Novel Dimerization Reactions of Styrene, α-Methylstyrene, and *p*-Chloro-α-methylstyrene. Codimerization of Styrene with α-Methylstyrene[1]

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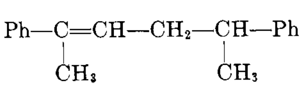
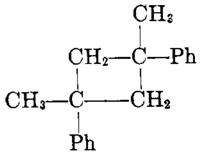
A novel dimerization reaction of α-methylstyrene was obtained by heating the olefin at 160° with catalytic amounts of potassium *t*-butoxide. The dimer produced in 80% yield was composed of 93% of 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XIII), the remainder being the open-chain dimer 2,5-diphenyl-2-hexene (XII). At 225°, 83% of the dimeric material consisted of 2,5-diphenyl-1- and 2-hexenes (XIV and XII); smaller amounts of XIII and of 1-methyl-1,3-diphenylcyclopentane (VI) also were formed. Similar dimerization products at the higher temperature were obtained in the absence of potassium *t*-butoxide. The use of sodium ethoxide as a possible catalyst for dimerization of α-methylstyrene was investigated. The dimerization of *p*-chloro-α-methylstyrene forms open chain and cyclic dimers having structures similar to those obtained from α-methylstyrene. The dimerization of styrene produces 1-phenyl-1,2,3,4-tetrahydronaphthalene in 11% yield. The codimerization of styrene and α-methylstyrene formed 1-methyl-1-phenyl- and 1-methyl-4-phenyl-1,2,3,4-tetrahydronaphthalene. The mechanism of dimerization is discussed. The structures of the dimers were established by independent syntheses.

The dimerization of α-methylstyrene has been studied over a period of about sixty years. Klages[3] was the first to dimerize α-methylstyrene during the dehydration of dimethylphenylcarbinol by means of 85% phosphoric acid. He proposed structure I for this dimer. Tiffeneau[4] obtained a solid material, m.p. 52°, on dimerization of α-methylstyrene in the presence of cold sulfuric acid to which he assigned structure of 1,3-dimethyl-1,3-diphenylcyclobutane (II). The same solid dimer was obtained by Staudinger and Breusch[5] by tin tetrachloride-catalyzed dimerization of α-methylstyrene and the same structure II was proposed by them. They also reported the formation of an oily product for which structure I and/or 2,5-diphenyl-3-hexene was suggested. Bergmann and co-workers[6] established the structure of the dimers by synthetic and degradative methods and they assigned structure III for the liquid and structure IV for the solid dimer.



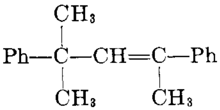
$\mathrm{Ph{-}\underset{CH_3}{C}{=}CH{-}CH_2{-}\underset{CH_3}{CH}{-}Ph}$

I



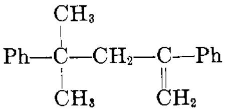
II

Hukki[7] established later that the liquid dimer obtained from the dimerization of α-methylstyrene with formic acid consisted of dimer III and its double bond isomer V.



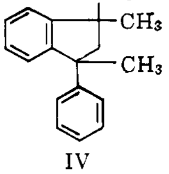
$\mathrm{Ph{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH{=}\underset{CH_3}{C}{-}Ph}$

III



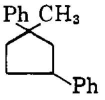
$\mathrm{Ph{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}\underset{\overset{\|}{CH_2}}{C}{-}Ph}$

V

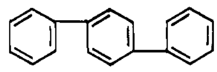


IV

Base-catalyzed dimerization of α-methylstyrene has been studied by Kolobielski and Pines using sodium–benzyl sodium as a catalyst.[8] The dimeric product consisted mainly of VI and of a small amount of VII; cumene was also obtained as part of a hydrogen transfer reaction. A carbanion chain mechanism was proposed for the dimerization reaction. Shabtai and Pines[9] found that on dimerization of α-methylstyrene in the presence of dispersed potassium the formation of VI is accompanied by small amounts of 2,5-diphenylhexenes as by-products.



VI

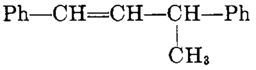


VII

The first styrene dimer was obtained by Fittig and Erdmann[10] during the decarboxylation of cinnamic acid by means of 40% aqueous sulfuric acid and they proposed the structures of 1,4-diphenyl-1-butene (VIII) and 1,3-diphenyl-1-butene (IX) for the dimers. Stoermer and Kootz[11] reinvestigated the product and concluded that it consisted mainly of IX admixed with 1,3-diphenyl-2-butene (X).

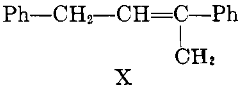
$\mathrm{Ph{-}CH{=}CH{-}CH_2{-}CH_2{-}Ph}$

VIII



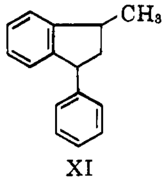
$\mathrm{Ph{-}CH{=}CH{-}\underset{CH_3}{CH}{-}Ph}$

IX



$\mathrm{Ph{-}CH_2{-}CH{=}\underset{CH_2}{C}{-}Ph}$

X



XI

Risi and Gauvin[12] dimerized styrene at reflux temperature in the presence of 53% sulfuric acid and reported that dimer IX was the main product and 1-methyl-3-phenylindan (XI) the minor product of the reaction. Spoerri and Rosen[13] found that the dimeriza-

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[1] Paper XXV of the series Base-Catalyzed Reactions. For paper XXIV, see A. Zwierzak and H. Pines, *J. Org. Chem.*, **27**, 4084 (1962).

[2] On leave of absence from Polytechnic Institute, Lodz, Poland.

[3] A. Klages, *Ber.*, **35**, 2633 (1902).

[4] M. Tiffeneau, *Ann.*, **10**, 158 (1907).

[5] H. Staudinger and F. Breusch, *Ber.*, **62**, 442 (1929).

[6] E. Bergmann, H. Taubadel, and H. Weiss, *ibid.*, **64**, 1493 (1931).

[7] J. Hukki, *Acta Chem. Scand.*, **3**, 279 (1949).

[8] M. Kolobielski and H. Pines, *J. Am. Chem. Soc.*, **79**, 5820 (1957).

[9] J. Shabtai and H. Pines, *J. Org. Chem.*, **26**, 4225 (1961).

[10] R. Fittig and E. Erdmann, *Ann.*, **216**, 179 (1883).

[11] R. Stoermer and H. Kootz, *Ber.*, **61**, 2330 (1928).

[12] J. Risi and D. Gauvin, *Can. J. Research*, **14B**, 255 (1936).

[13] P. E. Spoerri and M. J. Rosen, *J. Am. Chem. Soc.*, **72**, 4918 (1950).

tion of styrene in the presence of 62% sulfuric acid yielded only compound XI. Corson and co-workers obtained dimers IX and XI and small amounts of X by using phosphoric acid as catalyst.[14]

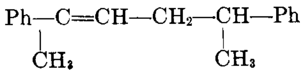
Free-radical inhibited thermal dimerization of styrene was recently reported by Bengelsdorf to produce small amounts of 1,2-diphenylcyclobutane.[15] Mayo[16] reported the formation of 1-phenyl-1,2,3,4-tetrahydronaphthalene on heating styrene with iodine.

Base-catalyzed dimerization of styrene does not seem to be described in the literature.

In the present paper we wish to report novel dimerization reactions of α-methylstyrene and styrene which are catalyzed by potassium *t*-butoxide.

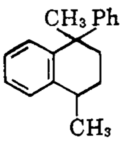
Dimerization of α-Methylstyrene in the Presence of Potassium *t*-Butoxide as Catalyst.—A dimeric product was obtained when α-methylstyrene was refluxed in the presence of 0.01 mole equivalent of $t\text{-}C_4H_9OK{\cdot}t\text{-}C_4H_9OH$. After 48 hr. of refluxing the yield of the dimers obtained amounted to 22%, based on the monomer used, and 80%, based on the monomer changed, the remainder being high molecular weight polymers. The dimeric product, which consisted of a viscous colorless oil, was composed of 6.7% of 2,5-diphenyl-2-hexene (XII) and 93.3% of 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XIII).

The structure of dimer XII was determined by means of selective hydrogenation to 2,5-diphenylhexane and by ozonolysis which yielded acetophenone. The presence of 2,5-diphenyl-1-hexene (XIV) was not detected in this particular experiment as the ozonolysis did not produce formaldehyde and gas chromatography did not show a peak corresponding to dimer XIV.

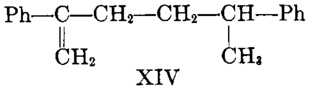


$Ph{-}\underset{CH_3}{C}{=}CH{-}CH_2{-}\underset{CH_3}{CH}{-}Ph$

XII



XIII

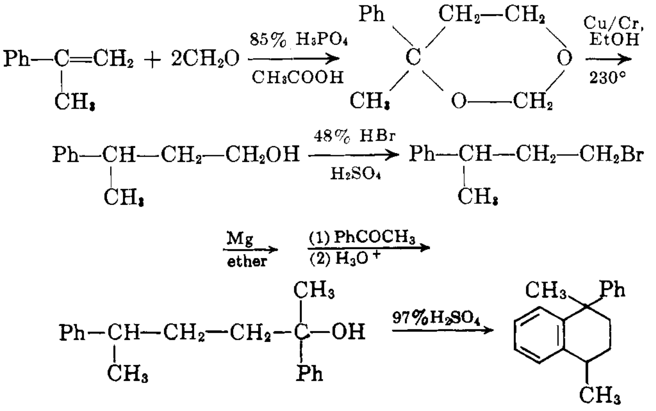


$Ph{-}\underset{\underset{CH_2}{\|}}{C}{-}CH_2{-}CH_2{-}\underset{CH_3}{CH}{-}Ph$

XIV

The structure of the main dimeric product, 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XIII) was established by independent synthesis, involving cyclodehydration of 2,5-diphenyl-2-hexanol with 97% sulfuric acid.[17,18] The synthetically produced hydrocarbon XIII was identical with the cyclic dimer XIII, according to infrared spectral analysis and gas chromatography.

Compound XIII was prepared by the sequence of reactions at the top of col. 2.



The relative rate of formation of dimer XII and XIII was determined by withdrawing liquid samples periodically during the reaction and subjecting them to selective hydrogenation and to gas chromatographic analysis before and after hydrogenation. Two sets of experiments were made at 160° using 0.01 and 0.05 mole equivalents of *t*-BuOK·*t*-BuOH, based on a α-methylstyrene. It was found that the rate of formation of the cyclic dimer XIII to open-chain dimer XII was constant and equal to about 16:1 (Table I, expt. 2).

In the absence of a catalyst (expt. 1) only about 2.2% of the α-methylstyrene dimerized and the product consisted mainly of the open-chain dimer XIV. Only 9.3% of the tetrahydronaphthalene dimer XIII was produced.

The dimerization reaction was strongly influenced by temperature. When the reaction was carried out at 225° under pressure (expt. 7) the dimerization proceeded much faster and the dimeric product was composed, after 48 hr. of heating, of the following hydrocarbons: 2,5-diphenyl-1-hexene (XIV), 68.1%; 2,5-diphenyl-2-hexene (XII), 15.3%; 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XIII), 11.0%; and 1-methyl-1,3-diphenylcyclopentane (VI), 5.6%. The composition of the dimeric material did not change drastically with the extent of the reaction.

The structure of both olefinic components was established by a combination of hydrogenation, gas chromatography, and ozonolysis. The reductive decomposition of the ozonide yielded crystalline formaldehyde–dimedone condensation product. Acetophenone was detected in the liquid part of the decomposed ozonide by means of gas chromatography. Compounds XIII and VI were determined quantitatively by gas chromatography.

At higher temperatures the dimerization reaction seems to proceed to a great extent noncatalytically as indicated by expt. 5. The presence of *t*-butylphenol does not inhibit the dimerization.

The striking difference between the results obtained at 160° and 225° suggests that different dimerization mechanisms are operating at the different temperatures.

The use of *t*-BuOK instead of *t*-BuOK·*t*-BuOH as a catalyst, either at 160° or 225°, had only a small effect upon the distribution of dimeric product (Table I). In the presence of *t*-BuOK the concentration of the tetrahydronaphthalene dimer XIII was smaller at the expense of the open-chain dimers XII and XIV.

Mechanism of Dimerization of α-Methylstyrene.—Two competitive dimerization reactions of α-methylstyrene occurred in the presence of potassium *t*-butoxide, leading to the formation of cyclic dimer XIII and open-chain dimer XII. The cyclic dimerization reaction can be interpreted by assuming the addition of

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[14] (a) B. B. Corson, J. Dorsky, J. E. Nickels, W. M. Kutz, and H. I. Thayer, *J. Org. Chem.*, **19**, 17 (1954); (b) B. B. Corson, W. J. Heintzelman, H. Moe, and C. R. Rousseau, *ibid.*, **27**, 1636 (1962).

[15] I. S. Bengelsdorf, *ibid.*, **25**, 1468 (1960).

[16] F. R. Mayo, Preprints of Papers, Division of Polymer Chemistry, 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961, Vol. 2, No. 2, p. 55.

[17] M. T. Bogert, and D. Davidson, *J. Am. Chem. Soc.*, **56**, 185 (1934).

[18] R. O. Roblin, Jr., D. Davidson and M. T. Bogert, *ibid.*, **57**, 151 (1935).

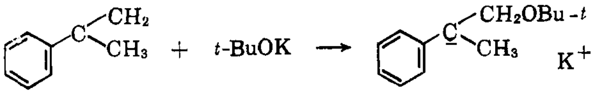
TABLE I

DIMERIZATION OF α-METHYLSTYRENE

Experiment	Catalyst (mole equiv.)	Temperature, °C.	Duration, hr.	Dimers produced	Composition of dimers[a]					
					XIII	XII	XIV	VI[b]	XVII	XVIIa
1	None	163	24	2.2	9.3		77.5	6[c]	——7.0——	
2	t-BuOK·t-BuOH (0.01)	160	4	2.0	100	Trace				
			8	4.1	94.2	5.8				
			16	7.8	93.8	6.2				
			24	11.2	93.5	6.5				
			36	16.3	93.2	6.8				
			48	21.3	93.3	6.7				
3	t-BuOK·t-BuOH (0.05)	160	48	25.1	94.2	5.8				
4	t-BuOK (0.01)	160	8	4.1	89.2	——10.8——				
			16	7.3	88.2	——11.8——				
			24	8.7	86.4	——13.6——				
			48	12.0	78.2	4.6	17.2			
5	None	215	24	15.9	12.5		73.8	11.4[c]	——2.3——	
6	p-t-Butylphenol	215	24	15.9	13.9		73.8	10.5[c]	——1.8——	
7	t-BuOK·t-BuOH (0.01)	225	8	19.1	22.9	——74.4——		2.7		
			16	30.9	15.7	——81.3——		3.0		
			24	42.4	12.8	——83.4——		3.8		
			48	60.6	11.0	15.3	68.1	5.6		
8	t-BuOK (0.01)	225	8	13.9	5.6	35.2	56.2	3.0		
			24	24.6	4.0	32.1	60.0	3.9		
			48	23.8	4.6	44.7	47.0	4.0		
9	$C_2H_5ONa \cdot 0.5C_2H_5OH$ (0.01)	160	8	0.2			100			
			24	1.7	14.0	13.7	65.3		——7.0——	
			48	4.3	22.1	12.6	57.1		——8.2——	
10	$C_2H_5ONa \cdot 0.5C_2H_5OH$ (0.01)	225	24	38.0	2.6	21.6	67.8	3.2	1.7	3.1
			48	41.5	2.6	20.0	69.1	3.8	1.6	2.9

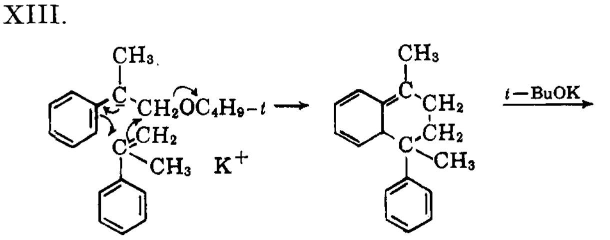
[a] XIII, 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene; XII, 2,5-diphenyl-2-hexene; XIV, 2,5-diphenyl-1-hexene; VI, 1-methyl-1,3-diphenylcyclopentane; XVII, 2,4-diphenyl-2-methylpentane; XVIIa, 2,4-diphenyl-2-methylpentenes. [b] Compound VI and the corresponding olefins. [c] After selective hydrogenation the retention time of this compound was close to compound VI. The structure of this compound will have to be verified by infrared spectroscopy.

the catalyst to the hydrocarbon as the first stage of the process. The deep purple-red color of the mixture produced after adding the catalyst to the monomer would indicate the formation of such an ionized compound XV.

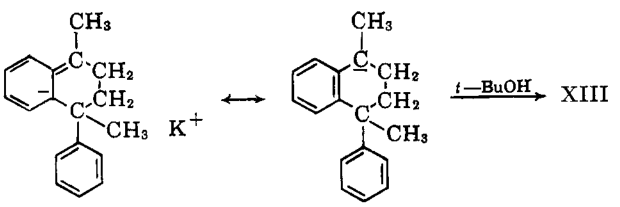


XV

The next step in the reaction could be presented by a concerted addition and elimination to form a dimer XVI, which by the usual base-catalyzed isomerization could be converted to the tetrahydronaphthalene dimer XIII.

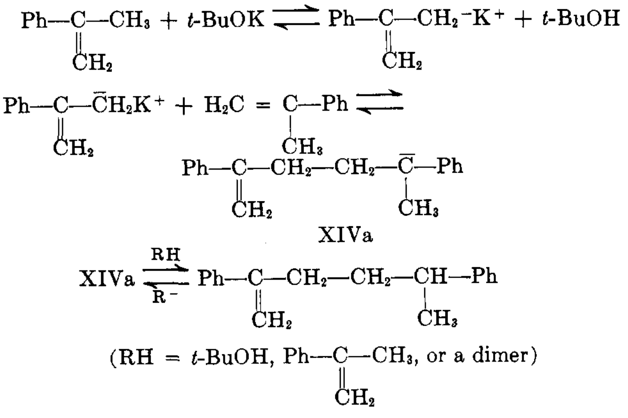


XVI



The formation of the small amount of 2,5-diphenyl-2-hexene (XII, Table I, expt. 1) at the exclusion of 2,5-diphenyl-1-hexene (XIV) is difficult to justify by any plausible mechanism.

An increase in the reaction temperature to 225° resulted in a significant increase in the production of the open-chain dimers (XII and XIV) at the expense of the tetrahydronaphthalene dimer XIII. Moreover, 2,5-diphenyl-1-hexene was the major component. In addition a small amount of 1-methyl-1,3-diphenylcyclopentane (VI) also was produced (Table I). All this indicates that at the higher temperature an alternate dimerization mechanism predominates, which in the presence of potassium t-butoxide may involve the abstraction of a proton from the allylic carbon in the α-methylstyrene molecule.



$$\mathrm{Ph{-}\underset{\substack{\|\\ CH_2}}{C}{-}CH_3} + t\text{-BuOK} \rightleftharpoons \mathrm{Ph{-}\underset{\substack{\|\\ CH_2}}{C}{-}CH_2^{-}K^{+}} + t\text{-BuOH}$$

$$\mathrm{Ph{-}\underset{\substack{\|\\ CH_2}}{C}{-}\bar{C}H_2K^{+}} + \mathrm{H_2C = \underset{\substack{|\\ CH_3}}{C}{-}Ph} \rightleftharpoons$$

$$\mathrm{Ph{-}\underset{\substack{\|\\ CH_2}}{C}{-}CH_2{-}CH_2{-}\underset{\substack{|\\ CH_3}}{\bar{C}}{-}Ph}$$

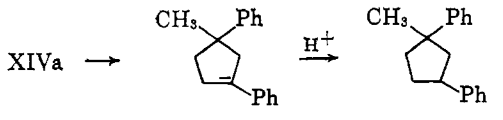
XIVa

$$\text{XIVa} \underset{R^-}{\overset{RH}{\rightleftharpoons}} \mathrm{Ph{-}\underset{\substack{\|\\ CH_2}}{C}{-}CH_2{-}CH_2{-}\underset{\substack{|\\ CH_3}}{CH}{-}Ph}$$

$$(\mathrm{RH} = t\text{-BuOH}, \mathrm{Ph{-}\underset{\substack{\|\\ CH_2}}{C}{-}CH_3}, \text{ or a dimer})$$

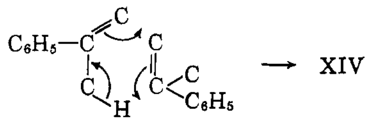
Open-chain dimer XII can be produced from XIV, according to the mechanism suggested previously.[1]

The formation of dimer VI can be explained by cyclization of XIVa followed by protonation.



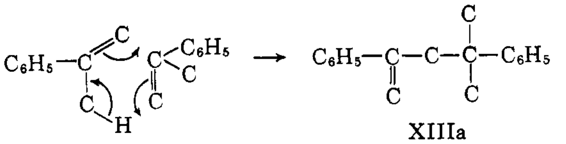
VI

In the absence of a catalyst another mechanism should be considered. The thermal dimerization does not seem to be a free-radical reaction inasmuch as the presence of p-t-butylphenol did not inhibit the dimerization rate of (Table I, expt. 6). The small amount of the cyclic dimer XIII produced could be explained by a Diels–Alder reaction leading to the intermediate formation of XVI. The formation of open-chain dimer can be accounted for by a concerted mechanism.



This type of mechanism occurring *via* a transient cyclic complex was first suggested by Arnold and Dowell[19] and also applied by others to explain thermal additions to olefins.[20,21]

The same mechanism could be used to explain the formation of the small amount of the open-chain dimer, which after selective hydrogenation yields 2-methyl-2,4-diphenylpentane.



XIIIa

Effect of t-Butyl Alcohol upon the Dimerization of α-Methylstyrene.—The dimerization of α-methylstyrene in the presence of potassium t-butoxide containing various amounts of t-butyl alcohol had been investigated (Table II). The alcohol added corresponded to 1, 2, 5, and 10 molar equivalents based on potassium t-butoxide used in the reaction; the temperature was maintained at 160°.

The addition of t-butyl alcohol to the catalyst seemed to have little effect upon the distribution of dimers, although the concentration of the cyclic dimer XIII was slightly lower when potassium t-butoxide as such was used as catalyst. The extent of dimerization was diminished however drastically when the molar ratio of t-butyl alcohol to potassium t-butoxide added was increased from five to ten.

Table II

Dimerization of α-Methylstyrene at 160° in the Presence of t-BuOK[a] Containing Various Amounts of t-BuOH

Experiment	Moles of t-BuOH per mole of t-BuOK	Duration, hr.	Dimers produced, wt. %	Composition of dimers[b] XIII	XIV	XII
11	0	8	5.9	91.9	4.7	3.4
		24	11.6	87.9	8.6	3.5
12	1	8	5.4	93.6	3.6	2.8
		24	13.9	91.9	5.1	3.0
13	2	8	4.0	94.5	3.7	1.8
		24	13.8	94.1	3.4	2.5
14	5	8	2.5	95.5	——4.5——	
		24	10.0	94.2	4.0	1.8
15	10	8	0.8			
		24	2.7	94.6	——5.4——	

[a] In each experiment 0.01 mole equivalent of t-BuOK was used. [b] XIII, 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene; XIV, 2,5-diphenyl-1-hexene; XII, 2,5-diphenyl-2-hexene.

Dimerization of α-Methylstyrene in the Presence of Sodium Ethoxide.—The dimerization was studied using 0.01 molar equivalent of sodium ethoxide–ethyl alcohol ($C_2H_5ONa{\cdot}0.5C_2H_5OH$). The experimental results given in Table I show that at 160° the rate of dimerization in the presence of sodium ethoxide was slower and that the composition of the dimeric product was different from that obtained with potassium t-butoxide as catalyst. With the ethoxide the open-chain dimers XIV and XII were the principal reaction products and in addition to the tetrahydronaphthalene dimer XIII, 2,4-diphenyl-2-methylpentane (XVII) together with the corresponding olefins was also produced. When the dimerization was carried out at 225° the only significant difference in activity between the two catalysts was that in the presence of sodium ethoxide the dimeric product contained compound XVII with the corresponding olefins.

The comparison of the results obtained in the presence and absence of sodium ethoxide suggests that the latter has only a slight catalytic effect at 160° and that the dimerization occurred primarily *via* a thermal reaction; at 225° the catalytic effect seems to be more pronounced. It is interesting also to note that dimers having a 2,4-diphenyl-2-methylpentane skeleton were formed only when the dimerization was made either in the absence of a catalyst or in the presence of sodium ethoxide. The formation of XII is an indication of a catalytic isomerization of XIV.

Dimerization of p-Chloro-α-methylstyrene.—The title compound was dimerized by means of 0.02 molar equivalent of t-BuOK·t-BuOH. At 165° the rate of reaction was very slow and after 48 hr. of heating only 2.8% of the monomer reacted, which compares with 21% of reaction observed with α-methylstyrene under similar conditions. A relatively high conversion of p-chloro-α-methylstyrene was obtained at 200° and 72 hours of heating. The product, after being washed, dried, and distilled under reduced pressure, yielded 26% of dimers based on monomer used, or 48% based on monomer reacted. A crystalline material separated from the dimeric distillate which melted at 84–85°; it was identified as 2,5-di(p-chlorophenyl)-2-hexene (XVIII).

The dimers were composed of compound XVIII, 51%; 2,5-di(p-chlorophenyl)-1-hexene (XIX), 20%; 1,4-dimethyl-1-(p-chlorophenyl)-1,2,3,4-tetrahydro-6-chloronaphthalene (XX), 19%; 1-methyl-1,3-di(p-chlorophenyl)cyclopentane (XXI) and skeletally identical cyclopentenes, 1.4%; 2-methyl-2,4-di(p-chlorophenyl)pentane and skeletally identical pentenes, 4%; and nonidentified dimers, 4.6%. The composition of the dimeric fraction was determined by the combined use of gas chromatography, selective hydrogenation, and dehalogenation of the original and of the selectively hydrogenated dimeric material.

The selective hydrogenation was made at atmospheric pressure using palladium catalyst; under these

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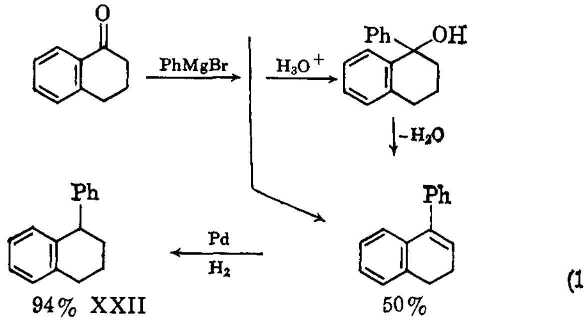
[19] R. T. Arnold and J. F. Dowell, *J. Am. Chem.Soc.*, **70**, 2590 (1948).

[20] M. J. Hogstedt and R. V. Lindsey, *ibid.*, **76**, 2305 (1954).

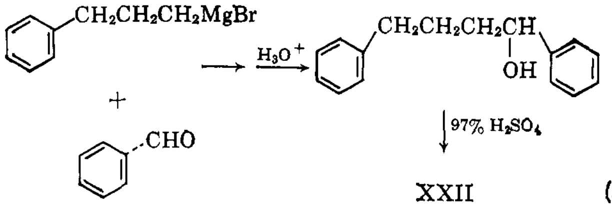
[21] C. J. Albisetti, N. G. Fisher, M. J. Hogsted, and R. M. Joyce, *ibid.*, **78**, 2637 (1956).

conditions only the olefinic double bonds underwent hydrogenation. The dehalogenation was made by treating the original and the selectively hydrogenated dimers in tetrahydrofuran solution with magnesium. After hydrolysis the dimers were converted to the corresponding hydrocarbons. The positions of the double bonds were not affected by the dehalogenation reaction.

Dimerization of Styrene.—We found that stabilized styrene undergoes dimerization in the presence of *t*-BuOK·*t*-BuOH as catalyst. The dimer produced in 11% yield, based on styrene reacted, was 1-phenyl-1,2,3,4-tetrahydronaphthalene (XXII); the remainder of the product was composed of high polymeric material. The structure of XXII was proved by two independent syntheses.



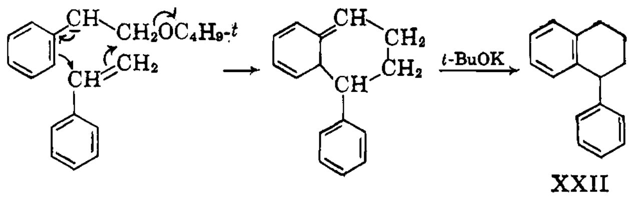
(1)



(2)

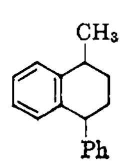
The two synthetic compounds XXII were found to be identical with the styrene dimer, according to gas chromatography and infrared spectroscopy.

The dimerization reaction can be explained by a mechanism similar to the one suggested for the dimerization of α-methylstyrene.

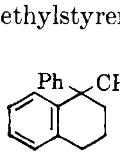


In the absence of the alkoxide after 4 hr. of heating, about 90% of styrene polymerized without detectable formation of dimers.

Codimerization of Styrene with α-Methylstyrene.—The reaction was carried out by refluxing for 24 hr. a solution consisting of 1 mole equivalent of styrene, (stabilized, purchased from Matheson Coleman and Bell, Cincinnati 12, Ohio), 0.5 of α-methylstyrene, and 0.01 of *t*-BuOK·*t*-BuOH as catalyst. The "dimers" which amounted to 12% by weight of α-methylstyrene used contained, according to the hydrogen number, 1–2% olefinic material. After selective hydrogenation the "dimers" were composed of 1-phenyl-1,2,3,4-tetrahydronaphthalene (XXII), 48%; 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XIII), 7%; 1 - methyl - 4 - phenyl - 1,2,3,4 - tetrahydronaphthalene (XXIII), 32%; and 1-methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XXIV), 13%. Compound XIII is a dimer of α-methylstyrene, while XXIII and XXIV are codimers of styrene with α-methylstyrene.



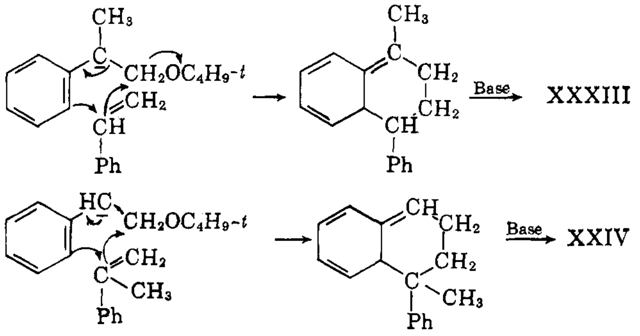
XXIII



XXIV

The composition of the product was established by means of gas chromatography, comparing the retention times of the product with the retention times of synthetically prepared compounds.

Compound XXIV was prepared by cyclodehydration of 2,5-diphenyl-2-pentanol with 97% sulfuric acid at room temperature, according to the procedure of Adkins and Davis.[22] The codimer XXIII was synthesized by a similar procedure starting from 1,4-diphenyl-1-pentanol. The formation of codimer XXIII and XXIV can be explained by the addition of the catalyst to α-methylstyrene and styrene, respectively, as the first step in the reaction, followed by reaction of the adducts with styrene and α-methylstyrene.



The codimerization reaction was accompanied by an extensive polymerization of styrene to high molecular weight compounds.

Experimental

A. **Gas Chromatography.**—The purity of all hydrocarbons prepared and the composition of reaction products were determined by gas chromatography using a F & M Model 300 programmed temperature gas chromatograph; the description of the columns is given in Table III. All quantitative determinations

TABLE III

DESCRIPTION OF GAS–LIQUID PHASE CHROMATOGRAPHIC COLUMNS USED IN ANALYSIS

Column	1	2	3	4
Liquid phase	8% silicone 550[a]	8% silicone gum rubber[b]	30% QF-1[c]	15% Carbowax 20 M[b]
Solid support		Chromosorb	P[b]	
Mesh	30/60	30/60	100/120	30/60
Length of column, m.	4	2.4	7.5	4.0
Theoretical plates	3000	1000	3500	2500
Flow rate (ml. He/min.)	75	75	50	75
Inlet pressure, atm.	2.4	2.4	3.4	2.4
Column temperature, °C.	215	225	200	225

[a] Dow Corning 550 fluid. [b] Supplied by Wilkens Instrument and Research Inc., Walnut Creek, Calif. [c] Dow Corning fluorinated silicone fluid.

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[22] H. Adkins and J. W. Davis, *J. Am. Chem. Soc.*, **71**, 2955 (1949).

TABLE IV

RELATIVE RETENTION TIMES OF DIMERS

Column	1 Silicone 550	2 Silicone gum		3 QF-1
Compound:				
1,2-Diphenylbutane	1.00	1.00		1.00
2-Methyl-2,4-diphenylpentane	1.58	1.22		
2,5-Diphenylhexane (*meso* and *dl*)	1.90[a]	1.74		
1-Phenyl-1,2,3,4-tetrahydronaphthalene (XXII)	1.98			1.69
1-Methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XXIV)	2.32			1.84
1-Methyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (XXIII)	2.32			1.95
2,5-Diphenyl-1-hexene (XIV)	2.38	2.10		
2,5-Diphenyl-2-hexene (XII)	2.85	2.32		
1,4-Dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XIII)	2.56	2.10	1.00	2.01
1-Methyl-1,3-diphenylcyclopentane (VI)	3.45	2.68		
2,5-Di(*p*-chlorophenyl)hexane		6.71	3.11	
2,5-Di(*p*-chlorophenyl)-1-hexene		7.71	3.57	
2,5-Di(*p*-chlorophenyl)-2-hexene		9.13	4.22	
1,4-Dimethyl-1-(*p*-chlorophenyl)-1,2,3,4-tetrahydro-6-chloronaphthalene		7.84	3.63	
1-Methyl-1,3-di(*p*-chlorophenyl)-cyclopentane		10.4	4.85	

[a] At 190° column temperature two peaks were observed having relative retention times of 2.03 and 2.10.

were made using 1,2-diphenylbutane as an internal standard. The peaks were identified using relative retention times listed in Table IV and the triangulation procedure was used for measuring the peak areas. In the case of overlapping peaks the method given by Bartlett and Smith[23] was used. Theoretical plate numbers for the different columns were obtained by the method described previously.[24]

B. Catalyst. 1. Preparation of *t*-BuOK·*t*-BuOH.—Freshly cut potassium metal, 13.6 g., was added to 250 g. of anhydrous *t*-butyl alcohol and the mixture refluxed for 6 hr., until a clear solution has been obtained. The excess alcohol was then removed at steam bath temperature and at 15–20-mm. pressure. The dry residue was powdered and kept for 2 days over phosphorus pentoxide. The catalyst (58 g.) thus prepared consisted, according to titration with 0.2 *N* hydrochloric acid, of the molecular compound $t\text{-}C_4H_9OK \cdot t\text{-}C_4H_9OH$.

2. Potassium *t*-Butoxide.—This alkoxide which was purchased from K and K Laboratories, Inc., Jamaica, N. Y., was 99% pure, as determined by titration.

3. Preparation of $C_2H_5ONa \cdot 0.5C_2H_5OH$.—The alkoxide was prepared from sodium and absolute ethanol, according to the procedure described previously for potassium *t*-butoxide.

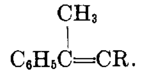
C. Dimerization of α-Methylstyrene. 1. Dimerization in the Presence of *t*-BuOK·*t*-BuOH at 160° (Expt. 2).—The catalyst, 9.3 g. (0.05 mole), was added to 590 g. (5 moles) of α-methylstyrene. An orange-red color appeared and evolution of heat was observed. The mixture was refluxed at 160° for 48 hr. and during the reaction liquid samples were withdrawn periodically for analysis. The main portion of the unchanged α-methylstyrene, 397 g., was removed at 45–50° (7 mm.), and the residue was poured into 250 ml. of water. The hydrocarbon layer was diluted with 300 ml. of diethyl ether, washed with water, dried over anhydrous magnesium sulfate, and distilled. The distillation afforded an additional 24 g. of α-methylstyrene and 131 g. of colorless viscous oil, b.p. 166–167° (7 mm.), $n^{20}D$ 1.5825. Resinous material left in the flask after distillation amounted to 32 g.

a. Hydrogenation of α-Methylstyrene Dimer.—The dimer 23.6 g. (0.1 mole) in 70 ml. of ethyl acetate was selectively hydrogenated at room temperature and at atmospheric pressure in the presence of 2 g. of 10% palladium on charcoal; 0.06 mole of hydrogen was absorbed per mole of dimers. The hydrogenated hydrocarbon was 2,5-diphenylhexane, as determined by gas chromatography.

The hydrogenated dimeric material was distilled on a Glover–Piros spinning-band column (H. S. Martin and Co., Evanston, Ill., Catalog N-8480). The fraction distilling at 150–150.5° (3.5 mm.), 9.8 g., $n^{20}D$ 1.5800, λ_{max} 2619 Å. (B-band), consisted of 96% 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene, as compared by gas chromatography and infrared spectroscopy with synthetically prepared hydrocarbon.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.45; H, 8.55. Found: C, 91.38; H, 8.61.

b. Ozonolysis of α-Methylstyrene Dimer.—The dimer, 4.7 g. (0.02 mole), dissolved in 25 ml. of carbon tetrachloride, was ozonized at −20°. The ozonide was then refluxed for 1 hr. with 5 ml. of acetic acid and 2 g. of zinc powder and the gases evolved were passed through a trap containing a solution of 0.5 g. of dimedone in 25 ml. of water and 10 ml. of 95% ethanol. A precipitate was not formed which indicates that formaldehyde was not produced and therefore the dimers did not contain hydrocarbons with a methylenic double bond. This is also in agreement with gas chromatographic analysis which failed to indicate the presence of dimer XII in the reaction product.

The liquid organic product from ozonolysis was analyzed by gas chromatography; acetophenone was detected which proves that the dimeric product contained hydrocarbons with a structure of  $C_6H_5\overset{CH_3}{\overset{|}{C}}{=}CR$.

c. Kinetic Studies of α-Methylstyrene Dimerization.—A profile of α-methylstyrene dimerization has been studied at 160° and 225° using potassium *t*-butoxide–*t*-butyl alcohol and potassium *t*-butoxide as catalysts. The results are summarized in Table I. Experiments were carried out using 59.0 g. (0.5 mole) of α-methylstyrene, 0.56 g. (0.005 mole) of potassium *t*-butoxide or 0.93 g. (0.005 mole) of potassium *t*-butoxide–*t*-butyl alcohol, and 1,2-diphenylbutane as an internal standard for chromatographic analysis. Reactions at 225° were made under 25 atm. of nitrogen in a rotating autoclave fitted with a glass liner and internal thermocouple well. Samples were taken out periodically, washed with water, dried over anhydrous magnesium sulfate, hydrogenated in the presence of 10% palladium-on-charocal catalyst and analyzed by gas chromatography. Owing to the overlapping of peaks of 2,5-diphenyl-2-hexene (XII) with 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XIII) on a silicone 450 column, the amount of compound XII was established by subtracting the per cent of 2,5-diphenyl-1-hexene present in the original dimer from the total 2,5-diphenylhexane obtained after hydrogenation of the dimer.

2. Ozonolysis of α-Methylstyrene Dimers (Expt. 7, Table I).—The dimers, 2.36 g. (0.01 mole), were dissolved in 25 ml. of carbon tetrachloride and ozonized at −20°. The ozonide was then reductively decomposed at reflux temperature with 10 ml. of acetic acid and 10 g. of zinc powder. The formaldehyde produced was trapped in a solution of 3 g. of dimedone in 150 ml. of water and 75 ml. of 95% ethanol. The crystalline precipitate thus formed, 1.75 g., melted at 188–189°. The yield of formaldehyde produced was 60%, based on 2,5-diphenyl-1-hexene present in the dimers.

The presence of acetophenone in the liquid product from ozonolysis was detected by gas chromatography using a Carbowax column.

3. Dimerization of α-Methylstyrene in the Presence of Potassium *t*-Butoxide Containing Various Amounts of *t*-Butyl Alcohol (Table II).—The experiments were made at 160° using 17.7 g. (0.15 mole) of α-methylstyrene, 0.17 g. (0.0015 mole) of potassium *t*-butoxide, 0 to 0.015 *M* of *t*-butyl alcohol, and 1,2-diphenylbutane as an internal standard. Potassium *t*-butoxide was mixed with the *t*-butyl alcohol just before use. Samples were taken after 8 and 24 hr. of reaction time. They were washed with water, dried, and analyzed by gas chromatography.

4. Dimerization of α-Methylstyrene in the Presence of Sodium Ethoxide.—The reaction has been studied at 160° and 225°. Experiments were carried out using 35.4 g. (0.3 mole) of α-methylstyrene, 0.27 g. (0.003 mole) of $C_2H_5ONa \cdot 0.5C_2H_5OH$ catalyst, and 1,2-diphenylbutane added as an internal standard for gas chromatographic analysis. The reaction at 225° was performed in a rotating autoclave, under 20 atm. of nitrogen according to the procedure described under 1c. Samples were worked up and analyzed by the method described previously. 2,4-Diphenyl-2-methylpentane was identified chromatographi-

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[23] J. C. Bartlett and D. M. Smith, *Can. J. Chem.*, **38**, 2057 (1960).

[24] S. M. Csicsery and H. Pines, *J. Chromatog.*, **9**, 34 (1962).

cally by comparison with synthetically prepared sample of this hydrocarbon. The results are summarized in Table I.

D. **Dimerization of *p*-Chloro-α-methylstyrene in the Presence of Potassium *t*-Butoxide Catalyst.**—Potassium *t*-butoxide–*t*-butyl alcohol catalyst, 2.9-g., (0.016 mole) was added to 122 g. (0.8 mole) of freshly distilled *p*-chloro-α-methylstyrene. A green-blue color appeared which turned slowly to brown. The mixture was heated at 200 ± 5° for 72 hr. in a rotating autoclave under 20 atm. of nitrogen. The product was diluted with 100 ml. of ether, washed with water, dried, and distilled under reduced pressure; 56 g. of unchanged monomer, b.p. 92–96° (18 mm.), and 32 g. of yellow, very viscous oil (dimers), b.p. 240–243° (18 mm.), were recovered. Brown hard resin, 31 g., remained in the distillation flask. The oil crystallized partially on standing for 24 hr. and the crystals 10.1 g., were filtered off with suction and washed with cold *n*-pentane. The solid on crystallization from methanol yielded white plates, m.p. 84–85°. It was identified as 2,5-di(*p*-chlorophenyl)-2-hexene.

Anal. Calcd. for $C_{18}H_{18}Cl_2$: C, 70.83; H, 5.94. Found: C, 71.23; H, 5.98.

The oily residue, 21.8 g., n^{25}_{D} 1.5850, was investigated separately.

1. **Hydrogenation of 2,5-di(*p*-chlorophenyl)-2-hexene.**—The olefin, 1.53 g., was dissolved in 20 ml. of ethyl acetate and hydrogenated at room temperature and atmospheric pressure over 10% palladium-on-charcoal catalyst. The theoretical amount of hydrogen was absorbed. After removing the solvent under reduced pressure, the residue was recrystallized from methanol; it produced small white plates, melting at 58–59°; yield, 1.50 g. or 97%.

Anal. Calcd. for $C_{18}H_{20}Cl_2$: C, 70.37; H, 6.56. Found: C, 70.55; H, 6.62.

2. **Dehalogenation of 2,5-Di(*p*-chlorophenyl)-2-hexene.**—A mixture of 1.53 g. (0.005 mole) of 2,5-di(*p*-chlorophenyl)-2-hexene, 0.48 g. (0.02 mole) of magnesium, 3 ml. of tetrahydrofuran, and 0.5 ml. of ethyl bromide, was refluxed for 6 hr.[25] The solution obtained was then decomposed with 20 ml. of 10% sulfuric acid, extracted with 15 ml. of ether, washed with water, and dried. After removal of the solvent a colorless oil was obtained, 1.0 g., n^{25}_{D} 1.5710, which was identified by gas chromatography as a pure sample of 2,5-diphenyl-2-hexene.

3. **Hydrogenation of the Oily Dimer.**—The oily dimer, 2.41 g., was dissolved in 10 ml. of ethyl acetate and hydrogenated at room temperature and atmospheric pressure over 10% palladium on charcoal. The hydrogen number calculated from the hydrogen uptake was 0.70. This value is in agreement with 71% of 2,5-di(*p*-chlorophenyl)hexene present in the product as determined chromatographically.

4. **Dehalogenation of the Oily Dimer.**—The dimer, 9.16 g., was hydrogenated and then dehalogenated according to the methods described previously. A yellow thick oil was obtained, 5.4 g., n^{25}_{D} 1.5573, 76% yield.

5. **Composition of the Dimeric Products.**—The dimeric material, after removal of the solid dimer which separated out, was analyzed by gas chromatography before and after hydrogenation and after respective dehalogenations. From the composite results it was established that the liquid dimeric fraction had the following composition: compound XIX, 29%; XVIII, 28%; XX, 27%; XXI, 2%; compounds which were not identified, 14%.

The hydrogenated and dehalogenated product was composed of 2,5-diphenylhexane, 58%; 2,4-diphenyl-2-methylpentane, 6%; the cyclic dimer XIII, 24%; 1-methyl-1,3-diphenylcyclopentane, 2%; compounds which were not identified, 10%.

The composition of the total dimers produced, including the solid dimer which separated out, was calculated and given in the text under "Dimerization of *p*-Chloro-α-methylstyrene."

E. **Dimerization of Styrene.**—Potassium *t*-butoxide–*t*-butyl alcohol, 7.4 g. (0.04 mole), was added to 208 g. (2 mole) of styrene (stabilized purchased from Matheson Coleman and Bell, Cincinnati 12, Ohio); a reddish violet color was produced which turned to lemon yellow on heating. The mixture was refluxed for 24 hr. and then flash distilled under reduced pressure. About 97 g. or 46% of styrene was recovered. The fraction boiling at 171–174° (13 mm.) was collected, diluted with 50 ml. of ether, washed with water, and dried. On redistillation 12.6 g. of colorless, blue fluorescent oil was obtained, boiling at 157° (6 mm.), n^{20}_{D} 1.5930, and which was 98% pure, according to gas chromatography. The product contained 1–2% of olefinic contaminants, according to selective hydrogenation at room temperature and pressure using palladium-on-charcoal catalyst and ethyl acetate as solvent.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.52; H, 8.09.

F. **Codimerization of Styrene and α-Methylstyrene.**—The mixture consisting of 177 g. (1.5 moles) of α-methylstyrene, 312 g. (3.0 moles) of stabilized styrene, and 11.2 g. (0.06 moles) of *t*-BuOK·*t*-BuOH was refluxed for 24 hr. The product was diluted with 500 ml. of benzene, washed with water, and dried. On distillation under reduced pressure 39.2 g. of colorless viscous oil was obtained which distilled at 157–160° (6 mm.), n^{25}_{D} 1.5861. The composition of the "dimeric" product, which is given in the discussion part, was established by gas chromatography.

G. **Synthesis of Hydrocarbons.** 1. **1-Phenyl-1,3-dimethyl-1,2,3,4-tetrahydronaphthalene.** a. **4-Methyl-4-phenyl-1,3-dioxane** was prepared from 708 g. (6 moles) of α-methylstyrene according to the method of Price, et al.[26] The fraction boiling at 116–144° (10 mm.) solidified on freezing. On recrystallization from *n*-pentane colorless needles were obtained melting at 39–40°, 484 g., 45% yield, lit.[26] m.p. 39–40°.

b. **3-Phenyl-1-butanol.**—4-Methyl-4-phenyl-1,3-dioxane, 178 g. in 200 ml. of absolute ethanol was hydrogenolyzed in a rocking autoclave at 230° and 120–200 atm. of hydrogen in the presence of 18 g. of copper chromite catalyst, according to the procedure of Emerson, *et al.*[27] On distillation a colorless oil was obtained, b.p. 121–122° (12 mm.), n^{25}_{D} 1.5168; yield, 125 g. or 85%; lit.[27] b.p. 121–123° (13 mm.), n^{25}_{D} 1.5165.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.71; H, 9.42.

c. **3-Phenylbutyl Bromide.**—A mixture consisting of 120 g. (0.8 mole) of 3-phenyl-1-butanol, 170 g. of 48% hydrobromic acid, and 45 g. of 97% sulfuric acid was refluxed for 4 hr. and then diluted with 1000 ml. of water. The bromide distilled at 110–111° (10 mm.), n^{25}_{D} 1.5340, 113 g., 66% yield, lit.[28] b.p. 108–110° (8 mm.).

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.36; H, 6.15. Found: C, 56.24; H, 6.21.

d. **Synthesis and Cyclodehydration of 2,5-Diphenyl-2-hexenol.**—The alcohol was prepared by the usual procedure from 32 g. (0.15 mole) of 3-phenylbutyl bromide, 3.6 g. (0.15 g.-atom) of magnesium, 24 g. (0.2 mole) of acetophenone, and 75 ml. of ether. The solvent and low-boiling contaminants were removed at below 100° under reduced pressure. The residual crude 2,5-diphenyl-2-hexanol, 36.0 g., was a thick yellow oil which could not be distilled without decomposition. It was placed in a 100-ml. three-necked flask fitted with a high-speed stirrer, thermometer, and a dropping funnel. Sulfuric acid (97%, 36 ml.) was added to it over 20 min., and the mixture was stirred for an additional 15 min. while the temperature of the mixture was kept at 15–20°, and then poured into 250 ml. of ice-cold water. The oil was extracted with ether, washed with 5% sodium carbonate solution, dried, and distilled under reduced pressure. On redistillation, 1,4-dimethyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XIII) was obtained of 98% purity; it distilled at 177–178° (10 mm.), n^{20}_{D} 1.5792, lit.[29] b.p. 155° (3 mm.), n^{25}_{D} 1.5801, and was identical, according to infrared spectroscopy and gas chromatography, with the saturated α-methylstyrene dimer XIII; yield, 14 g. or 38%.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.45; H, 8.55. Found: C, 91.13; H, 8.61.

2. **2-Methyl-2,4-diphenylpentane.** a. **4-Methyl-4-phenyl-2-pentanone.**—The ketone was prepared in 70% yield, according to the procedure described by Hoffman[30]; it distilled at 108–112° (7 mm.), n^{20}_{D} 1.5120.

b. **2-Methyl-2,4-diphenylpentenes** were prepared from the corresponding alcohol. The alcohol was synthesized from 44 g. (0.25 mole) of 4-methyl-4-phenyl-2-pentanone, 39 g. (0.25 mole) of bromobenzene, and 6.1 g. (0.25 g.-atom) of magnesium. The crude alcohol was dehydrated by refluxing with 50 ml. of 20%

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[25] H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn, and R. S. Cserr, *J. Org. Chem.*, **22**, 1202 (1957).

[26] C. C. Price, F. L. Benton, and C. J. Schmidle, *J. Am. Chem. Soc.*, **71**, 2860 (1949).

[27] W. S. Emerson, R. L. Heider, R. I. Longley, Jr., and T. C. Shafer, *ibid.*, **72**, 5314 (1950).

[28] J. v. Braun, A. Grabowski, and G. Kirschbaum, *Ber.*, **46**, 1266 (1913).

[29] M. S. Hogsed (to E. I. du Pont de Nemours and Co.). U. S. Patent 2,714,621; *Chem. Abstr.*, **50**, P7139 (1956).

[30] A. Hoffman, *J. Am. Chem. Soc.*, **51**, 2542 (1929).

sulfuric acid for 1 hr. and the olefins produced, 33.0 g. (56% yield), distilled at 164–165° (9 mm.), n^{20}D 1.5700. According to gas chromatography the olefins consisted of a mixture of *cis*- and *trans*-2,4-diphenyl-4-methyl-2-pentene together with 4-methyl-2,4-diphenyl-1-pentene.

c. **2-Methyl-2,4-diphenylpentane.**—The olefinic mixture, 7.1 g., was dissolved in 10 ml. of ethyl acetate and hydrogenated at room temperature and atmospheric pressure over 0.5 g. of 5% palladium on charcoal. The hydrogenated product, 6.1 g. (85%), distilled at 149–149.5° (6 mm.), n^{20}D 1.5476, and was chromatographically pure.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.63; H, 9.20.

3. **1-Methyl-1,3-diphenylcyclopentane.**—This compound was produced by the dimerization of α-methylstyrene in the presence of sodium.[8] The sodium (2.3 g., 0.1 g.-atom) was dispersed by means of a high-speed stirrer in 59.0 g. (0.5 mole) of freshly distilled α-methylstyrene and the dark brown mixture obtained was refluxed for 4 hr. The catalyst was decomposed by adding 30 ml. of ethanol and the solution was poured into 250 ml. of water. The oil was extracted with benzene, washed with water, and dried. The product was separated by means of distillation into the following fractions: (1) b.p. 167–174° (7 mm.), 3.0 g., n^{25}D 1.5630; (2) 174–184°, 16.0 g., n^{25}D 1.5696; (3) 184–193°, 6.0 g., n^{25}D 1.5752. Cut 2 was redistilled on a column of about sixty theoretical plates and the following fractions were collected: (a) b.p. 167–172° (7 mm.), 2.4 g.; (b) 172–174.5°, 1.8 g., n^{20}D 1.5666; (c) 175–178°, 3.8 g., n^{20}D 1.5706; (d) 178–179.5°, 5.1 g., n^{20}D 1.5743. Cuts b and c contained 85–95% of 1-methyl-1,3-diphenylcyclopentane. Cut d was 98% pure according to gas chromatography. Its infrared spectrum was the same as obtained previously.[8]

Anal. Calcd. for $C_{18}H_{20}$: C, 91.45; H, 8.55. Found: C, 91.40; H, 8.35.

4. **1,2-Diphenylbutane.**—To a stirred Grignard reagent prepared from 31.6 g. (0.25 mole) of benzyl chloride and 6.1 g. (0.25 g.-atom) of magnesium in 100 ml. of ether was added 33.5 g. (0.25 mole) of propiophenone in 35 ml. of ether. The alcohol thus obtained was dehydrated with 30 ml. of acetic acid and 0.5 ml. of 96% sulfuric acid and refluxed for 6 hr. The olefins produced distilled at 175–178° (20 mm.), n^{25}D 1.5946, and, according to the gas chromatography, consisted of a mixture of *cis*- and *trans*-1,2-diphenyl-1- and 2-butenes. The diphenylbutenes were hydrogenated at atmospheric pressure and temperature in the presence of 10% palladium-on-charcoal catalyst. The 1,2-diphenylbutane thus obtained, 26.8 g., distilled at 165–166° mm.), n^{25}D 1.5498; it was 99% pure.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.14; H, 8.63.

5. **1-Phenyl-1,2,3,4-tetrahydronaphthalene**. a. **3-Phenylpropyl bromide** which was prepared from 136 g. (1 mole) of 3-phenyl-1-propanol, 204 g. (1.2 moles) of 48% hydrobromic acid, and 55 g. of 97% sulfuric acid,[31] distilled at 102–103° (9 mm.), n^{25}D 1.5439; yield, 130 g. or 65%; lit.[31] b.p. 110–113° (11 mm.), n^{25}D 1.5440.

b. **1,4-Diphenyl-1-butanol.**—To the Grignard reagent, prepared from 6.1 g. (0.25 g.-atom) of magnesium and 50 g. (0.25 mole) of 3-phenylpropyl bromide in 100 ml. of ether, was added 26.5 g. (0.25 mole) of benzaldehyde in 30 ml. of ether. Distillation afforded 40.5 g., 71% yield, of colorless viscous oil, b.p. 197–198° (9 mm.), n^{25}D 1.5636, which solidified on standing. On crystallization from *n*-pentane thin long needles were obtained which melted at 50°.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.06; H, 7.79.

c. **1-Phenyl-1,2,3,4-tetrahydronaphthalene (XXII).**—The cyclodehydration of 22.6 g. of 1,4-diphenyl-1-butanol to the title compound was made according to the procedure described under G1d of Experimental. Compound XXII which was obtained in 63% yield, distilled at 166–167° (10 mm.), n^{20}D 1.5925, and was 99% pure and identical, according to infrared spectra and gas chromatography, with the dimer secured from styrene.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.74; H, 7.52.

6. a. **1-Phenyldihydronaphthalene.**—The compound was prepared as described by Weiss and Woidich[32] from 3.6 g. (0.15 g.-atom) of magnesium, 23.6 g. (0.15 mole) of bromobenzene, and 21.9 g. (0.15 mole) of α-tetralone in 85 ml. of ether. On crude distillation *in vacuo* 15.5 g. (50%) of thick yellow oil was collected. After redistillation it boiled at 175–176° (10 mm.), n^{25}D 1.6291, and was found to be about 99% pure (lit.[32] b.p. 175–177° at 12 mm.).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16%, H, 6.84%. Found: C, 93.25%; H, 6.62%.

b. **1-Phenyl-1,2,3,4-tetrahydronaphthalene.**—1-Phenyldihydronaphthalene (6.2 g., 0.03 mole) was hydrogenated in 10 ml. of ethyl acetate over 0.5 g. of 5% palladium on charcoal at room temperature and atmospheric pressure. The distillation yielded 5.9 g., 94% yield, of a colorless oil, b.p. 167–168° (10 mm.), n^{20}D 1.5950, which was about 95% pure according to gas chromatography. The compound was found to be identical with the authentic hydrocarbon prepared according to procedure 5.

7. **1-Methyl-1-phenyl-1,2,3,4-tetrahydronaphthalene (XXIV).**—2,5-Diphenyl-2-pentanol prepared from 6.1 g. (0.25 g.-atom) of magnesium, 50 g. (0.25 mole) 3-phenylpropyl bromide, and 30 g. (0.25 mole) acetophenone, was cyclodehydrated by means of sulfuric acid, according to the method described in a preceding section. Compound XXVI thus obtained, 16.5 g. (50% yield), distilled at 175–177° (12 mm.), n^{25}D 1.5855, and was 98% pure; lit.[22] b.p. 129–131° (1 mm.), n^{25}D 1.5853.

Anal. Calcd. for $C_{17}H_{28}$: C, 91.84; H, 8.16. Found: C, 91.75; H, 8.35.

8. **1-Methyl-4-phenyl-1,2,3,4-tetrahydronaphthalene (XXIII).** a. **1,4-Diphenyl-1-pentanol** was prepared from 53.3 g. (0.24 mole) of 3-phenylbutyl bromide, 6.1 g. (0.25 g.-atom) of magnesium, and 26.5 g. (0.25 mole) of benzaldehyde in 150 ml. of ether. The alcohol distilled at 201–202° (11 mm.), n^{25}D 1.5553; yield, 40 g. or 67%.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.78; H, 8.69.

b. **1-Methyl-4-phenyl-1,2,3,4-tetrahydronaphthalene.**—1,4-Diphenyl-1-pentanol, 24 g. (0.1 mole) was cyclized by the method described under G1d. On distillation a colorless viscous oil was obtained, b.p. 177–178° (12 mm.), n^{20}D 1.5825; yield, 13.5 g. or 61%. The compound was 99% pure by gas chromatography; lit.[33] b.p. 175° (12 mm.), n^{20}D 1.5910.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.62; H, 8.35.

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