was transferred to a refrigerator at 5° for 4 hr. to complete the crystallization. The supernatant liquid was decanted and the crystals were triturated with ether. These hygroscopic, electrostatic crystals were transferred to an analytical boat and dried to a constant weight prior to analysis. The infrared spectrum (Nujol) was not free of O–H absorption.

Anal. Calcd. for $C_7H_{13}BF_4O_2S$: C, 33.89; H, 5.28. Found: C, 34.07; H, 5.50.

Co-Reductions with Alkali Metals. I. Styrene and Acetone with Sodium

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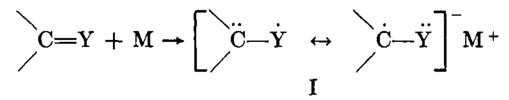
Received February 8, 1963

The reductive condensation of styrene and acetone by sodium metal to form phenylmethylbutanols, dimethylphenylhexanediol, dimethyldiphenyloctanediols, and related co-reduction products has been examined. The formation and distribution of these condensation products are highly solvent dependent. It is postulated that the styrene radical-anion, $PhCH\overset{\cdot}{=}CH_2$, is the intermediate directly responsible for the products of co-reduction. The mechanism of the reactions is discussed with respect to the nucleophilic properties of the styrene radical-anion and the effect of solvent on the dimerization equilibrium to form styrene dimer dianion, $[Ph\ddot{C}H—CH_2-CH_2—\ddot{C}HPh]Na_2$. Initiation by electron transfer from sodium to styrene *via* the ketyl of acetone is discussed.

The addition of alkali metals to multiple bonds of organic compounds to form ion-radical intermediates I is a relatively common process.



(1)

I

Y = C, O, N, etc.
M = alkali metal.

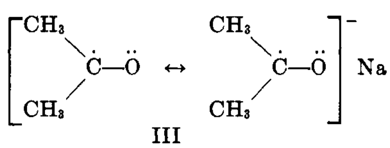
With compounds which contain carbon–carbon unsaturation, such species as I (Y = carbon) have been postulated in the sodium or lithium ammonia[2a] and amine[2b] reduction of aromatic compounds, in displacement reactions[3a] and the polymerization of conjugated olefins such as butadiene[3b,c] and styrene.[4a,b] Such intermediates as I from aromatic compounds also have been detected and studied spectroscopically.[5] In a similar manner heteropolar multiple bonds, especially between carbon and oxygen (Y = oxygen), have been subjected to reaction by alkali metals as in the pinacolic reduction of ketones,[6] acyloin condensation of esters,[7] and reduction of esters to alcohols.[8] Metal ketyls (I, Y = oxygen) have been postulated as intermediates in the reduction of these carbonyl-containing compounds, and also as "carriers" for electron transfer reactions from sodium to peroxides[9] and unsaturated compounds.[10]

In many of these cases where ion-radicals from unsaturated compounds or metal ketyls from carbonyl compounds are formed as intermediates, condensations to yield dimers or polymers as well as simple reduction products result. Although crossed products from unlike unsaturated compounds (for example in the anionic copolymerization of monomers)[3c] or from unlike metal ketyls in mixed acyloin condensations[11] have been effected, crossed condensation between ion radicals from unsaturated compounds and ketyls appears not to have been studied.

In this series of studies we examined the chemistry of radical ions and ketyls derived *simultaneously* as intermediates from alkali metals and such organic compounds possessing unsaturated centers as aromatic, olefinic, carbonyl, and nitrile-containing compounds. In this report we wish to describe the co-reduction[12] of styrene and acetone with sodium. The possible ion-radical intermediates in this case are the styrene radical-anion (II) and the ketyl (III) from acetone.

$$[C_6H_5—\dot{C}H—\ddot{C}H_2 \longleftrightarrow C_6H_5—\ddot{C}H—\dot{C}H_2]^-Na^+$$

II



III

These co-reductions, under conditions in which the unsaturated and carbonyl compounds react together with sodium, differ from those condensations of alkali metal adducts of hydrocarbons with electrophilic reagents such as carbon dioxide[13] and ethylene oxide[14] described recently. In the latter cases the alkali metal is first treated with the unsaturated compound to *preform* the organoalkali metal adduct which is then treated with the electrophilic reagent in a subsequent step. These reactions are, thus, essentially those of "conventional" carbanions such as Grignard,[15] organolithium,[16]

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(1) Department of Chemistry, Case Institute of Technology.

(2)(a) A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959); J. J. Eisch and W. C. Kasha, *J. Org. Chem.*, **27**, 3745, 4171 (1962); (b) R. A. Benkeser, *J. Am. Chem. Soc.*, **77**, 3230, 3378, 6042 (1955).

(3)(a) D. R. Weyenberg and L. H. Toporcer, *ibid.*, **84**, 2844 (1962); (b) M. Sittig, "Sodium," Reinhold Publishing Co., New York, N. Y., 1956, pp. 313 ff.; (c) A. V. Tobolsky, *et al.*, *J. Polymer Sci.*, **31**, 115, 123 (1958).

(4)(a) M. Szwarc, M. Levy, and R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2657 (1956); (b) C. Geacintov, J. Smid, and M. Szwarc, *ibid.*, **84**, 2508 (1962).

(5)(a) D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, **80**, 5342 (1958); 116 (1956); *J. Chem. Phys.*, **21**, 2227 (1953); **25**, 188 (1956); (b) T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954); ref. 27, p. 159 f.

(6)(a) G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 793 ff.; (b) J. Wieman, *Bull. soc. chim. France*, 63 (1954); *Compt. rend.*, **232**, 1941, 2029 (1951).

(7) M. Kharasch, E. Sternfeld, and F. Mayo, *J. Org. Chem.*, **5**, 362 (1940).

(8)(a) Ref. 4a, p. 286 ff.; (b) G. Darzens, *Compt. rend.*, **224**, 570 (1947); (c) S. M. McElvain, *Org. Reactions*, **4**, Chap. 4 (1948).

(9) J. F. Garst, D. Walmsley, and W. R. Richards, *J. Org. Chem.*, **27**, 2924 (1962).

(10) A. Zilkha, P. Neta, and M. Frankel, *Proc. Chem. Soc.*, 364 (1960).

(11) J. Kapron, *Compt. rend.*, **223**, 421 (1946); *Ann. chim.*, 12, **3**, 117 (1948).

(12) We wish to apply the term "co-reduction" to those condensations effected by alkali metals or related reducing agents in the presence of both components simultaneously.

(13) T. M. Lyssy, *J. Org. Chem.*, **27**, 5 (1962); C. E. Frank and W. E. Foster, *ibid.*, **26**, 303 (1961); C. E. Frank, *et al.*, *ibid.*, **26**, 307 (1961).

(14) J. F. Nobis and E. A. Allgeier, U. S. Patent 2,850,538 (1958).

(15) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954.

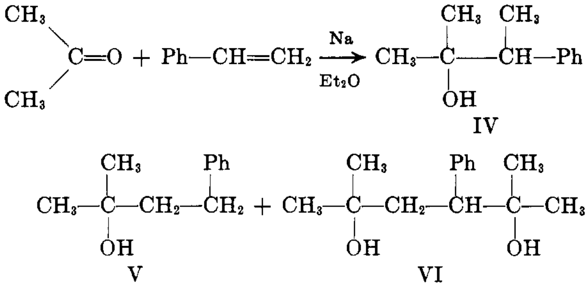
sodium,[17] and aluminum[18] reagents. Although the stoichiometry of both types of reactions is the same, the co-reductions we wish to describe here are more related to the chemistry of radical-anion intermediates.

Results

The reaction of acetone and styrene with sodium is an exothermic one. In most cases the temperature was regulated between −10° and +10°, but, if the reaction was allowed to warm up, a reaction ensued which led to polymerization of styrene.

To maintain control, acetone that was diluted in solvent was added dropwise to a stirred mixture of styrene in ethereal solution and freshly pressed sodium wire at the requisite low temperatures. Styrene is polymerized by sodium in ether solvents even at −10°. In order to obviate the anionic polymerization of the styrene, it was added to the mixture of sodium and ethereal solvent at −78°. Acetone prevented the polymerization of styrene and, if a small amount was added at −78° and the temperature was slowly allowed to rise to −10°, the co-reduction could be carried out smoothly with very little polymerization of styrene.

The products obtained from the co-reduction of styrene and acetone are highly dependent on the solvent employed. In diethyl ether the most important products were the 1:1 acetone–styrene adducts, 2-methyl-3-phenylbutanol-2 (IV) (26%) and 2-methyl-4-phenylbutanol-2 (V) (28%), in addition to the 2:1 adduct, 2,5-dimethyl-3-phenylhexanediol-2,5 (VI) (6%).

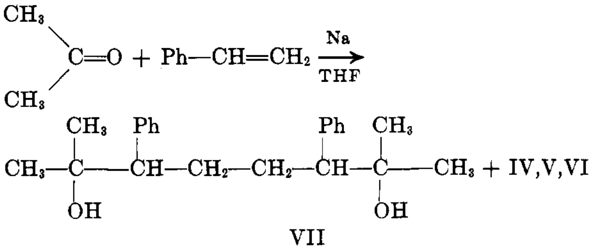


$$(CH_3)_2C{=}O + Ph{-}CH{=}CH_2 \xrightarrow[Et_2O]{Na} \underset{IV}{CH_3{-}\overset{CH_3}{\underset{OH}{C}}{-}\overset{CH_3}{CH}{-}Ph} + \underset{V}{CH_3{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_2{-}\overset{Ph}{CH_2}} + \underset{VI}{CH_3{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_2{-}\overset{Ph}{CH}{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_3} \quad (2)$$

Structures of the isomeric 1:1 adducts IV and V were proved by comparison of their infrared and nuclear magnetic resonance spectra and phenyl carbamate derivatives with authentic samples. The Grignard reaction was used to prepare authentic 2-methyl-3-phenylbutanol-2 from α-phenethylmagnesium bromide and acetone and 2-methyl-4-phenylbutanol-2 from ethyl hydrocinnamate and methylmagnesium iodide.

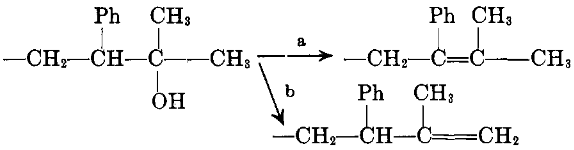
The structure of the diol VI was assigned primarily on the basis of its elemental and hydroxyl group analysis and molecular weight. The infrared spectrum indicated the presence of a monosubstituted benzene ring and this, together with the nuclear magnetic resonance spectrum indicating two pairs of nonequivalent methyl groups, further strengthened the case for the assignment of structure VI.

In tetrahydrofuran as solvent, the most important product was the 2:2 acetone–styrene adduct, 2,7-dimethyl-3,6-diphenyloctanediol-2,7 (VII) (31%), in addition to 1:1 adducts (13%) IV and V, and the 2:1 adduct (2%) VI.



$$(CH_3)_2C{=}O + Ph{-}CH{=}CH_2 \xrightarrow[THF]{Na} \underset{VII}{CH_3{-}\overset{CH_3}{\underset{OH}{C}}{-}\overset{Ph}{CH}{-}CH_2{-}CH_2{-}\overset{Ph}{CH}{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_3} + IV,V,VI \quad (3)$$

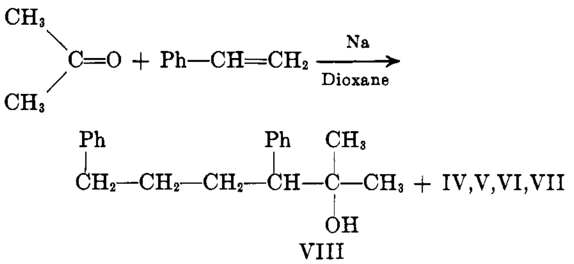
Diol VII was isolated in two diastereomeric forms which melted at 118° and 138°. These two isomers, which exhibited different solubility behavior, both underwent facile iodine-catalyzed dehydration to a mixture of diolefins. In each case the mixture of diolefins was ozonized to yield 1,2-dibenzoylethane in 21% (118° isomer) and 46% (138° isomer) yields, in addition to other ketonic products which were not identified. Although electronic factors controlling the dehydration of a tertiary alcohol such as VII would favor the internal olefin (a), it is possible that steric control[19] may be imposed by the neighboring groups to cause a significant amount of dehydration to the terminal position (b). The less than quantitative yields of dibenzoylethane are attributed to partial dehydration through route b.



$$-CH_2{-}\overset{Ph}{CH}{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_3 \xrightarrow{a} -CH_2{-}\overset{Ph}{C}{=}\overset{CH_3}{C}{-}CH_3$$
$$-CH_2{-}\overset{Ph}{CH}{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_3 \xrightarrow{b} -CH_2{-}\overset{Ph}{CH}{-}\overset{CH_3}{C}{=}CH_2$$

Infrared spectra of the ketonic by-products indicated the presence of carbonyl groups at saturated (5.82 μ) center as well as at unsaturated centers (5.95 μ) and are compatible with a mixture consisting of diacetyl and acetyl–benzoyl end groups.

In dioxane–diethyl ether solutions (80% by volume) a mixture of all four compounds, IV (7%), V (8%), VI (16%), and VII (27%), in addition to the 1:2 acetone–styrene adduct, 2-methyl-3,6-diphenylhexanol-2 (VIII) (27%), was formed.



$$(CH_3)_2C{=}O + Ph{-}CH{=}CH_2 \xrightarrow[Dioxane]{Na} \underset{VIII}{\overset{Ph}{CH_2}{-}CH_2{-}CH_2{-}\overset{Ph}{CH}{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_3} + IV,V,VI,VII \quad (4)$$

Diphenylhexanol VIII was easily dehydrated with iodine to yield an olefin which, on ozonolysis, yielded, 1,4-diphenylbutanone-1 (IX) in 88% yield. (see p. 1962, col. 1)

In addition to these alcohols the simple reduction products isopropyl alcohol and ethylbenzene were formed in small yields. The homobimolecular reduction product from styrene, 1,4-diphenylbutane (X), was formed in varying yields depending on the temperature of the reaction. The isomeric 1,3-diphenyl- and 2,3-diphenylbutanes were not formed.

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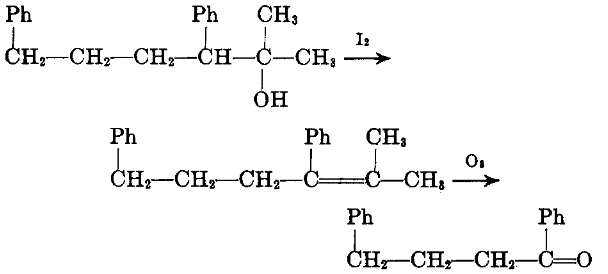
[16] D. L. Esmay, in "Metal-Organic Compounds," Advances in Chemistry Series, American Chemical Society, Washington, D. C., 1959, p. 46 ff.

[17] J. F. Nobis, L. F. Moormeir, and R. E. Robinson, *ibid.*, p. 63 ff.

[18] K. Ziegler, in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p. 194 ff.

[19] H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **77**, 3607, 3610, 3614, 3619, 3623 (1955).



IX (5)

$$2PhCH{=}CH_2 \xrightarrow[DMK]{Na} PhCH_2{-}CH_2{-}CH_2{-}CH_2Ph \quad (6)$$

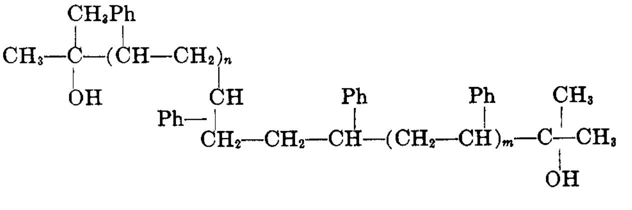
X

Bimolecular reduction product from acetone, pinacol, was not found, although under the alkaline conditions of the experiments the acetone condensation products, mesityl oxide, isophorone, and a crystalline ketone, were present, especially when acetone was added in excessive amounts. In tetrahydrofuran in the absence of olefin, acetone was reduced by sodium solely to isopropyl alcohol.

The effect of a *carbon dioxide atmosphere* on the reaction is a *retarding one.* In the presence of carbon dioxide the reaction of sodium with acetone and styrene was very slow under the usual reaction conditions. However, at elevated temperatures the reaction proceeded quite readily. Thus, if a nitrogen atmosphere is replaced by carbon dioxide, the reaction in diethyl ether could be carried out at 65° and slight excess carbon dioxide pressure in a controllable manner, whereas under the usual operating conditions extensive homopolymerization of styrene would have resulted at these temperatures.

It is interesting to note that the yields of 1,4-diphenylbutane and ethylbenzene at 65° were significantly higher under these conditions than at 0° and the absence of carbon dioxide. The low yields of carboxylic acids formed under a carbon dioxide atmosphere indicated that the concentration of carbon dioxide in solution at the elevated temperatures was small (probably due to the high partial pressure of the solvent).

In addition to solvent and temperature effects the yields of products also were dependent on the concentration of the olefinic component. In fairly concentrated solutions, telomers higher than the 2:2 adduct were formed. Polystyrene (mol. wt., 150,000), containing the dimethylcarbinol end groups, in addition to an amorphous mixture of lower molecular weight (~500) material which contained three and four styrene units associated with two acetone moieties, was observed. The structures of these compounds taken by analogy with lower condensation products are assigned as XI.



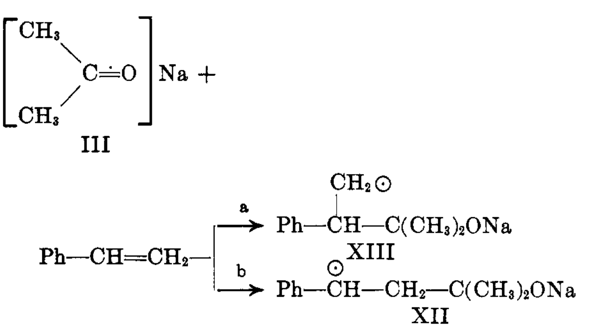
XI

Conditions for the optimum formation of these higher molecular weight products were not explored further.

The reaction of diacetone alcohol and styrene with sodium yielded products which are the same as those obtained with acetone. Less contamination from mesityl oxide and isophorone, however, was apparent. The retroaldol reaction of diacetone alcohol is apparently faster than the condensation with styrene under these conditions.

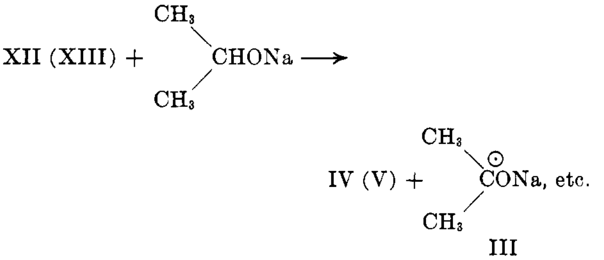
Discussion

The co-reduction of styrene and acetone with sodium is more akin in many ways to the anionic polymerization of styrene than the pinacolic reduction of acetone. Although sodium ketyl may be actually the first intermediate in the reaction (*vide infra*), the actual intermediate which leads directly to products appears to be the styrene radical-anion II. There is no direct evidence that sodium ketyl reacts with styrene in a reaction such as 7 to form the radical-alkoxides XII or XIII, and ultimately to yield the 1:1 reduction products IV and V, respectively, by either an electron transfer to the anion-alkoxide followed by proton transfer or by a free radical chain transfer of hydrogen.



(7)

With respect to the latter, isopropyl alcohol or its sodium salt, which are reasonably effective radical chain transfer agents for free alkyl radicals such as XII or XIII, did not increase the yield of either IV or V. The possibility of a radical chain addition (7, 8) of sodium isopropoxide to styrene *via* a ketyl intermediate was, therefore, not realized.



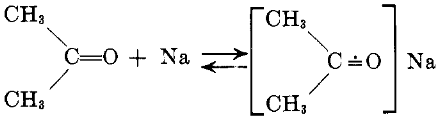
(8)

On the contrary, active hydrogen compounds decreased the yields of co-reduction products by reacting directly with sodium metal. Furthermore the addition, if possible, of sodium ketyl to styrene is expected not to differ significantly from the behavior of other free radicals to styrene.[20] The formation of the 1:1 adduct IV in amounts equal to the isomeric V by a ketyl addition to styrene as in reactions 7 is highly unlikely since free radical addition would be expected to occur more readily at the β-position of styrene to produce the more stable benzylic radical XIII. That ketyl is formed is indicated by the formation of small amounts of isopropyl alcohol from acetone even in the presence of styrene. The ketyl itself, how-

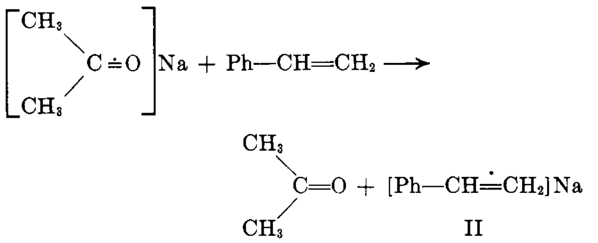
(20) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

ever, does not appear to be the addendum directly responsible for the co-reduction products.

On the other hand, if the styrene radical-anion II is postulated as the intermediate leading directly to products, a more coherent reaction path can be delineated. This olefin radical-anion could be formed in the primary step from sodium as evidenced by the formation initially of colored intermediates when styrene is added to sodium; the color is readily discharged by carbonylic compounds. We have observed qualitatively that the rate of co-reduction of styrene with carbonyl compounds varies significantly[21] with the structure of the carbonyl component. For this reason we prefer an alternative postulation in which the styrene radical-anion is formed by electron transfer from an initially formed sodium ketyl to styrene.



(9)

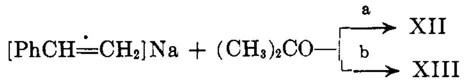


(10)

It can be argued, mainly on intuitive grounds, that the more electronegative carbonyl group would be reduced to the anion-radical in competition with the olefin moiety. The relative rates of reduction of compounds such as these by sodium are unknown, but *thermodynamic* values of the energy changes involved may be of some guide. Streitwieser[22a] has shown that in a series of related compounds, the polarographic reduction potentials are related to the energies of the lowest unoccupied molecular orbital. The half-wave potentials[22b] of acetone (-2.46 *vs.* S.C.E.) and styrene (-2.35 volts *vs.* S.C.E.) in 75% dioxane are similar. We have made crude Hückel molecular orbital calculations of the energies of the lowest unoccupied molecular orbitals in acetone and styrene, and they indicate that the formation of the ketyl III requires about 2 kcal./mole less energy than the formation of the styrene radical-anion II. Thus, the relative values of the polarographic reduction potentials of acetone and styrene are reasonably consistent with the calculated energies of the lowest unoccupied molecular orbital. If these gross thermodynamic comparisons are valid, it might be expected that they may be interpreted in terms of activation processes[22c] if, in addition, the electronegative oxygen atom in acetone facilitates the rate of electron transfer from the sodium surface.

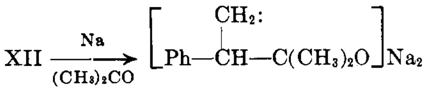
The variation in rates of reaction with the carbonyl component is then attributed to the formation of ketyls in the initial step. The subsequent electron transfer from ketyl to olefin[10] has been demonstrated with benzophenone ketyl[9] and the naphthalene radical-anion[23] as initiators in anionic polymerizations and as reducing agents.

The styrene radical-anion in diethyl ether solvent reacts as a nucleophile[24] with acetone at either the α- or β-position to produce the isomeric 4-phenylbutyl and 3-phenylbutyl radicals XII and XIII, respectively.[25]



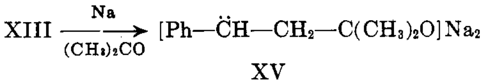
$$[\mathrm{PhCH{\doteq}CH_2}]\mathrm{Na} + (\mathrm{CH_3})_2\mathrm{CO}-\left\{\begin{array}{l}\xrightarrow{a} \mathrm{XII}\\ \xrightarrow{b} \mathrm{XIII}\end{array}\right. \qquad (11)$$

The radical-alkoxides XII and XIII are easily reduced[7] further by sodium or ketyl to the dianions XIV and XV, respectively, which react with acetone by proton



$$\mathrm{XII} \xrightarrow[(\mathrm{CH_3})_2\mathrm{CO}]{\mathrm{Na}} \left[\mathrm{Ph{-}\overset{\overset{\displaystyle CH_2:}{|}}{C}H{-}C(CH_3)_2O}\right]\mathrm{Na_2} \qquad (12)$$

XIV



$$\mathrm{XIII} \xrightarrow[(\mathrm{CH_3})_2\mathrm{CO}]{\mathrm{Na}} [\mathrm{Ph{-}\ddot{C}H{-}CH_2{-}C(CH_3)_2O}]\mathrm{Na_2} \qquad (13)$$

XV

transfer to yield the isomeric 1:1 adducts, IV and V, or by addition to the carbonyl group to yield the 1:2 styrene–acetone adduct, VI.

Since this bimolecular reaction must compete with the polymerization of styrene, the free energy of activation of the addition of the styrene radical-anion to acetone must be lower than that of the addition to styrene. The anionic polymerization of styrene is exothermic and the activation energy of the propagation step is low (1.0 kcal./mole in tetrahydrofuran).[4,25] It can be concluded on the basis of Hammond's postulate[26] that the transition state of the addition of styrene radical-anion to styrene has a high degree of *carbanionic* character. By the same token, the transition state for the addition of the styrene radical-anion to acetone must have at least as much or more carbanionic character. Therefore, the relative spin densities at various positions in the styrene radical-anion can serve as a suitable model for determining the relative rates of reaction of acetone at these positions of the radical-anion. In Fig. 1 is given the calculated spin densities in the radical-anion, using the simple Hückel molecular orbital method.[27]

This model correctly predicts[28a] that nucleophilic centers of the styrene radical-anion reside at both the

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[21] See following paper, J. K. Kochi, *J. Org. Chem.*, **28**, 1969 (1963).

[22] (a) Ref. 27, p. 173 ff. (b) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience Publishers, New York, N. Y., 1952, pp. 635, 661. (c) The correlation between electron density and the rate of proton transfer has been applied to the reduction of unsaturated hydrocarbons at the dropping mercury electrode by Hoijtink [*Rec. trav. chim.*, **76**, 885 (1957); **72**, 691 (1953); **71**, 1089 (1952)] and by Streitwieser (ref. 27, p. 425) to the reduction of aromatic compounds by alkali metals in the presence of a proton source. See also discussion presented earlier.

[23] (a) M. Szwarc, *Makromol. Chem.*, **35**, 133 (1960); (b) M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **82**, 521 (1960); (c) A. V. Tobolsky and D. B. Hartley, *Ibid.* **84**, 1391 (1962).

[24] The rate of addition of styrene radical-anion to acetone is certainly not so fast as the reaction of a conventional organosodium compound since the negative charge is delocalized in the radical-anion. The relative rate of addition of these nucleophiles to acetone compared to styrene should be much faster if taken in analogy with organometallic reagents such as Grignard compounds, etc.[15-18]

[25] Radical alkoxides XII and XIII are the same intermediates as those produced by the addition of acetone ketyl to styrene by another mechanism (*vide supra*).

[26] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

[27] A. Streitwieser, "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961.

[28] (a) This assumes that the additions are irreversible and that the subsequent reduction followed by protonation of the radical-alkoxides, XII and XIII, proceed in comparable fashion. See also J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, New York, N. Y., 1956, p. 207 ff. (b) The relative high electron density at the *para*-position would indicate the formation of another isomer, *p*-ethylphenyldimethyl carbinol, as a possibility. We observed no such product.

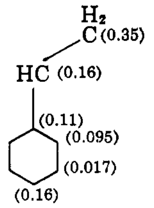


Fig. 1.—Spin densities at various positions in the styrene radical-anion.

α- and β-carbon atoms. The formation of the isomeric (1:1) adducts IV and V are in accord with this.[28b]

The same result, however, is obtainable if a styrene dianion XVI is postulated as an intermediate whose condensation with acetone occurs more or less randomly at either the α- or β-position. It is unlikely that

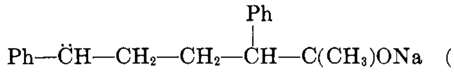
$$[\mathrm{Ph{-}CH\dot{=}CH_2}]\mathrm{Na} + \mathrm{Na} \rightleftharpoons [\mathrm{Ph{-}\ddot{C}H{-}\ddot{C}H_2}]\mathrm{Na_2} \quad (14)$$
$$\text{XVI}$$

$$2[\mathrm{Ph{-}CH\dot{=}CH_2}]\mathrm{Na} \rightleftharpoons \mathrm{PhCH{=}CH_2} + [\mathrm{Ph{-}\ddot{C}H{-}\ddot{C}H_2}]\mathrm{Na_2} \quad (15)^{28}$$

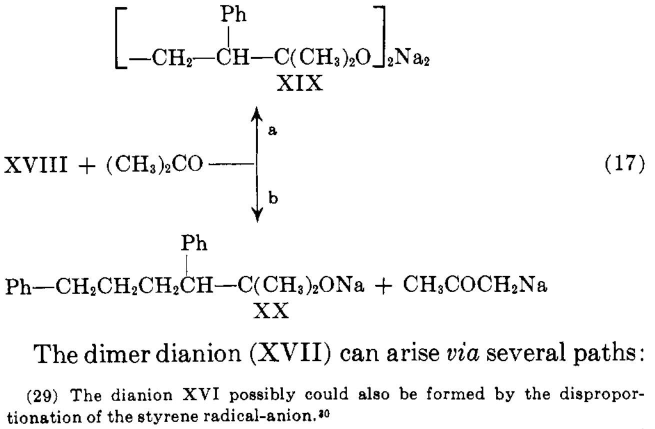
the formation of such a dianion from the styrene radical-anion[29] can compete with such processes of low activation energy as condensation or proton transfer with acetone or polymerization. Moreover, there is no *a priori* basis for styrene radical-anion to be reduced more easily to the dianion by electron transfer in ether than in tetrahydrofuran[31] (*vide infra*). The formation of ethylbenzene is not necessarily evidence in favor of the styrene dianion XVI since it is possible for it to arise *via* two successive pairs of electron and proton transfers from styrene.

In tetrahydrofuran as solvent, the 1:1 and 2:1 acetone–styrene adducts are replaced largely by 2:2 (VII) and 1:2 (VIII) adducts and 1,4-diphenylbutane, which arise from the dimer dianion XVII by condensation with either two or one acetone moieties or by proton transfer.

$$[\mathrm{Ph{-}\ddot{C}H{-}CH_2{-}CH_2{-}\ddot{C}H{-}Ph}]\mathrm{Na_2} + \mathrm{(CH_3)_2CO} \longrightarrow$$
$$\text{XVII}$$



$$\mathrm{Ph{-}\ddot{C}H{-}CH_2{-}CH_2{-}CH(Ph){-}C(CH_3)ONa} \quad (16)$$
$$\text{XVIII}$$



$$\left[\mathrm{{-}CH_2{-}CH(Ph){-}C(CH_3)_2O}\right]_2\mathrm{Na_2}$$
$$\text{XIX}$$

$$\text{XVIII} + \mathrm{(CH_3)_2CO} \longrightarrow \text{a: XIX; b: XX} \quad (17)$$

$$\mathrm{Ph{-}CH_2CH_2CH_2CH(Ph){-}C(CH_3)_2ONa} + \mathrm{CH_3COCH_2Na}$$
$$\text{XX}$$

The dimer dianion (XVII) can arise *via* several paths: the dimerization of styrene radical-anion (18)[4a] or the addition of the styrene radical-anion to styrene (19)

$$2[\mathrm{Ph{-}CH\dot{=}CH_2}]\mathrm{Na} \rightleftharpoons [\mathrm{Ph\ddot{C}H{-}CH_2CH_2{-}\ddot{C}HPh}]\mathrm{Na_2} \quad (18)$$
$$\text{XVII}$$

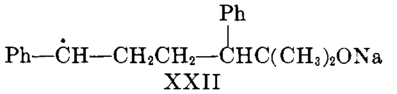
to form the dimer anion-radical XXI followed by reduction (20) by electron transfer to the dimer dianion XVII.

$$[\mathrm{Ph{-}CH\dot{=}CH_2}]\mathrm{Na} + \mathrm{Ph{-}CH{=}CH_2} \longrightarrow [\mathrm{Ph{-}\ddot{C}H{-}CH_2CH_2{-}\dot{C}H{-}Ph}]\mathrm{Na} \quad (19)$$
$$\text{XXI}$$

$$\text{XXI} + \mathrm{Na(S)} \longrightarrow \text{XVII} \quad (20$$

The formation of the 2:2 diastereomeric adducts VII by the former path through the dimer dianion (equations 16–17) is preferred to alternative paths. Since the activation energies for the dimerization of carbon radicals is generally low, the coupling of the radical alkoxide XIII to the dialkoxide XIX should not be favored particularly over the coupling of the isomeric radical-alkoxide XII or the mixed coupling of XII and XIII. Therefore, the absence of structural isomers of the 2:2 adducts VII precludes the formation of the latter by this route. Alternatively, the dimer anion-radical XXI could condense with acetone to form the dimer radical-alkoxide XXII as an intermediate which subsequently is reduced by electron transfer to the dimer

$$\text{XXI} + \mathrm{(CH_3)_2CO} \longrightarrow$$



$$\mathrm{Ph{-}\dot{C}H{-}CH_2CH_2{-}CH(Ph)C(CH_3)_2ONa} \quad (21)$$
$$\text{XXII}$$

anion-alkoxide XVIII followed by reaction 17. However, it is not expected that the free radical intermediates are of such reactivity to enable these reactions to compete with their facile destruction by electron transfer.[2,4,23,25,32]

The validity of the latter alternative path (equations 19 and 21) for the formation of 2:2 adducts is difficult to assess, but we question whether the dimer anion-radical XXI or the dimer radical-alkoxide XXII are significant intermediates in these reactions.

Szwarc in his extensive studies of the mechanism of anionic polymerization has indicated that with olefins such as 1,1-diphenylethylene[33] and α-methylstyrene,[34] the rate constants for dimerization of the radical-anion, and the addition of the radical-anion to another olefin unit are within orders of magnitude the same. Our qualitative results, of course, cannot serve to distinguish between these two possibilities for the formation of the dimer dianion XVII.[35] However, we disfavor the dimer radical-anion as an intermediate in our co-reduction reactions. There is a rather striking alteration in the complexion of the reaction from the formation of monomeric styrene products (*i.e.*, 1:1 and 2:1 acetone–styrene adducts) in diethyl ether to largely dimeric styrene products (2:2 and 1:2 acetone–styrene adducts)

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[29] The dianion XVI possibly could also be formed by the disproportionation of the styrene radical-anion.[30]

[30] J. F. Garst and R. S. Cole, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N.J., September, 1962, p. 5Q.

[31] However, Garst and Cole[30] have shown recently that in an equilibrium such as 15 involving tetraphenyl ethylene, good solvating media such as dimethoxyethane favor the radical-anion and diethyl ether favors the dianion. The analogy applicable to tetraphenylethylene cannot be extended easily to styrene because the absence of phenyl groups to stabilize the methylene carbanionic center in the styrene dianion XVI.

[32] Since the electron transfer reaction is partially heterogeneous, the surface area as well as the state of the surface of the sodium and the steady state concentration of ketyls will affect these rates.

[33] G. Spach, H. Monteiro, M. Levy, and M. Szwarc, *Trans. Faraday Soc.*, **58**, 1809 (1962).

[34] M. Szwarc and R. Asami, *J. Am. Chem. Soc.*, **84**, 2269 (1962).

[35] That is, after electron transfer to the dimer anion-radical formed by the addition process.

in tetrahydrofuran. This is difficult to reconcile with the occurrence of a reaction sequence such as 19 and 21 (which involve the dimer radical-anion XXI as an intermediate) as a major route for the production of dimeric styrene adducts XIX and XX.[36] It is known that solvents such as tetrahydrofuran facilitate solvation of alkali ketyls[37] and anion-radicals.[39] The change in the course of the co-reduction with solvent can be reasonably accommodated if the dimerization of styrene radical-anion (equation 18) is considered reversible.[40] The variation in the complexion of the products with solvent can then be attributed to the different equilibrium (or steady state) concentrations of the styrene radical-anion as monomer II or dimer XVII in tetrahydrofuran, dioxane, and diethyl ether solvents. The equilibrium constant for formation of the dimer dianion would be expected to be favored by such solvents as tetrahydrofuran, dioxane and, to a higher degree, dimethoxyethane (a solvent unfortunately not employed in these studies) and less favored by the relatively poorly solvating diethyl ether.[41,42]

The inhibitory effect of carbon dioxide is at present not explained too adequately. Since the reaction is heterogeneous the surface of the sodium is an important factor to be considered. It is possible that the carbon dioxide reacts with either styrene radical-anion or the dimer dianion[13] to form insoluble sodium carboxylates. This is apparent by the dull surface of the sodium when a carbon dioxide atmosphere is maintained. Whether carbon dioxide also prevents electron transfer from sodium by some other mechanism is unclear.

Experimental

Materials.—Sodium: A. R. grade, Mallinckrodt Chemical Works. Ether: A. R. grade, Mallinckrodt Chemical Works. Tetrahydrofuran: Du Pont Co., refluxed with lithium aluminum hydride two days and distilled, under nitrogen, b.p. 68°. Dioxane: Du Pont Co., distilled from potassium hydroxide and then from lithium aluminum hydride. Styrene: Eastman Kodak, distilled, b.p. 49.5–50.5 (25 mm.). Carbon dioxide: Pureco (99.87 +%) passed over manganous oxide (gas reduced, Foote Chemical Co.), at 150° then through a tube packed with lithium aluminum hydride.

Synthesis of 1-Methyl-3-phenylbutanol-2.—The Grignard reagent of α-bromoethylbenzene (50 g.) was prepared from 12 g. of magnesium. It was treated with 20 g. of acetone in 50 ml. of ether. The reaction mixture separated into two liquid layers, but it was worked up in the usual manner using ammonium chloride. The crude ethereal solution on distillation yielded 5 g. of desired alcohol, 2-methyl-3-phenylbutanol-2 (b.p. 62–63° (1 mm.); m.p. 40–42°; $n^{20}D$ 1.5161; lit.[43] b.p. 105–107° (12 mm.); $n^{20}D$ 1.5193) and 33 g. of 2,3-diphenylbutane (recrystallized from methylcyclohexane–petroleum ether, (b.p. 40–50°)) (m.m.p. 125–126°). The phenylurethane of 2-methyl-3-phenylbutanol-2 was made by heating on a steam bath a solution of 1 g. of the alcohol, 0.5 g. of phenyl isocyanate, and 1 drop of pyridine in a sealed tube for 36 hr. It was recrystallized twice from petroleum ether (b.p. 40-50°) (m.p. 101.5–102.0°).

Anal. Calcd. for 2-methyl-3-phenylbutanol-2 ($C_{11}H_{16}O$): C, 80.5; H, 9.82. Found: C, 79.67, 79.82; H, 9.87, 9.86.

Anal. Calcd. for urethane of 2-methyl-3-phenylbutanol-2 ($C_{18}H_{21}NO_2$): C, 76.4; H, 7.48; N, 4.95. Found: C, 76.3; H, 7.7; N, 5.00.

Anal. Calcd. for 2,3-diphenylbutane ($C_{16}H_{18}$): C, 91.4; H, 8.6. Found: C, 91.7; H, 8.6.

Synthesis of 2-Methyl-4-phenylbutanol-2.—This alcohol was prepared by K. Dewhirst from ethyl hydrocinnamate and methylmagnesium iodide. Further rectification through a spinning band column gave material boiling at 86–87° (1 mm.) ($n^{20}D$ 1.5103). The urethane was prepared by heating a mixture of 1 g. of alcohol with 0.5 g. of phenyl isocyanate and 1 drop of pyridine in a sealed tube over a steam bath for 18 hr.; recrystallization from petroleum ether (b.p. 40–50° yielded material melting at 138.5–139.5° (lit.[44] m.p. 138–139°)).

Anal. Calcd. for 2-methyl-4-phenylbutanol-2 ($C_{11}H_{16}O$): C, 80.5; H, 9.86. Found: C, 79.6; H, 9.8.

Anal. Calcd. for urethane of 2-methyl-4-phenylbutanol-2 ($C_{18}H_{21}NO_2$): C, 76.4; H, 7.48; N, 4.95. Found: C, 76.1; H, 7.6; N, 4.92.

Synthesis of 1,4-Diphenylbutane.—Phenethyl Grignard reagent was prepared from α-phenethyl chloride (10 g.) and magnesium (4 g.) in ether. Anhydrous cobaltous chloride (1 g.) and α-phenethyl chloride (5 g.) were added and the reaction refluxed for 1 hr. Water was added and the reaction worked up in the usual manner. 1,4-Diphenylbutane was obtained in 31% yield (b.p. 127-131° (3.5 mm.), m.p. 52–53°).

Anal. Calcd. for 1,4-diphenylbutane ($C_{16}H_{18}$): C, 91.5; H, 8.63; mol. wt. (cryoscopic in dioxane), 210. Found: C, 91.5; H, 8.6; mol. wt., 185 ± 5.

Synthesis of 2,5-Dimethyl-3-phenylhexanediol-2,5.—The subject diol was obtained from the reaction of styrene and acetone with sodium in ether (*vide infra*) and represented the condensation of two acetone units with one of styrene. After repeated rectification it was obtained pure (b.p. 130–132° (2 mm.), $n^{20}D$ 1.5272). On prolonged standing it crystallized into dense crystals, m.p. 73–74°. The crystalline diol, however, after melting, supercooled badly and was difficult to crystallize. A solution of the diol in isopentane on chilling in a Dry Ice bath absorbed enough moisture to deposit fine needles of hemihydrate, m.p. 62–63°.

Anal. Calcd. for 2,5-dimethyl-3-phenylhexanediol-2,5 ($C_{14}H_{22}O_2$): C, 75.6; H, 9.97; hydroxyl value (equiv./100 g.), 0.900; mol. wt., 222. Found: C, 75.4, 75.7; H, 10.0, 10.1; hydroxyl value, 0.894; mol. wt., 228 ± 7.

Anal. Calcd. for 2,5-dimethyl-3-phenylhexanediol-2,5-hemihydrate ($C_{14}H_{22}O_2 \cdot {}^1/_2\, H_2O$): C, 72.8; H, 10.0; mol. wt. (ethanol azeotrope), 231.3; hydroxyl value ($LiAlH_4$), 0.862; water (% weight) (Fischer), 3.9. Found: C, 72.9, 72.7; H, 10.1, 10.0; mol. wt., 242 ± 7; hydroxyl value, 0.85; water, 3.8.

Synthesis of 2-Methyl-3,6-diphenylhexanol-2 ($C_{19}H_{24}O$).—The subject alcohol was a product obtained from the reaction of styrene and acetone with sodium in dioxane (*vide infra*) and represented the incorporation of two styrene moieties with each acetone. Distillation yielded material boiling at 168–175° at 2.5 mm. which was a viscous liquid ($n^{25}D$ 1.5483), but could not be crystallized. A urethane was prepared from a mixture of 2 g. of the alcohol, 1 g. of phenyl isocyanate, and 1 drop of pyridine heated in a sealed tube on a steam bath for 60 hr. It was recrystallized from *n*-hexane to yield phenylurethane melting at 122.5–123.0°.

Anal. Calcd. for 2-methyl-3,6-diphenylhexanol-2 ($C_{19}H_{24}O$):

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[36] Unless solvent plays a larger role in the addition of the styrene radical-anion to styrene than it does with addition to acetone. Alternatively the formation of the dimer radical-anion could be reversible and the equilibrium constant highly solvent dependent.

[37] The mechanism of this solvation has not been fully developed.[38,41]

[38] J. F. Garst, *et al., J. Am. Chem. Soc.*, **83**, 5034 (1961); J. F. Garst and R. J. Cole, *ibid.*, **84**, 4352 (1962).

[39] R. L. Ward and S. I. Weissman, *ibid.*, **79**, 2086 (1957).

[40] M. Szwarc and R. Asami[34] have given a value, however, for the activation energy of the dimer dianion from 1,1-diphenylethylene as approximately 10 kcal., and the rate of dissociation (8 × 10^{-7} sec.$^{-1}$ at 30°) is estimated to be approximately an order of magnitude faster than that of the dimer dianion of α-methylstyrene.

[41] (a) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936); (b) G. E. Coates, "Organo-Metallic Compounds," Methuen and Co., London, 1960, p. 33.

[42] For example the dimerization equilibrium of benzophenone ketyl is highly solvent dependent.[6a]

$$2[Ph_2C\doteq O]Na \rightleftharpoons (Ph_2CO)_2Na_2 \qquad (22)$$

However, at present the effect solvents will have on such reversible equilibria as 18 and 22 is difficult to state unequivocably. If solvents such as tetrahydrofuran and dimethoxyethane solvate the metal cations,[41] they also would serve to put more of an effective charge on the anionic centers. If such is the case, these solvents should increase the forces of coulombic repulsions in the dimer dianion and *decrease* the formation constants of these dianions relative to those in poorly solvating media. If these solvents affect the degree or kind of ionic aggregates in solution,[38] they may well stabilize dianions.

[43] A. Lepin, *Chem. Zentr.*, **IIb**, 2080 (1912).

[44] A. Birch, *J. Chem. Soc.*, 809 (1945).

C, 85.0; H, 9.03; mol. wt., 268.4; hydroxyl value (equiv./100 g.), 0.373. Found: C, 84.5, 84.7; H, 9.2, 9.1; mol. wt., 284 ± 5; hydroxyl value, 0.368, 0.405.

Anal. Calcd. for urethane of methyldiphenylhexanol ($C_{25}H_{27}O_2N$): C, 80.3; H, 7.28; N (Kjeldahl), 3.75. Found: C, 80.60, 80.68; H, 7.55, 7.62; N, 3.61, 3.69.

The Proof of Structure of 2-Methyl-3,6-diphenylhexanol-2. Iodine Dehydration.—A mixture of 6 g. of 2-methyl-3,6-diphenylhexanol-2 and 0.1 g. of iodine was intimately ground.[45] It was then heated to 130° for 0.5 hr. under nitrogen. Water and iodine were then distilled *in vacuo*. The residue (containing no hydroxyl bands in the infrared spectrum) was taken up in isopentane, washed twice with sodium bisulfite solution, and then added dropwise to a refluxing mixture of 13 g. of zinc dust and 75 ml. of ethanol over 0.5 hr. The mixture after refluxing for 2 hr. was diluted with water and extracted with *n*-pentane. The solution after drying overnight with calcium chloride was distilled *in vacuo* to yield 4.5 g. of hydrocarbon boiling at 147.5–149.5° at 2 mm. ($n^{25}D$ 1.5542–1.555). The infrared spectra of all the fractions were the same.

Anal. Calcd. for 2-methyl-3,6-diphenylhexene-2 ($C_{19}H_{22}$): C, 91.1; H, 8.85; bromine no. (g./100 g.), 63.8. Found: C, 91.1, 91.3; H, 8.8, 9.0; bromine no., 69.3.

Ozonolysis.—A solution of 2.3 g. of 2-methyl-3,6-diphenylhexene-2 in 15 ml. of methylene chloride was ozonized at −78°.[46] The methylene chloride solution was added dropwise to a refluxing 50% solution of aqueous acetic acid and 3 g. of zinc dust. The mixture was refluxed for 1.5 hr. after the methylene chloride had distilled. It was then taken up in ether, and the ethereal solution washed with aqueous sodium iodide (2%), dilute sodium hydroxide (8%), dilute hydrochloric acid, and twice with water, and dried with calcium chloride. Distillation of the ether yielded a ketonic oil. Sublimation of the oil (50–65° at 3 mm.) yielded a colorless solid (1.8 g., 88%, m.p. 55.0–55.5°) identified as 1,4-diphenylbutanone-1 (lit.[47] m.p. 55–56°).

Anal. Calcd. for 1,4-diphenylbutanone-1 ($C_{16}H_{16}O$): C, 85.7; H, 7.15. Found: C, 85.4; H, 7.2.

A 2,4-dinitrophenylhydrazone derivative recrystallized from ethyl acetate–ethanol solutions yielded orange needles (m.p. 145.0–145.5°; lit.[48] m.p. 144.5–145.0°).

Anal. Calcd. for 1,4-diphenylbutanone-1 2,4-dinitrophenylhydrazone ($C_{22}H_{20}N_4O_4$): C, 65.3; H, 4.98; N, 13.84. Found: C, 65.1; N, 4.8; N, 13.9.

Synthesis of 2,7-Dimethyl-3,6-diphenyloctanediol-2,7.—The diol, 2,7-dimethyl-3,6-diphenyloctanediol-2,7, exists as two diastereoisomers, *dl* and *meso*. Both compounds were isolated from the reaction of styrene and acetone with sodium in dioxane or tetrahydrofuran and represented the condensation of two styrene and two acetone units. They were crystalline compounds recrystallizable from methylcyclohexane and were roughly separable by cooling their concentrated solution in isopentane, whereupon the higher melting isomer crystallized quickly. Filtration and further standing allowed the lower melting isomer to separate. They were further purified by recrystallization from absolute ethanol in which the higher melting isomer was quite soluble and the lower melting isomer crystallized in beautiful hexagonal crystals containing loose molecules of solvation. The ethanol of solvation deliquesced in air to leave a colorless white solid (m.p. 118–119°; b.p. 192–196° (1 mm.)). The higher melting isomer was recrystallized from methylcyclohexane to yield colorless crystals melting at 135.5–136.0°. The diurethane of the 118° isomer melted with decomposition at 188.5°.

Anal. Calcd. for 2,7-dimethyl-3,6-diphenyloctanediol-2,7 ($C_{22}H_{30}O_2$) (118° isomer): C, 81.0; H, 9.27; hydroxyl value (equiv./100 g.; $LiAlH_4$), 0.613. Found: C, 81.44, 81.38; H, 9.32, 9.33; hydroxyl value, 0.605.

Anal. Calcd. for bisphenylurethane of dimethyldiphenyloctanediol-2,7 ($C_{36}H_{40}O_4N_2$) (118° isomer): C, 76.6; H, 7.15; N, 4.96. Found: C, 76.7, 76.9; H, 7.3, 7.4; N, 4.97.

Anal. Calcd. for 2,7-dimethyl-3,6-diphenyloctanediol-2,7 ($C_{22}H_{30}O_2$) (136° isomer): C, 81.0; H, 9.27; hydroxyl value, 0.613. Found: C, 81.0; H, 9.3; hydroxyl value, 0.606.

Proof of Structure of 2,7-Dimethyl-3,6-diphenyloctanediol-2,7 118° Isomer.—A mixture of 1.50 g. of diol and 0.05 g. of iodine was heated under nitrogen for 1 hr. The water and iodine were vacuum distilled and the residue taken up in chloroform. The chloroform solution was added to a refluxing mixture of zinc and ethanol and heated for an additional hour after distilling the chloroform. The mixture was diluted with water and taken up in *n*-hexane. The hexane solution was washed with sodium thiosulfate and water, dried with calcium chloride, and distilled from zinc dust. The first fraction (b.p. 146–148° (2 mm.)) crystallized on standing. Recrystallization from isopentane yielded colorless crystals (m.p. 112–114°). The presence of infrared absorption bands at 10.25 and 10.9 μ indicated that the olefin probably contained the *isopropenyl* structure.

Anal. Calcd. for $C_{22}H_{26}$: C, 91.0; H, 9.0. Found: C, 91.0; H, 9.1.

The major dehydration product (1 g.) boiled at 148–149° at 2 mm. ($n^{25}D$ 1.5588) and could not be crystallized. It was ozonized in methylene chloride solution at −78°. The ozonide was treated with refluxing ethanol and zinc dust to yield 0.8 g. of ketonic oil and 0.25 g. (21%) of dibenzoylethane. Recrystallization of the 1,2-dibenzoylethane from absolute alcohol yielded colorless needles (m.p. 144.5–145.5°).

Anal. Calcd. for 1,2-dibenzoylethane ($C_{16}H_{14}O_2$): C, 80.6; H, 5.92. Found: C, 79.8, 79.9; H, 6.0, 6.2.

The infrared spectrum (potassium bromide) was identical with an authentic sample.[49] The ketonic oil was treated with DNP reagent but yielded a mixture of 2,4-dinitrophenylhydrazones which were not further investigated.

The crystallized olefin was also ozonized but did not yield the easily identifiable dibenzoylethane. The ketonic product was treated with DNP reagent to give a yellow DNP (m.p. 150–154°, recrystallized twice from aqueous ethanol solutions).

136° Isomer.—The diol (10 g.) was dehydrated by heating with iodine (0.1 g.) at 140–150°. The water and iodine were vacuum distilled and the residue treated with zinc and ethanol in the usual manner to yield 8 g. of hydrocarbon boiling at 151–152° ($n^{25}D$ 1.5582–1.5588). The infrared spectrum was quite similar (especially in the fingerprint region) to the liquid olefin obtained from the dehydration of the 118° isomer.

Anal. Calcd. for $C_{22}H_{26}$: C, 91.0; H, 9.04; bromine no., 110. Found: C, 91.06, 90.96; H, 9.07, 9.04; bromine no., 115, 115.

The olefin (1.38 g.) was ozonized in the usual manner to yield 0.46 g. (46%) 1,2-dibenzoylethane.

Reaction of Styrene and Acetone with Sodium.—In a typical experiment a 1-l., three-neck round-bottom flask equipped with a reflux condenser, trubore stirrer, and gas inlet was flushed with dry oxygen-free nitrogen and a head of nitrogen pressure was maintained in all of the subsequent operations. The solvent was added and sodium wire (1.5-mm. diameter) was pressed directly into the kettle. It was then cooled to the appropriate temperature and 5 to 10 ml. of the carbonyl component added with stirring. The latter was necessary particularly if the olefinic component is susceptible to anionic polymerization (*e.g.*, butadiene and styrene). As the olefin was added the surface of the sodium turned yellow to red depending on the olefin; the color probably was due to the formation of a carbanion since it was readily discharged by the addition of the carbonyl compound. The progress of the reaction was readily followed by the disappearance of the sodium. With reactive systems (carbonyl component) the surface of the sodium remained shiny until it was consumed completely.

Reaction of Styrene and Acetone with Sodium in Diethyl Ether.—Sodium (30 g.) was pressed in wire form into 600 ml. of absolute ether. The mixture was continuously flushed with dry nitrogen. It was cooled to −40° and 10 ml. of anhydrous acetone added. This was followed by the simultaneous addition of 150 ml. of styrene and 95 ml. of acetone at such a rate to maintain the temperature at approximately −10° (∼1 hr.). As the reaction proceeded the surface of the sodium remained shiny and appeared molten. The reaction was stirred for an additional hour until the sodium was completely consumed; the mixture was homogeneous and appeared faintly gray. Acetic acid (100 ml.) and water were added simultaneously and the temperature maintained at 0°. The mixture was poured into an ice–water slurry and extracted twice with ether. The colorless ethereal extract was washed with sodium bicarbonate twice and dried to yield a colorless ethereal solution. Vacuum distillation yielded unchanged styrene (19 g., b.p. 49–52° (30 mm.)) contaminated with

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(45) F. Whitmore, *J. Am. Chem. Soc.*, **51**, 1485 (1929); **56**, 180 (1934).

(46) A. Henne and P. Hill, *ibid.*, **65**, 752 (1943).

(47) von Auwers, *J. prakt. Chem.*, **109**, 124 (1925); J. Brewster, *J. Am. Chem. Soc.*, **74**, 5179 (1952).

(48) C. Rondesvedt, *J. Org. Chem.*, **19**, 548 (1954); D. Cram; *J. Am. Chem. Soc.*, **76**, 726 (1954).

(49) I. Bengelsdorf, *J. Org. Chem.*, **25**, 1468 (1960).

mesityl oxide and ethylbenzene. The latter were identified by gas–liquid chromatography using a 6-ft. DC-710 silicone firebrick column operated at 105–107° and 9 p.s.i. The emergence times are mesityl oxide, 7.5 min., ethylbenzene, 10.3 min., and styrene, 14.5 min. The infrared spectrum of the trapped ethylbenzene g.l.c. peak was the same as that of an authentic sample. Mesityl oxide was identified by its 2,4-dinitrophenylhydrazone (m.p. 202°). In addition, there was obtained 58.1 g. of a mixture of the isomeric 3-phenyl- and 4-phenyl-2-methylbutanol-2's (b.p., 62–71° (3 mm.)). Rectification of this mixture resolved it into its component alcohols consisting of 53.5% 3-phenyl-2-methylbutanol-2 (b.p. 62 (2 mm.)) and 46.5% 4-phenyl-2-methylbutanol-2 (b.p. 86° (2 mm.)). The material (17.7 g.) boiling at 110–121° at 3 mm. was predominantly 2,5-dimethyl-3-phenylhexanediol-2,5. The high boiling residue (3.6 g.) was predominantly 2-methyl-3,6-diphenylhexanol-2.

To a mixture of 30 g. of sodium wire and 350 ml. of absolute ether at −75° were added 5 ml. of acetone and 200 ml. of styrene in approximately 5 min. Acetone was then added dropwise to maintain the temperature at −15° to −10° (1 hr.). The reaction was stirred for an additional hour at −10° until most of the sodium was consumed. The homogeneous solution was then cooled to −20° and 130 ml. of acetic acid and occasional portions of water were added to maintain the temperature of 0°. The reaction was then poured into an ice–water slurry and extracted twice with ether. The combined ethereal extracts were washed with water, potassium carbonate solution and water again, and dried over sodium sulfate. The volatile components consisting of ether and styrene were then removed by vacuum distillation to yield 109 g. of styrene and 11 g. of ethylbenzene. The latter was obtained by comparing the relative areas of styrene and ethylbenzene in a g.l.c. chromatogram with known mixtures. There also was obtained 51.5 g. of phenylmethylbutanols (b.p. 76–86° (2.5 mm.)), 17.8 g. of phenyldimethylhexanediol, and 3.1 g of high boiling residues.

The previous reaction was repeated at 0° and yielded 119 g. of recovered styrene, 10 g. of ethylbenzene, 52.4 g. of isomeric phenylmethylbutanols (b.p., 77–90° (4 mm.)), 21.4 g. of dimethylphenylhexanediol (b.p. 125–134° (3 mm.)), 2.0 g. of 1,4-diphenylbutane, and 6.7 g. of high boiling residues.

Reaction of Styrene and Acetone with Sodium and Carbon Dioxide in Ether.—A mixture of 30 g. of sodium wire in 500 ml. of ether was chilled to −78° and 10 ml. of acetone and 150 ml. of styrene were added. The system was then pressured with two atmospheres of carbon dioxide and acetone was added dropwise at a rate such that the temperature was maintained at 0°. The surface of the sodium remained dull. After 60 ml. of acetone had been added the temperature was allowed to rise to 32° (1 hr.). The surface of the sodium appeared dull and a small amount of flocculent solid was found suspended in the ether. The carbon dioxide pressure was replaced with argon and after a short induction period (approximately 5 min.) the temperature rose rapidly (40°, 0.5 hr.). The carbon dioxide pressure was reinstituted but the temperature continued to rise (65°). At this temperature the partial pressure of carbon dioxide in solution was low. With a 0.5-atm. carbon dioxide applied pressure, the addition of acetone was continued and the temperature remained at 60–65°. The reaction mixture became orange and solidified. To the mixture water was added slowly and the whole poured into ice–water. The ether extracts were washed twice with saturated sodium bicarbonate and then water. The sodium bicarbonate extracts were decolorized with Norit and filtered to yield a clear cream-colored solution. It was acidified with dilute sulfuric acid at 0° and reextracted twice with ether. The ether solutions after drying yielded 3.5 g. of a viscous carboxylic acid(s) which was not identified further.

Distillation of the original ethereal solution yielded 60.9 g. of isomeric methylphenylbutanols, 12.1 g. of 1,4-diphenylbutane, 18.5 g. of dimethylphenylhexanediol, 5.5 g. of an unidentified crystalline ketone, 6.3 g. of dimethyldiphenyloctanediol, and 8.5 g. of nondistillable residues. The unidentified ketone was recrystallized from methylcyclohexane and sublimed *in vacuo* to yield colorless crystals (m.p. 127.0–127.5°). The infrared spectrum showed absorption bands at 5.87 (very strong), 6.82 (strong), 6.90 (strong), 7.08 (strong), 7.20 (medium), 7.33 (strong), 7.49 (strong), 7.85 (very strong), and 8.15 (very strong) μ. The characteristic aromatic bands were absent.

Anal. Calcd. for unidentified ketone ($C_{15}H_{24}O_2$): C, 76.2; H, 10.25. Found: C, 76.3, 76.4; H, 10.3, 10.4.

The ketone was treated with DNP reagent to form a yellow DNP which was recrystallized from ethyl acetate (m.p. 240–241°, with decomposition in vacuum capillary). No lower melting derivative was formed.

Anal. Calcd. for $C_{15}H_{24}O_2 \cdot 2$ DNP ($C_{27}H_{32}N_8O_8$): C, 54.5; H, 5.41; N, 18.8. Found: C, 54.4, 54.4; H, 5.4, 5.5; N, 18.8, 18.6.

The material is, therefore, a diketone. This diketone was derived from acetone exclusively since it was also obtained when styrene was not present (*vide infra*).

Since the dimethylphenylhexanediol, 1,4-diphenylbutane, and the ketone codistill it was necessary to separate them by crystallization from isopentane in which the ketone and diphenylbutane were insoluble in the cold. The ketone was separated from the hydrocarbon by recrystallization from isopentane. The dimethylphenylhexanediol was obtained most conveniently as the hemihydrate by chilling an isopentane solution in a Dry Ice bath and allowing atmospheric moisture to condense. It could be purified by sublimation as a supercooled liquid or by distilling off the water of hydration.

If the reaction was repeated continuously maintaining the applied total pressure of carbon dioxide at two atmospheres, the reaction was sluggish. It was moderately exothermic, however, and after half an hour the temperature rose to 37° (90 ml. of acetone added). After an hour the reaction temperature reached 40° and the reaction became more vigorous and maintained itself despite applied carbon dioxide pressure at 56°. At the end of 2.5 hr. the reaction was complete. Under these conditions it appeared that the applied carbon dioxide pressure moderated the reaction and enabled it to be carried out at higher temperatures. Under these conditions 45.0 g. of phenylmethylbutanols, 19.5 g. of dimethylphenylhexanediol, and 5.7 g. of nondistillable residues were obtained.

Reaction of Acetone with Sodium in Tetrahydrofuran.—To 15 g. of sodium wire in 200 ml. of tetrahydrofuran at −20° was added 60 ml. of acetone dropwise. The addition was carried out at a rate such that the temperature was kept at 0–5° (1 hr.). After the reaction was stirred an additional hour, acetic acid (80 ml.) was added and the reaction mixture poured into water. The colorless solution was vacuum distilled directly to yield 15.3 g. (0.255 mole, 78%) of isopropyl alcohol determined by nitrite ester. The residues were extracted with benzene continuously but yielded no pinacol.

Reaction of Styrene and Acetone with Sodium in Tetrahydrofuran.—To 30 g. of sodium wire in 350 ml. of tetrahydrofuran at −60° was added 10 ml. of acetone. Acetone (150 ml.) and 230 ml. of styrene were then added dropwise simultaneously to maintain the temperature at −25° (1 hr.). The reaction was then stirred for 2 hr. at 0°. Acetic acid (100 ml.) and water were added at 0° and the reaction mixture poured into an ice–water slurry. When the mixture was extracted with ether a colorless solid (6 g.) separated. It was identified as polystyrene (with hydroxyl end groups). The intrinsic viscosity was determined in toluene at 25° to be 0.61 dl./g. Applying the equation, mol. wt. = $3.09 \times 10^5 \eta^{1.41}$, the viscosity average molecular weight was 150,000.

Anal. Calcd. for polystyrene $(C_8H_8)_n$: C, 92.3; H, 7.74. Found: C, 92.1, 92.1; H, 7.8, 7.8.

The viscous ethereal solution was treated with 1.5 l. of methanol whereupon more colorless solid (11 g.) precipitated. The analysis was consistent with a compound consisting of three styrene units for each two acetone units. The structure was probably 2,9-dimethyl-3,5-triphenyldecanediol-2.9.

Anal. Calcd. for $(C_8H_8)_3 \cdot (C_3H_7O)_2 = C_{30}H_{38}O_2$: C, 83.7; H, 8.9; mol. wt., 431. Found: C, 82.8; H, 9.1; mol. wt., 412 ± 16.

Vacuum distillation of the ether–methanol solution yielded a very viscous oil and a crystalline solid. When it was treated with petroleum ether it deposited more heavy crystalline precipitate. The crystalline precipitate (66.6 g.) was a mixture of the diasteriomeric dimethyldiphenyloctanediols with the higher melting isomer predominating (~90%). The viscous oil was fractionated into 14.1 g. of methylphenylbutanols, 5 g. of isophorone (2,4-dinitrophenylhydrazone, m.p. 129°), 3 g. of dimethylphenylhexanediol, and 94.7 g. of nondistillable residues (b.p. >140° at 2 mm.).

Anal. Calcd. for isophorone 2,4-dinitrophenylhydrazone ($C_{15}H_{20}N_4O_4$): C, 56.3; H, 6.29; N (Dumas), 17.5. Found: C, 57.5, 56.5; H, 6.1, 5.9; N, 17.7, 17.7.

Anal. Calcd. for residues $(C_8H_8)_4 \cdot (C_3H_7O)_2 = C_{38}H_{46}O_2$: C, 85.4; H, 8.5; mol. wt., 535; hydroxyl value, 0.372. Found: C, 86.2, 85.9; H, 8.6, 8.6; mol. wt., 551 ± 12; hydroxyl value, 0.348, 0.398.

A mixture of 30 g. of sodium wire and 350 ml. of tetrahydrofuran was chilled to −75°. Initially 5 ml. of acetone was added and then 150 ml. of acetone and 130 ml. styrene were added simultaneously at −40° to −35° (10 min.). The reaction was stirred at 0° and after 20 min. the reaction was viscous and opaque. An additional 120 ml. of acetone was added at 0° (1 hr.) and the reaction stirred for an additional hour. Acetic acid (130 ml.) and water were added to the mixture and the whole poured into an ice–water slurry. The reaction was extracted with ether; the ethereal extract was washed with saturated sodium bicarbonate and water. No polystyrene was formed. Vacuum distillation of the ether and styrene yielded a heterogeneous mixture of a viscous liquid and a crystalline solid. The ethereal distillate was a mixture containing styrene (10.1 g.), ethylbenzene (4.8 g.), and mesityl oxide (3.9 g.). Petroleum ether was added to the semisolid mixture to separate the crystalline insoluble material which was dimethyldiphenyloctanediol (78 g.). The petroleum ether solution on vacuum distillation yielded 17.9 g. of a mixture of methylphenylbutanols, 3.2 g. of isophorone, and 60.5 g. of a light yellow amorphous solid (b.p. >140° (3 ml.)).

The nondistillable amorphous residues showed an hydroxyl absorption at 2.8 μ and characteristic aromatic bands in the infrared spectrum. Its analysis was compatible with a structure consisting of three sytrene and two acetone units.

Anal. Calcd. for $(C_8H_8)_3 \cdot (C_3H_7O)_2 = (C_{30}H_{38}O_2)$: C, 83.7; H, 8.9; hydroxyl value (equiv./100 g.), 0.464; mol. wt. (ebull. ethanol, ebull. methylene chloride), 431. Found: C, 83.8; H, 9.0; hydroxyl value, 0.464; mol. wt., ethanol, 315 ± 20, methylene chloride, 350 ± 17.

Reaction of Styrene and Acetone with Sodium and Carbon Dioxide in Tetrahydrofuran.—To 30 g. of sodium wire in 500 ml. of tetrahydrofuran at −45° were added 15 ml. of acetone and then 150 ml. of styrene. The nitrogen was replaced with carbon dioxide and the total applied pressure maintained at 2 atm. Acetone (120 ml.) was added over 1 hr. at 0° but the reaction did not appear to be going. The temperature was allowed to rise to 35° by removing the cold bath (0.5 hr.) and the reaction allowed to proceed at 35–40° for an additional hour. The gray but homogeneous mixture was quenched by pouring it into an ice–dilute sulfuric acid solution. Approximately 10 g. of unchanged sodium remained in the kettle. The light brown mixture was extracted with ether and the ether solutions washed with saturated sodium bicarbonate threee times. The dark brown bicarbonate extracts were treated with Norit and carefully reacidified to yield 3 g. of carboxylic acid(s). Its infrared spectrum was similar to that obtained in ether. The original ether extract yielded styrene (103 g.), methylphenylbutanol (14.1 g.), 1,4-diphenylbutane (3 g.), dimethyldiphenylhexanediol (5.1 g.), and 17 g. of nondistillable residues (b.p. >160°(1 mm.)).

Anal. Calcd. for residues $(C_8H_8)_4 \cdot (C_3H_7O)_2 = C_{38}H_{46}O_2$: C, 85.4; H, 8.5; mol. wt., 535; hydroxyl value, 0.372 (equiv./100 g.). Found: C, 86.5; H, 8.5; hydroxyl value, 0.385, 0.356.

Reaction of Styrene and Acetone with Sodium in Dioxane.—To 30 g. of sodium wire in 400 ml. of dioxane and 100 ml. of ether at 3° were added dropwise simultaneously 150 ml. of styrene and 100 ml. of acetone at a rate (0.5 hr.) to maintain the temperature at 3° with external cooling. This was followed by an additional 100 ml. of acetone (1 hr.). Most of the sodium was consumed. The clear colorless fairly viscous solution was treated with 150 ml. of acetic acid and water, and then poured onto 500 ml. of ice–water slurry and extracted with ether. After drying with sodium sulfate the ethereal solution was vacuum distilled to remove styrene (2 g.) and ethylbenzene (3 g.). The residue was a viscous oil (197 g.). Isopentane (100 ml.) was added and the solution on setting overnight deposited crystals of dimethyldiphenyloctanediol (m.p. 135–138°), 30.5 g. More isopentane (50 ml.) was added and the solution cooled to 0° whereupon 6.5 g. of the diasteriomeric dimethyldiphenyloctanediol (m.p. 113–117°) was obtained. The higher melting isomer was purified by crystallization from methylcyclohexane, vacuum sublimation, and recrystallization (m.p. 135.0–135.7°). The lower melting isomer was purified by crystallization from absolute ethanol from which it crystallized as transparent platelets containing ethanol of solvation which was removed by vacuum drying (m.p. 118–119°).

The remaining isopentane mother liquor was vacuum distilled to yield 17.5 g. of isomeric methylphenylbutanols (b.p. 71–94° (3 mm.); $n^{25}D$ 1.4878–1.5202), 22.1 g. of dimethylphenylhexanediol (b.p. 130–147° (3 mm.); $n^{25}D$ 1.5382–1.5453), 46.4 g. of diphenylhexanol (b.p. 168–176° (3 mm.); $n^{25}D$ 1.5483–1.5495), 19.6 g. of additional dimethyldiphenyloctanediol (b.p. 176–192° (1 mm.); $n^{25}D$ 1.5498–1.5490), 7 g. of 1,4-diphenylbutane, and 25.8 g. of nondistillable residues (b.p. >200° (2 mm.)). The latter analyzed approximately for a compound consisting of three styrene and two acetone units.

Anal. Calcd. for residue $(C_8H_8)_3 \cdot (C_3H_7O)_2 = C_{30}H_{38}O_2$: C, 83.7; H, 8.9; mol. wt., 431; hydroxyl value, 0.464. Found: C, 83.8; H, 9.2; mol. wt., 392 ± 14; hydroxyl value, 0.497.

Reaction of Styrene and Diacetone Alcohol with Sodium in Ether.—To a mixture of 30 g. of sodium wire in 450 ml. of ether at −54° were added 10 ml. of diacetone alcohol and then 150 ml. of styrene. Diacetone alcohol (100 ml.) was then added dropwise at such a rate as to maintain the temperature at 0–5° (2 hr.). The clear homogeneous solution was chilled to −5° and 100 ml. of acetic acid and 100 ml. of water added. The mixture was then poured into an ice–water slurry and extracted with ether. The ethereal solution yielded 66.4 g. of methyl phenylbutanols (b.p. 68–87° (2.5 mm.); $n^{25}D$ 1.4951–1.5090), 23.6 g. of dimethylphenylhexanediol (b.p. 124–137° (2.5 mm.); $n^{25}D$ 1.5292–1.5211), 14.5 g. of diphenylhexanol (b.p. 163–184° (2.5 mm.); $n^{25}D$ 1.5427–1.5437), and only 4.1 g. of nondistillable residue (b.p. > 185° (2.5 mm.)).

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