraction lines are [10] 5.86; [4] 6.75, 3.92; [3] 3.69; [2] 3.56, 3.48.

The mother liquor was concentrated to half its volume, the solute was redissolved, and the solution was cooled to 0°. The *dd,ll*-dimethyldiphenylhexane, 0.88 g., m.p. 95–98°, separated. The mother liquor was evaporated, redissolved in 20 ml. of petroleum ether (b.p. 40–60°) and adsorbed on a 1.5 × 40 cm. column of activated alumina which was then eluted with 350 ml. of petroleum ether. The evaporated eluate, crystallized from methanol, gave 0.05 g. of *meso* diastereomer and, on further cooling, 0.31 g. of *dd,ll* diastereomer. Total yield of the latter compound was 45% of theoretical. The column was further eluted with 98:2 petroleum ether-methanol to remove 0.08 g. (4%) of impure stilbene, m.p. 109–117°. The non-crystalline product was oily, b.p. 118–119° (1.5 mm.), wt. 0.34 g., n_D^{20} 1.5280 or 15% as 3-methyl-1,2-diphenylethane.

The *dd,ll* diastereomer was purified by adsorption on alumina which was eluted with petroleum ether first to remove the *meso* isomer and then to remove the *dd,ll* diastereomer which was twice crystallized from methanol (0.75 ml. per g.), m.p. 98–99°. The five strongest x-ray diffraction lines are [10] 7.93, 5.77; [4] 8.30, 4.16, 4.02.

Anal. Calc'd for $C_{20}H_{26}$: C, 90.2; H, 9.84.

Found: C, 90.2; H, 10.0.

In a variation of this procedure diethyl ether was used instead of dioxahexane. The system at −80° was first deep red in color, but it had faded after eight hours. This and other variations reported in Table I were processed as outlined above.

B. *With stilbene-monosodium adduct.* The deep red solution of stilbene-disodium adduct (0.01 mole) in 80 ml. of 2,5-dioxahexane was added to 1.80 g. (0.01 mole) of stilbene. The resulting brownish-green solution, chilled and stirred at −80°, was treated with 2.30 ml. (0.025 mole) of 2-chloropropane in 10 ml. of dioxahexane during ten minutes. After 30 hours at −80° the color had disappeared. The dioxahexane was vacuum-evaporated and the residue was washed with diethyl ether into a filter. Sodium chloride was washed from the polymer (XXI, 0.13 g.) by washing the filter with water. This infusible polymer was exhaustively extracted with boiling benzene.

Anal. Calc'd for $C_{14}H_{12}$ (stilbene): C, 93.4; H, 6.82.

Calc'd for $C_{17}H_{19}$ (isopropylstilbene): C, 91.4; H, 8.57.

Found: C, 92.1; H, 7.46; ash, 0.40.

The etherous filtrate was evaporated and the residue (4.14 g.) was dissolved in 10 ml. of hot absolute ethanol. The cooled system precipitated 0.71 g. of stilbene, m.p. 118–120°. Evaporation of the alcoholic filtrate left 3.43 g. which was adsorbed from petroleum ether (b.p. 40–60°) on a 2.0 × 73 cm. column of activated alumina. Elution with 25 ml. of petroleum ether removed 0.025 g. (0.47%) of *meso*-2,5-dimethyl-3,4-diphenylhexane, m.p. 145–150°, together with 1.31 g. of an unsaturated, unidentified oil. Further elution with 95:5 petroleum ether-methanol yielded first (200 ml.) a solid, m.p. 129–141° (0.50 g.), and then (45 ml.) another solid, m.p. 73–115° (0.84 g.). The first solid was extracted with 5 ml. of boiling methanol to remove stilbene and oil, leaving 0.18 g., m.p. 153–155°. When crystallized from acetic acid (10 ml./g.) it melted at 157–158°.

Anal. Calc'd for $C_{34}H_{38}$: C, 91.4; H, 8.57; Mol. wt., 447.

Found: C, 91.5; H, 8.50; Mol. wt. (Rast), 449.

The second solid was extracted with 5 ml. of boiling absolute ethanol to remove stilbene and oil, leaving 0.10 g., m.p. 225–240°. When crystallized from acetic acid (10 ml./g.) it melted at 258–259°.

Anal. Calc'd for $C_{34}H_{38}$: C, 91.4; H, 8.57; Mol. wt., 447.

Found: C, 91.4; H, 8.40; Mol. wt. (Rast), 464.

The extracts from these two compounds yielded 0.43 g. of stilbene, m.p. 115–120° after evaporation and crystallization from 10 ml. of methanol. Total yield of stilbene (authenticated by mixture melting point) is thus 32% of the total used in the reaction.

3-Methyl-1,2-diphenylbutane. Dehydration of 3-methyl-1,2-diphenylbutanol-2 (6) (20 g., 0.083 mole) was effected by heating to 95° in 50 ml. of acetic anhydride containing 0.18 g. of concentrated sulfuric acid for 20 hours. The system was added to ice; after hydrolysis the mixture was made alkaline and was extracted with ether. The dried extract was distilled at 95–115° (0.5–0.8 mm.), n_D^{20} 1.5290, d_4^{20} 0.977, as an 87% yield of mixed 3-methyl-1,2-diphenylbutene-2 and butene-1. The presence of these two compounds was demonstrated by ozonization which yielded desoxybenzoin and isobutyrophenone. The mixed alkenes (2.22 g., 0.01 mole) were reduced in 50 ml. of ethanol containing 4 g. of W-1 Raney Nickel at 40 lb./in². Subsequent distillation gave 1.82 g. (82%) of 3-methyl-1,2-diphenylbutane, b.p. 118.5–119.5° (1.5 mm.), n_D^{20} 1.5278, d_4^{20} 0.966.

Anal. Calc'd for $C_{17}H_{20}$: C, 91.1; H, 9.02.

Found: C, 90.8; H, 9.2.

4,4'-Dinitro-3-methyl-1,2-diphenylbutane. A solution of 0.5 g. (0.0022 mole) of methyl-diphenylbutane in 5 ml. of acetic anhydride was chilled to 0° and a solution of 3 ml. of 99% nitric acid (*d*.1.52, 0.0724 mole) in 5 ml. of acetic anhydride was added during two minutes. After one hour the system was poured into ice. The precipitated gum was dissolved in 1 ml. of hot acetic acid; 0.079 g. (11%) of dinitromethyldiphenylbutane, m.p. 120–123°, separated. Two crystallizations from a 0.75-ml. portion of absolute ethanol raised the m.p. to 124–125.5°. Oxidation with dichromate yielded *p*-nitrobenzoic acid.

Anal. Calc'd for $C_{17}H_{18}N_2O_4$: C, 64.9; H, 5.77; N, 8.91.

Found: C, 65.4; H, 6.00; N, 9.06.

A mixture melting point of this product with that obtained from 3-methyl-1,2-diphenyl-ethane prepared by alkylation of the stilbene-disodium was not lowered.

SUMMARY

1. The stability of the stilbene-disodium adduct in various ethers has been examined.

2. Dialkylation of the adduct with triethyl phosphate has been accomplished.

3. Mono- and di-alkylation of the adduct with a series of primary, secondary, and tertiary alkyl halides has been accomplished. The competing reaction of coupling also occurs.

4. Addition of stilbene to the stilbene-disodium adduct causes the adduct to behave as if it were in equilibrium with a stilbene-monosodium adduct.

5. While the useful reactions of the stilbene-disodium adduct seem to proceed by molecular coördination, the monosodium adduct seems to react by radical mechanisms.

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