[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Free Radical Addition Reactions Involving Possible Rearrangement[1]

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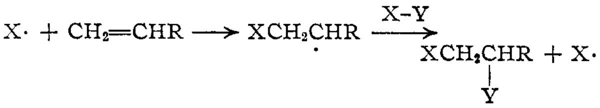
The free radical addition of thiolacetic acid and butyl mercaptan to 3,3-diphenyl-1-butene proceeds without any detectable rearrangement. A similar addition of *n*-butyraldehyde goes with rearrangement to form 6,7-diphenyl-4-octanone. These data support the concept that rearrangement proceeds from the intermediate radical formed by the addition of a radical to the olefin and that the amount of rearrangement is a function of the lifetime of the intermediate.

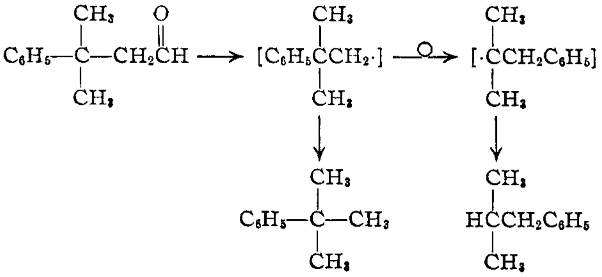
The study of free radical addition reactions to olefins which has been under investigation for many years[3] has led to the idea that the addition after initiation occurs in two steps.



$$X\cdot + CH_2{=}CHR \longrightarrow XCH_2\underset{\cdot}{C}HR \xrightarrow{X-Y} XCH_2\underset{\substack{|\\ Y}}{C}HR + X\cdot$$

This paper describes some work undertaken with the purpose of developing a new method for determining the relative rates of the second step for a number of X–Y substances.

In an investigation of the rearrangement of the β-phenylisobutyl radical derived from the decarbonylation of β-phenylisovaleraldehyde, Seubold[4] found that the amount of rearrangement is proportional to the concentration of aldehyde in the reaction mixture.



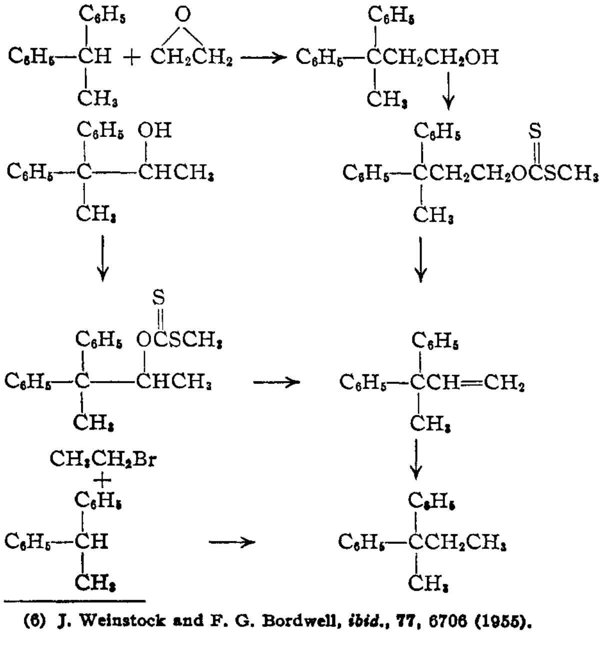
$$\begin{array}{ccccc} C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2\overset{O}{\overset{\|}{C}}H & \longrightarrow & [C_6H_5\underset{CH_3}{\overset{CH_3}{C}}CH_2\cdot] & \xrightarrow{O} & [\cdot\underset{CH_3}{\overset{CH_3}{C}}CH_2C_6H_5] \\ & & \downarrow & & \downarrow \\ & & C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 & & H\underset{CH_3}{\overset{CH_3}{C}}CH_2C_6H_5 \end{array}$$

This was taken to mean that the β-phenylisobutyl radical is formed as a discrete intermediate without the aid of bridging involving the phenyl group and that rearrangement and hydrogen abstraction compete as alternative paths for the decomposition of the β-phenylisobutyl radical. Since the rate of rearrangement in a similar radical $R_1R_2C(C_6H_5)-\dot{C}HCH_2X$ derived from an addition reaction should be essentially independent of the substituent X, the amount of phenyl migration occurring during such an addition should be a measure of the rate at which the unrearranged radical abstracts the atom Y from the substance X–Y being added. The faster that the abstraction proceeds the less will be the amount of phenyl migration that has time to take place.

In a study of the effect of aldehyde structure on the amount of rearrangement during the decarbonylation reaction, Curtin and Hurwitz[5] found that the change from β-phenylisovaleraldehyde to β,β-diphenylbutyraldehyde increased the amount of rearrangement from about 50 to 100%. On this basis 3,3-diphenyl-1-butene seemed to be a reasonable choice for an olefin that might undergo partial rearrangement during some addition reactions.

The synthesis of 3,3-diphenyl-1-butene was achieved by two independent methods. 3,3-Diphenyl-2-butanone was reduced by sodium borohydride to 3,3-diphenyl-2-butanol, and this was converted *via* the lithium salt[6] to the methyl xanthate. Pyrolysis of this gave the olefin in 80% yield. For the alternate synthesis, which was more adaptable for large scale work, 3,3-diphenyl-1-butanol was prepared by the reaction of the sodium salt of 1,1-diphenylethane with ethylene oxide in liquid ammonia. This was converted *via* the lithium salt to the methyl xanthate in 80% yield. Pyrolysis of this xanthate also gave an 80% yield of olefin but at a higher temperature.

The structure of the olefin was established by converting it by catalytic hydrogenation to 2,2-diphenylbutane. This material had the same infrared spectrum as an authentic sample prepared by the reaction of the sodium salt of diphenylethane with ethyl bromide. The absence of rearrangement to 2,3-diphenyl-2-butene during the pyrolysis further illustrates the excellence of the Chugaev procedure for the preparation of unstable olefins and provides evidence for the absence of any phenyl participation during the pyrolysis.



$$\begin{array}{ccc} C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}H + \overset{O}{CH_2CH_2} & \longrightarrow & C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}CH_2CH_2OH \\ & & \downarrow \\ C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-\overset{OH}{C}HCH_3 & & C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}CH_2CH_2O\overset{S}{\overset{\|}{C}}SCH_3 \\ \downarrow & & \downarrow \\ C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}-\overset{O\overset{S}{\overset{\|}{C}}SCH_3}{C}HCH_3 & \longrightarrow & C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}CH{=}CH_2 \\ & & \downarrow \\ \begin{array}{c} CH_3CH_2Br \\ + \\ C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}H \end{array} & \longrightarrow & C_6H_5-\underset{CH_3}{\overset{C_6H_5}{C}}CH_2CH_3 \end{array}$$

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[3] For a recent review of this field see J. I. G. Cadogen and D. H. Hey, *Quart. Revs.*, **8**, 308 (1954).

[4] F. H. Seubold, THIS JOURNAL, **75**, 2532 (1953).

[5] D. Y. Curtin and M. J. Hurwitz, *ibid.*, **74**, 5381 (1952).

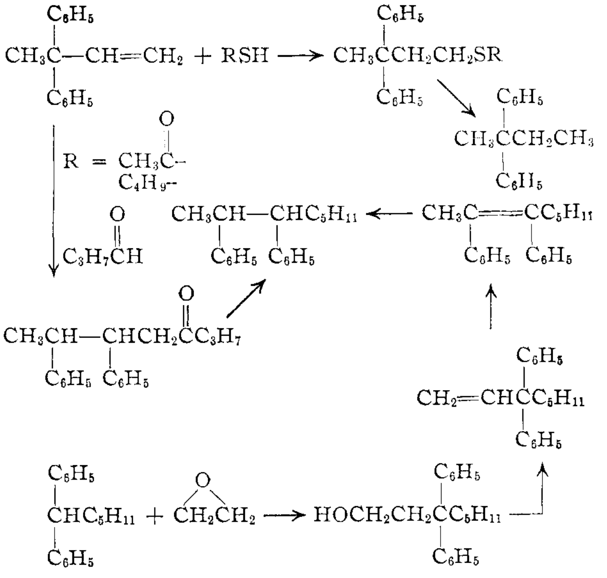
[6] J. Weinstock and F. G. Bordwell, *ibid.*, **77**, 6706 (1955).

The addition of thiolacetic acid to 3,3-diphenyl-1-butene was unsuccessful when carried out using ultraviolet or visible light to initiate the reaction. However, in the presence of *t*-butyl hydroperoxide and a tenfold excess of thiolacetic acid, a fair yield of thiol ester was obtained. Desulfurization of this with Raney nickel[7] gave a 92% yield of material whose infrared spectrum was identical with that of authentic 2,2-diphenylbutane.

The *t*-butyl hydroperoxide-catalyzed addition of *n*-butyl mercaptan to 3,3-diphenyl-1-butene in a tenfold excess of mercaptan gave about a 25% yield of sulfide. Desulfurization of this with Raney nickel gave a quantitative yield of 2,2-diphenylbutane whose infrared spectrum was identical with that of the authentic sample.

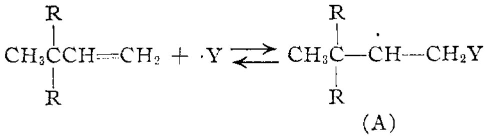
The absence of rearrangement in the above reactions raised the possibility that this system for some reason could not undergo radical rearrangement. In order to give the intermediate radical a lifetime similar to that of the radicals which had previously been found to rearrange,[4,5] the addition of butyraldehyde[8] to 3,3-diphenyl-1-butene was run under the same conditions as the thiol additions. Only a 6.7% yield of product was obtained, but much starting material was recovered. The product had a strong band at 5.8 μ in the infrared spectrum which was indicative of its ketonic nature. On Wolff–Kishner reduction it gave a 37% yield of a product whose infrared spectrum was essentially identical with that of an authentic sample of 2,3-diphenyloctane and different than that of an authentic sample of 2,2-diphenyloctane.

Authentic 2,2-diphenyloctane was prepared by the alkylation of the sodium salt of 1,1-diphenylethane with *n*-hexyl chloride in liquid ammonia. Authentic 2,3-diphenyloctane was prepared by the following procedure. The sodium salt of diphenylmethane was alkylated in liquid ammonia with *n*-amyl bromide to give 1,1-diphenylhexane. The sodium salt of this was treated with ethylene oxide in liquid ammonia to give 3,3-diphenyl-1-octanol which was converted to the methyl xanthate *via* the lithium salt. Pyrolysis of the xanthate gave 3,3-diphenyl-1-octene which had an infrared spectrum very similar to that of 3,3-diphenyl-1-butene. Rearrangement of the olefin by 5% sulfuric acid in glacial acetic acid gave 2,3-diphenyl-2-octene whose infrared spectrum did not have the peaks at 6.08, 7.07 and 10.83 μ characteristic of the vinyl group.[8a] This olefin was reduced by sodium in liquid ammonia[9] to 2,3-diphenyloctane. It is likely that the products obtained by this reduction and from the free radical reaction have the same configuration because in both cases a hindered trisubstituted carbon (either as an anion or as a radical) must abstract a hydrogen to give the final product, and it is probable that the anion and radical would have the same conformation determined so as to minimize steric repulsions.[10]



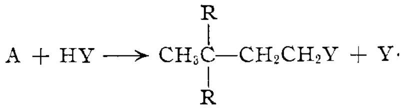
Discussion

The main course of the additions to 3,3-diphenyl-1-butene after initiation may be represented schematically as (R = phenyl)

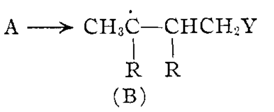


$$CH_3\overset{R}{\underset{R}{C}}CH{=}CH_2 + \cdot Y \rightleftarrows CH_3\overset{R}{\underset{R}{C}}-\dot{C}H-CH_2Y \qquad (1)$$

(A)

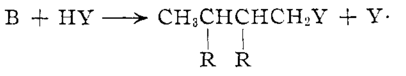


$$A + HY \longrightarrow CH_3\overset{R}{\underset{R}{C}}-CH_2CH_2Y + Y\cdot \qquad (2)$$



$$A \longrightarrow CH_3\underset{R}{\dot{C}}-\underset{R}{C}HCH_2Y \qquad (3)$$

(B)



$$B + HY \longrightarrow CH_3\underset{R}{C}H\underset{R}{C}HCH_2Y + Y\cdot \qquad (4)$$

The lack of rearrangement found in the additions of thiolacetic acid and butyl mercaptan to the olefin shows that for these substances reaction 2 must be much faster than reaction 3. The difficulty encountered in the thiolacetic acid addition contrasted to the usual ease of such additions[11] may be attributed to a retardation of reaction 2 due to steric hindrance which allows the reverse of reaction 1 to occur. A radical addition-elimination of this kind has been proposed as the explanation for the equilibration of *cis*- and *trans*-2-butene during the addition of bromotrichloromethane[12] and for the iodine-catalyzed isomerization of *cis*- and *trans*-diiodoethylene.[13]

The complete rearrangement observed in the addition of butyraldehyde indicates that in this case reaction 3 is faster than reaction 2. The low

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(7) R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, THIS JOURNAL, **65**, 1013 (1943).

(8) M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

(8a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 31–47.

(9) K. N. Campbell and B. K. Campbell, *Chem. Revs.*, **31**, 77 (1942).

(10) It is of interest in this connection that W. R. Brasen, S. W. Kantor, P. S. Skell and C. R. Hauser, THIS JOURNAL, **79**, 398 (1957), report that the sodium in liquid ammonia reduction of both *threo* and *erythro*-2-chloro-2,3-diphenylbutane gave *meso*-2,3-diphenylbutane.

(11) F. G. Bordwell and W. A. Hewett, *ibid.*, **79**, 3493 (1957).

(12) P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955).

(13) R. M. Noyes, R. G. Dickinson and V. Schomaker, *ibid.*, **67**, 1319 (1945).

yield of product obtained is probably due to a reversal of reaction 1 and the disappearance of the butyryl radical by alternative pathways such as decarbonylation and dimerization.

The different courses of the mercaptan additions and the aldehyde addition are not surprising when considering the relative reactivity of *n*-butyl mercaptan and *n*-butyraldehyde toward radicals as revealed in chain transfer constant measurements. Walling[14] has found that in the system styrene–*n*-butyl mercaptan at 60° the chain transfer constant is 22 ± 3 and Gregg and Mayo[15] found that in the system styrene–*n*-butyraldehyde at 60° the chain transfer constant is about 5.7×10^{-4}. Thus the benzyl-type radical in these systems can abstract a hydrogen from *n*-butyl mercaptan about 40,000 times as readily as it can from *n*-butyraldehyde. A less stable radical than the benzyl type would probably be somewhat less selective.

The rearrangement results provide further evidence that free radical rearrangements involving phenyl migration do not take place simultaneously with the formation of a radical capable of rearranging.[4] Some more recent support for this view is the observation[16] that the presence of benzyl mercaptan during the decarbonylation of β-phenylisovaleraldehyde decreases the amount of rearranged product formed. In this case the mercaptan acts as a chain transfer agent[17] and decreases the lifetime of the neophyl radical.

The lack of rearrangement during the addition of mercaptans to 3,3-diphenyl-1-butene helps to clarify the absence of rearrangement observed during the addition of *p*-thiocresol to norbornene[18] and its analog, *exo-cis*-3,6-endomethylene-Δ^4-tetrahydrophthalic anhydride.[19] In these cases rearrangement was inhibited not only by an olefin not prone to rearrange during radical reactions[20] but also by a reaction involving a relatively short lifetime for the intermediate radical.

The complete phenyl migration observed in the butyraldehyde addition and the lack of rearrangement found in the mercaptan additions shows in a crude manner that the amount of rearrangement is related to the relative rates of the abstraction step (reaction 2) of the addition. However, in order to get information regarding the relative rates of reaction 2 for different HY substances, it would be necessary to work in systems where several different additions give varying amounts of both rearranged and unrearranged products.

Experimental[21]

3,3-Diphenyl-2-butanol.—2,3-Diphenyl-2,3-butandiol was prepared in 58% yield by the reaction of phenylmagnesium bromide and biacetyl by the method of Wegmann and Dahn.[22] This was converted into 3,3-diphenyl-2-butanone in 75% yield by refluxing in 62% sulfuric acid.[23] To a solution of 78.7 g. (0.35 mole) of this ketone in 300 ml. of methanol was added dropwise a solution of 13.6 g. (0.35 mole) of sodium borohydride in 30 ml. of water. The mixture was refluxed for 2 hr., 235 ml. of methanol removed by distillation and the residue dissolved in 300 ml. of water. The organic material was extracted with pentane and then washed successively with aqueous saturated sodium bisulfite, aqueous saturated sodium chloride and then dried over magnesium sulfate. The pentane was removed under vacuum and the residue distilled to give 70.9 g. (90%) of a colorless oil, b.p. 147–148° (0.7 mm.), $n^{25}\mathrm{D}$ 1.5827.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.93; H, 8.02. Found: C, 85.07; H, 7.85.

1,1-Diphenylethane was prepared by a modification of the method of Szmant and Yonkoskie.[24] A mixture of 1 l. of thiophene-free benzene and 200 ml. of 96.5% sulfuric acid was stirred at room temperature while 170 g. (1.64 moles) of styrene in 300 ml. of benzene was added over a 4-hr. period. The reaction mixture was stirred an additional 3 hr., poured into a separatory funnel and the sulfuric acid sludge removed. The benzene was removed under vacuum and the residue distilled to give 186 g. of crude material, b.p. 145–150° at 20 mm. On chilling overnight at 5° a small amount of a low melting solid came out of solution. This was removed by filtration and the filtrate distilled to give 155 g. (53%) of a colorless liquid, b.p. 146–149° (20 mm.), $n^{25}\mathrm{D}$ 1.5700. The original method[24] gave a 41% yield of material, b.p. 126–129° (0.8 mm.), $n^{25}\mathrm{D}$ 1.5719. The present method avoids the troublesome emulsions encountered in the original method.

3,3-Diphenyl-1-butanol.—To a suspension of sodamide prepared from 19.5 g. (0.85 gram atom) of sodium and 1 l. of liquid ammonia was added 140 g. (0.77 mole) of 1,1-diphenylethane and 100 ml. of dry ether and the mixture stirred for 30 minutes. Then about 70 g. (1.6 moles) of ethylene oxide was added and the stirring continued for 2 hr. After the addition of 100 ml. of concentrated ammonium hydroxide, the ammonia was allowed to evaporate, 300 ml. of water added and the organic material extracted with ether. The organic layer was washed with saturated ammonium chloride solution and then water, dried with magnesium sulfate and distilled to give 38.8 g. (28% recovery) of diphenylethane, b.p. 98–100° (1.6 mm.), and 106.7 g. (62%) of a colorless oil, b.p. 158–179° (1.6 mm.), which on standing crystallized to a white solid, m.p. 47–50°.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.93; H, 8.02. Found: C, 84.97; H, 7.93.

Methyl 3,3-Diphenyl-2-butylxanthate.—To a phenyllithium solution prepared from 60 ml. of bromobenzene and 7.8 g. of lithium in 400 ml. of ether was added dropwise 65 g. (0.29 mole) of 3,3-diphenyl-2-butanol. After 1 hr. 60 ml. of carbon disulfide was added and after 2 additional hr. 60 ml. of methyl iodide added. The mixture was refluxed 3 hr., allowed to stand overnight and 15 ml. of methyl iodide added followed by an additional 1 hr. reflux. The reaction was then poured on crushed ice, extracted with ether and the organic layer washed with water and dried over magnesium sulfate. After the ether and other volatile materials were removed under vacuum, the residue partially crystallized to give 72 g. (80%) of bright yellow crystals, m.p. 83.5–84.5°. Recrystallization from ethanol gave colorless prisms, m.p. 85–85.5°.

Anal. Calcd. for $C_{18}H_{20}S_2O$: C, 68.31; H, 6.37. Found: C, 68.33; H, 6.23.

Methyl 3,3-diphenyl-1-butylxanthate was prepared as described above except that the product did not spontaneously crystallize on removal of the ether. The residue obtained was taken up in ethanol, heavily charcoaled, diluted with water and the product extracted with ether. The ether was washed with water, dried over magnesium sulfate, the solvent removed and on trituration of the residue with ethanol 7.4 g. (38%) of a white solid obtained, m.p. 62–63°.

Anal. Calcd. for $C_{18}H_{20}S_2O$: C, 68.31; H, 6.37. Found: C, 68.72; H, 6.16.

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(14) C. Walling, This Journal, **70**, 2561 (1948).

(15) R. A. Gregg and F. R. Mayo, *ibid.*, **75**, 3530 (1953).

(16) S. Winstein, R. Heck, S. Lapporte and R. Baird, *Experientia*, **12**, 138 (1956).

(17) E. F. P. Harris and W. A. Waters, *Nature*, **170**, 212 (1952).

(18) S. J. Cristol and G. D. Brindell, This Journal, **76**, 5699 (1954).

(19) J. A. Berson and W. M. Jones, *ibid.*, **78**, 6045 (1956).

(20) J. Weinstock, Abstracts of the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September, 1955, p. 19-O.

(21) Microanalyses were carried out by Miss Hilda Beck. Melting points and boiling points are uncorrected. Infrared spectra were determined in chloroform solution on a Baird Spectrophotometer.

(22) J. Wegmann and H. Dahn, *Helv. Chim. Acta*, **29**, 101 (1946).

(23) K. Sisido and H. Nozaki, This Journal, **70**, 776 (1948).

(24) H. H. Szmant and R. Yonkoskie, *J. Org. Chem.*, **21**, 78 (1956).

3,3-Diphenyl-1-butene. A.—Methyl 3,3-diphenyl-2-butylxanthate (64 g., 0.20 mole) was pyrolyzed in an oil-bath heated round-bottomed flask vented through a mercury bubbler and a 50% aqueous potassium hydroxide trap. Smooth decomposition started at about 140°, and complete decomposition was obtained by heating at 220° for 1 hr. The pot residue was taken up in pentane and then washed successively with a 5% aqueous solution of sodium hydroxide and water and dried over magnesium sulfate. Distillation gave 35 g. (81%) of a colorless liquid, b.p. 107–110° (1.5 mm.), n^{25}D 1.5772.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.27; H, 7.73. Found: C, 92.68; H, 7.36.

B.—Methyl 3,3-diphenyl-1-butylxanthate (3.8 g., 0.012 mole) was pyrolyzed as described above. Smooth decomposition started at about 225°, and 30 minutes at 250° was used to obtain complete decomposition. Distillation in a short-path still at 1.5 mm. gave a few drops of a yellow liquid at a bath temperature of 115° and 2.0 g. (80%) of a colorless oil, n^{25}D 1.5776, at a bath temperature of 125°. This product had an infrared spectrum identical with that of the product prepared by method A.

On a larger scale run using crude xanthate obtained from 105 g. (0.47 mole) of 3,3-diphenyl-1-butanol, 60.3 g. (68%) of a red liquid, b.p. 113–128° (1.7 mm.), n^{25}D 1.5796, was obtained. This was purified by refluxing for 2 hr. with 100 ml. of a 5% solution of sodium hydroxide in ethanol–water. On diluting with water, extracting with pentane, drying over magnesium sulfate and distilling there was obtained 49.0 g. (91% recovery) of a colorless liquid, b.p. 111–115° (1.5 mm.), n^{25}D 1.5780. The infrared spectrum of this material was identical with that of the previous preparations.

C.—To a sodamide suspension prepared in the usual manner from 3.5 g. (0.15 gram atom) of sodium and 300 ml. of liquid ammonia was added slowly 26.5 g. (0.14 mole) of 1,1-diphenyl-1-propene,[25] m.p. 48–49°, in 75 ml. of dry ether. After 10 minutes the maximum intensity of a blood red color was attained, and 9 ml. of methyl iodide was added over a period of 5 minutes and the color was dispelled. An excess of 5 ml. of methyl iodide was added and the mixture stirred for 2 hr., 50 ml. of concentrated aqueous ammonium hydroxide added and the ammonia allowed to evaporate overnight. The residue was taken up in water and pentane and the organic layer washed in turn with saturated aqueous ammonium chloride and water and dried over magnesium sulfate. Distillation gave 20 g. of a colorless liquid, b.p. 113–118° (1.6 mm.), n^{25}D 1.5863. Infrared comparisons using mixtures of known composition of 1,1-diphenyl-1-butene and 3,3-diphenyl-1-butene indicated that the product contained about 50% of each of the isomers. Assuming a linear relationship between refractive index and composition and taking n^{25}D 1.5904 for 1,1-diphenylbutene,[26] the product contained about 70% of 1,1-diphenylbutene.

Hydrogenation of 3,3-Diphenyl-1-butene.—A suspension of 1.0 g. of 3,3-diphenyl-1-butene in 15 ml. of 95% ethanol and 0.10 g. of 10% palladium-on-charcoal was stirred in a hydrogen atmosphere until 1 equivalent of hydrogen was taken up. Distillation of the product in a short-path still at a bath temperature of 140° and a pressure of 0.8 mm. gave 0.70 g. (70%) of a colorless liquid, n^{25}D 1.5653. The infrared spectrum of this material was identical with that of an authentic sample of 2,2-diphenylbutane (see below).

Anal. Calcd. for $C_{16}H_{18}$: C, 91.38; H, 8.62. Found: C, 91.62; H, 8.25.

2,2-Diphenylbutane.—To a sodamide suspension prepared in the usual way from 4.2 g. (0.18 gram atom) of sodium and 300 ml. of liquid ammonia was added 30 g. (0.165 mole) of 1,1-diphenylethane. After stirring the red solution for 20 minutes, 20 g. (0.18 mole) of ethyl bromide was added over a 1-hr. period and the ammonia allowed to evaporate. The mixture was diluted with 100 ml. of water and acidified with 6 *N* sulfuric acid. The organic material was taken up in pentane, the pentane layer washed with water, dried over magnesium sulfate and distilled to give: (1) 3.1 g. of a liquid, b.p. 106–111° (1.5 mm.), n^{25}D 1.4645; (2) 8.5 g., b.p. 112–115° (1.5 mm.), n^{25}D 1.5672; and (3) 14.5 g., b.p. 116–118° (1.5 mm.), n^{25}D 1.5657. The infrared spectra of (2) and (3) were identical with each other and with that of the material obtained by hydrogenation of 3,3-diphenyl-1-butene.

3,3-Diphenyl-1-butyl Thiolacetate.—To a stirred solution of 20.8 g. (0.10 mole) of 3,3-diphenyl-1-butene and 76 g. (1.0 mole) of freshly distilled thiolacetic acid in an 80° oil-bath was added 1.0 g. (0.011 mole) of *t*-butyl hydroperoxide. The temperature of the solution rose to 90°, but it returned to 80° within 10 minutes. After 5 hr. an additional 0.2 g. of *t*-butyl hydroperoxide was added which caused the internal temperature to rise temporarily 1.5°. After a total of 24 hr. at 80°, the thiolacetic acid and a 2.6-g. fraction, b.p. 115° at 1.5 mm., were removed to give 25.3 g. (95%) of a reddish-brown viscous oil. Distillation of a portion of this in a short path still at 1.0 mm. at a bath temperature of 210–220° gave an orange oil, n^{25}D 1.5843.

Anal. Calcd. for $C_{18}H_{20}SO$: C, 76.02; H, 7.09. Found: C, 75.58; H, 6.91.

3,3-Diphenyl-1-butyl Butyl Sulfide.—To a stirred solution of 4.16 g. (0.02 mole) of 3,3-diphenyl-1-butene and 18.04 g. (0.20 mole) of freshly distilled *n*-butyl mercaptan at 80° was added 0.1 g. (0.001 mole) of *t*-butyl hydroperoxide. Additional 0.1-g. portions of hydroperoxide were added after 5 and after 17 hr. After a total of 24 hr. at 80 ± 2°, 10 ml. of toluene was added and the excess mercaptan and some toluene distilled out at a bath temperature of 125°. Distillation of the residue gave (1) 2.23 g. (54% recovery) of 3,3-diphenyl-1-butene, b.p. 109–113° (1.5 mm.); (2) 0.50 g., light yellow liquid, b.p. 130–179° (1.5 mm.); and (3) 1.50 g. (25%) of a light yellow oil, b.p. 180–181° (1.5 mm.), n^{25}D 1.5682. Fraction 3 was taken for analysis.

Anal. Calcd. for $C_{20}H_{26}S$: C, 80.47; H, 8.78. Found: C, 80.58; H, 8.60.

Desulfurization of 3,3-Diphenyl-1-butyl Thiolacetate.—To a solution of 5.00 g. of the undistilled product in 175 ml. of absolute ethanol was added 20 g. of Raney nickel which had been washed with absolute alcohol. The mixture was refluxed on a steam-bath for 18 hr., allowed to stand at room temperature for two days, filtered and the solvent removed under vacuum. Distillation of the residue in a short path still at 1.5 mm. and at a bath temperature of 130–160° gave 3.40 g. (92%) of a colorless liquid, n^{25}D 1.5643. The infrared spectrum of this material was identical in all respects with that of authentic 2,2-diphenylbutane.

Desulfurization of 3,3-Diphenyl-1-butyl Butyl Sulfide.—A mixture of 1.25 g. of the sulfide, 50 ml. of absolute ethanol and 5 g. of Raney nickel was refluxed on a steam-bath for 19 hr. and worked up in the above manner. Distillation of the product in a short path still at 1.2 mm. and a bath temperature of 125° gave 0.87 g. (100%) of a colorless liquid, n^{25}D 1.5643. The infrared spectrum of this compound was identical in all respects with that of an authentic sample of 2,2-diphenylbutane.

Addition of Butyraldehyde to 3,3-Diphenyl-1-butene.—To a stirred solution of 8.32 g. (0.04 mole) of 3,3-diphenyl-1-butene in 28.8 g. (0.4 mole) of freshly distilled *n*-butyraldehyde kept at 80° was added a total of 0.80 g. (0.009 mole) of *t*-butyl hydroperoxide in six equal portions over a period of 6 hr. The low boiling material was removed under vacuum and distillation of the residue gave (1) 1.64 g. of a colorless liquid, b.p. 85–105° (1.0 mm.), n^{25}D 1.5623; (2) 5.40 g., b.p. 105–107° (1.0 mm.), n^{25}D 1.5743; (3) 0.4 g. of a yellow liquid, b.p. 107–155° (1.0 mm.), n^{25}D 1.5660, and (4) 0.75 g. (6.7%) of a yellow liquid, b.p. 155–160° (1.0 mm.), n^{25}D 1.5553. A dark brown residue of 0.87 g. remained. A study of the infrared spectra of the fractions showed that (1) is probably a mixture of butyroin[27] and 3,3-diphenyl-1-butene, that (2) is 3,3-diphenyl-1-butene and that (4) is ketonic in nature.

Wolff–Kishner Reduction of 6,7-Diphenyl-4-octanone.—A stirred solution of 0.60 g. of the ketonic material (fraction 4 above) obtained from the addition of butyraldehyde to 3,3-diphenyl-1-butene and 5 ml. of 85% hydrazine hydrate in 15 ml. of ethanol was refluxed for 10 hr. To this was then added 30 ml. of diethylene glycol and 3.0 g. of potassium hydroxide and the mixture heated according to the Huang-Minlon procedure[28] at 200° for 4.5 hr. The residue after cooling was diluted with water, the organic material extracted with ether and the ether layer washed successively with 5% aqueous hydrochloric acid and water and dried over magnesium sulfate. Distillation in a short-path still at a bath temperature of 150° at 1.0 mm. gave 0.20 g. (37%) of a

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[25] A. Klages and S. Heilmann, *Ber.*, **37**, 1447 (1904).

[26] A. W. Schmidt and C. Hartmann, *ibid.*, **74**, 1325 (1941).

[27] R. I. Huang, *J. Chem. Soc.*, 1749 (1956).

[28] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

colorless oil, n^{25}D 1.5453. The infrared spectra of this material were essentially identical with that of authentic 2,3-diphenyloctane and exhibited marked differences from that of authentic 2,2-diphenyloctane.

2,2-Diphenyloctane.—To a sodamide suspension prepared from 4.2 g. (0.18 gram atom) of sodium and 300 ml. of liquid ammonia was added 29.8 g. (0.164 mole) of 1,1-diphenylethane. The blood red solution was stirred for 20 minutes and then 20 g. (0.166 mole) of 1-chlorohexane added over a 15-minute period. The reaction mixture was worked up in the usual fashion and on distillation gave 10.5 g. of recovered 1,1-diphenylethane and 7.0 g. (15%) of a colorless liquid, b.p. 150° (1.5 mm.), n^{25}D 1.5412.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.17; H, 9.83. Found: C, 89.68; H, 9.88.

1,1-Diphenylhexane.—To a sodamide suspension prepared from 7.5 g. (0.325 gram atom) of sodium and 500 ml. of liquid ammonia was added 50 g. (0.297 mole) of diphenylmethane in 50 ml. of dry ether. After the maximum color intensity was obtained, 45 g. (0.297 mole) of 1-bromopentane was added as rapidly as possible. Working up in the usual manner gave 38.1 g. (53%) of a colorless liquid, b.p. 135° (1.0 mm.), n^{30}D 1.5422; reported[29] b.p. 164° (10 mm.).

Anal. Calcd. for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.78; H, 8.86.

3,3-Diphenyl-1-octanol.—To a sodamide suspension prepared from 3.0 g. (0.13 gram atom) of sodium and 400 ml. of liquid ammonia was added 30.9 g. (0.13 mole) of 1,1-diphenylhexane and 250 ml. of ether. To the red suspension was then added 25 g. (0.57 mole) of ethylene oxide and the mixture stirred for 2 hr. Then another 10 g. of ethylene oxide was added and the mixture stirred an additional 4 hr. On working up in the usual manner 18.8 g. (61%) of the starting hydrocarbon was recovered, and there was obtained 10.2 g. (28%) of a very viscous colorless oil, b.p. 185–190° (1.0 mm.), n^{28}D 1.5533, which on standing crystallized to a white solid, m.p. 75–78°.

Anal. Calcd. for $C_{20}H_{27}O$: C, 85.06; H, 9.33. Found: C, 84.96; H, 9.11.

3,3-Diphenyl-1-octene.—To a stirred phenyllithium solution prepared from 0.6 g. of lithium and 5 ml. of bromobenzene in 100 ml. of dry ether was added 6.0 g. (0.021 mole) of 3,3-diphenyl-1-octanol and the solution refluxed for 1 hr. Then 5 ml. of carbon disulfide was added, the solution refluxed an additional hour and 10 ml. of methyl iodide added. After standing overnight at room temperature, an additional 5 ml. of methyl iodide was added and the mixture refluxed for 1 hr. The product, which was isolated in the manner described above for methyl 3,3-diphenyl-2-butylxanthate, was a light red oil. The crude xanthate was pyrolyzed in the usual manner, decomposition starting at about 220° and becoming complete after 30 minutes at 255°. The residue was refluxed with a mixture of 25 ml. of 10% aqueous potassium hydroxide and 25 ml. of ethanol for 2 hr., the mixture diluted with water, extracted with ether and the ether extract dried over magnesium sulfate. Distillation gave 3.5 g. (55%) of a colorless liquid, b.p. 138–140° (1.0 mm.), n^{25}D 1.5542. The infrared spectrum of this product resembled that of 3,3-diphenyl-1-butene.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 91.12; H, 9.22.

2,3-Diphenyl-2-octene.—A stirred solution of 3.0 g. of 3,3-diphenyl-1-octene and 40 ml. of 5% sulfuric acid in glacial acetic acid was heated for 3 hr. at 78°. On cooling, the mixture was diluted with water, extracted with ether, the ether washed with water until neutral and then dried over magnesium sulfate. Distillation gave 1.80 g. (60%) of a colorless liquid, b.p. 130–132° (1.0 mm.), n^{25}D 1.5513. The infrared spectrum of this material lacked bands at 6.08, 7.06 and 10.82 μ characteristic of the terminal vinyl group which were present in the infrared spectrum of the starting material.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.78; H, 8.77.

2,3-Diphenyloctane.—A mixture of 1.00 g. (0.0038 mole) of 2,3-diphenyl-2-octene and 200 ml. of liquid ammonia was stirred vigorously while 0.20 g. (0.0087 gram atom) of sodium was added in small portions.[30] The initial blue color imparted by the sodium faded until one equivalent was added. On addition of the remainder of the sodium the blue color persisted while the solution was stirred for 30 minutes. Solid ammonium chloride was added until the blue color was discharged; then 100 ml. of saturated aqueous ammonium chloride was added and the ammonia allowed to evaporate. The mixture was diluted with water, extracted with ether, the ether washed with aqueous ammonium chloride and with water, dried over magnesium sulfate and distilled. This gave 0.80 g. (80%) of a colorless liquid distilling at a bath temperature of 170° at 0.8 mm., n^{25}D 1.5388. The infrared spectrum of this material differed markedly from that of the starting material and that of 2,2-diphenyloctane.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.17; H, 9.83. Found: C, 90.65; H, 9.43.

Infrared Spectra.—Herewith are given the positions in microns of characteristic infrared bands used to identify some of the above compounds. All spectra were taken in chloroform solution on a Baird spectrophotometer. All of the spectra had a peak at 6.20 μ which may be used as an internal standard of wave length calibration.

3,3-Diphenyl-1-butene: 6.07, 6.67, 6.79(sh), 6.88, 7.05, 7.25, 9.68, 9.90, 10.85
2,2-Diphenylbutane: 6.67, 6.88, 7.20, 9.68(s)
3,3-Diphenyl-1-octene: 6.08, 6.67, 6.78(sh), 6.88, 7.06, 7.21, 9.62, 9.87, 10.82
2,3-Diphenyl-2-octene: 6.66, 6.78(w), 6.88, 7.22, 9.26, 9.68
2,3-Diphenyloctane: 6.67, 6.78(sh), 6.85, 7.23, 9.65(w)
2,2-Diphenyloctane: 6.67, 6.79, 6.90, 7.24, 9.67(s)

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(29) H. Masson, *Compt. rend.*, **135**, 533 (1902).

(30) C. B. Wooster and J. F. Ryan, This Journal, **56**, 1133 (1934).