This is the same precision encountered in the over-all process including extraction as was shown by a comparison of concentrations calculated from zero-time aliquots and from the weights of the samples. Because of a decrease in total ketone concentration, probably due to sulfonation, rates were not determined beyond the second half-life.

Specific rates for the rearrangements of hexamethylacetone and methyl triphenylmethyl ketone and for the cleavage of methyl pentamethylethyl ketone were determined from the slopes of log A *versus* time plots. Rate constants for the cleavage reaction also were obtained from the expression

$$k' = \frac{-2.3}{t} \log \left[\frac{A}{A_0} - \frac{B}{A_0}\left(\frac{k'}{k} - 1\right)\right]$$

where A and B are the concentrations of hexamethylacetone and methyl pentamethylethyl ketone at time t, A_0 is the initial concentration of hexamethylacetone and k is the specific rate of the rearrangement. Values were assigned to k', both sides of the equation were plotted against k' and the intersection of the two curves was determined. The values of k' were fairly constant for points near the maximum concentration of methyl pentamethylethyl ketone.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Syntheses with Triarylvinylmagnesium Bromides. α,γ-Bisdiphenylene-β-phenylallyl, a Stable Free Radical

BY C. F. KOELSCH

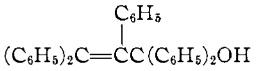
RECEIVED[1] APRIL 10, 1957

Unlike α,α,β,γ,γ-pentaphenylallyl alcohol, α,γ-bisdiphenylene-β-phenylallyl alcohol can be converted into a chloride because its geometry hinders it from cyclization to an indene. The chloride has been converted into the corresponding free radical, a substance which is highly dissociated and remarkably stable to oxygen.

Ziegler's[2] tetraphenylallyl radical, $(C_6H_5)_2C{=}CH{-}C(C_6H_5)_2$, and its substituted derivatives are particularly remarkable in that although they contain only two aryl groups on the methane carbon atom, molecular weight determinations show them to be largely monomolecular. Their deep colors in solution or in the solid state, and their sensitivity toward oxygen also attest their high degree of dissociation. This degree of dissociation, so much exceeding that of triphenylmethyl, was explained by Ziegler on the ground that as 1,1-diphenylethylene is more unsaturated than benzene, diphenylvinyl has a larger "valence requirement" than phenyl.

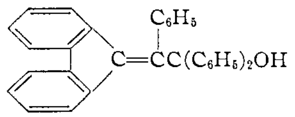
The completely phenylated allyl radical, pentaphenylallyl, as yet unknown, is of interest because of the intermediate position of the constituent triphenylvinyl group between tetraphenylethylene, whose double bond does not add bromine, and 1,1-diphenylethylene, which adds bromine readily.

A previous paper[3] described the difficulties which were encountered when an attempt was made to synthesize the pentaphenylallyl radical and suggested a means for avoiding these. When pentaphenylallyl alcohol (I) is treated with any acidic reagent, a necessary step in its conversion into a radical, it loses water to form 1,1,2,3-tetraphenylindene. α,α,β-Triphenyl-γ-diphenyleneallyl alcohol (II) is unable to lose water directly, but acidic reagents cause it to undergo an allylic rearrangement followed by the formation of 1-diphenylene-2,3-diphenylindene. α,γ-Bisdiphenylene-β-phenylallyl alcohol (III) is hindered in indene formation, since no matter whether the hydroxyl group is on carbon 1 or 3 the same steric effect tends to prevent the approach of this atom to an *ortho* position of a diphenylene group. Linkage of these positions is therefore difficult.[4] The present paper describes the successful conversion of this alcohol into a radical.

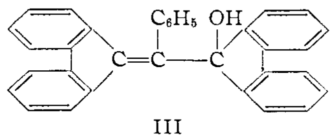


$$(C_6H_5)_2C{=}\overset{C_6H_5}{\overset{|}{C}}C(C_6H_5)_2OH$$

I



II



III

α,γ-Bisdiphenylene-β-phenylallyl alcohol treated with dilute methyl or ethyl alcoholic sulfuric acid gave nearly quantitative yields of the expected ethers. With hydrogen chloride in benzene, α,γ-bisdiphenylene-β-phenylallyl chloride was formed.

The ethers were of no value in the preparation of the radical. When they were treated with sodium amalgam in ether, they yielded deep blue solutions, believed to contain the expected sodio deriva-

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(1) The experimental work in the present paper was done in the Converse Memorial Laboratory of Harvard University in 1931–1932, when the author was a National Research Council fellow. A paper describing the work was submitted to THIS JOURNAL June 9, 1932, but it was not accepted for publication. The referee held that the properties of the chief compound, α,γ-bisdiphenylene-β-phenylallyl, could not be those of a radical.

Recent quantum mechanical calculations by M. M. Kreevoy (to be published in *J. Chem. Phys.*), however, now indicate that a radical of the structure named would be unusually resonance-stabilized, and that the properties reported for the substance in question would be not at all inconsistent with the structure claimed. A study of the thermodynamics of addition of sodium to the substance [N. B. Keevil, THIS JOURNAL **59**, 2104 (1937)] hinted that the compound might be unusually stable as a radical. And finally, recent studies by J. E. Wertz and J. L. Vivo, using electron spin resonance methods (briefly reported in OSR Technical Note 55-203, May 1955, p. 133, and to be published in detail in *J. Chem. Phys.*) indicate that the substance is highly dissociated, has an unusually narrow line-width, and is very stable. A sample kept in air 23 years is unchanged in appearance and shows a high free-radical content.

Because the structure originally suggested appears to be confirmed, and because many requests for samples and preparational details are being received, it appears desirable to publish the work now. In the interest of historical accuracy, the only important changes in the original paper are the additions of footnotes 5, 6 and 8.

(2) K. Ziegler and C. Ochs, *Ber.*, **55**, 2257 (1922); K. Ziegler, *Ann.*, **434**, 34 (1923).

(3) C. F. Koelsch, THIS JOURNAL, **54**, 3384 (1932).

(4) C. F. Koelsch, *ibid.*, **54**, 4744 (1932).

tive. But this sodio derivative did not react with tetramethylethylene dibromide. Its ether solution was not decolorized until a considerable amount of alcohol was added. When 40% sodium amalgam was used to cleave the ethers, the blue solutions first formed became red on continued shaking and then contained trisodium compound, whose hydrolysis gave α,γ-bisdiphenylene-β-phenylpropane.[5]

α,γ-Bisdiphenylene-β-phenylallyl chloride reacted with mercury to form the radical, α,γ-bisdiphenylene-β-phenylallyl. The molecular weight of this radical in boiling benzene indicated that it was largely dimolecular (α = 5.6%), and this was also evidenced by its great resistance to atmospheric oxidation.[6] The radical could be recovered in part unchanged after oxygen has been passed through its solution in boiling benzene for six hours. Bromine cleaved the radical slowly, but the reaction was complicated by partial formation of unworkable substitution products. It is difficult, however, to reconcile the behavior of the substance toward sodium with a low degree of dissociation; it is cleaved immediately by even 1% amalgam. Also the deep color of the substance, green in the solid state and red in solution, appears to be much too intense to be caused only by the fulvene groups present in a dimer.

In order to be able to ascribe the anomalous behavior of α,γ-bisdiphenylene-β-phenylallyl to the presence of the diphenylene groups or to the fifth (β) aryl group, it is planned to investigate tetraarylallyl radicals containing two diphenylene groups.[7]

Experimental

α,γ-Bisdiphenylene-β-phenylallyl Methyl Ether.—A solution of 6 g. of α,γ-bisdiphenylene-β-phenylallyl alcohol[4] in 360 ml. of hot methanol was cooled rapidly and mixed with 5 ml. of concd. sulfuric acid in 20 ml. of methanol. After ten hours, the product was removed by filtration and washed with methanol containing ammonia. Recrystallization from benzene–ligroin gave 5.7 g. of pale yellow prisms, m.p. 184–186°.

Anal. Calcd. for $C_{34}H_{24}O$: C, 91.1; H, 5.3. Found: C, 91.1; H, 5.5.

The ethyl ether had m.p. 187–190°.

Anal. Calcd. for $C_{35}H_{26}O$: C, 90.8; H, 5.6. Found: C, 90.5; H, 5.7.

A solution of 1 g. of the methyl ether in 35 ml. of ether was shaken with an excess of 1% sodium amalgam for several hours, or with an excess of 40% amalgam until the first tinge of green was noticed. The amalgam was frozen, and the deep blue solution, in which was suspended shining crystalline plates, was decanted under nitrogen. Hydrolysis of the solution gave a brick-red amorphous substance which could not be crystallized. Many attempts were made to carbonate the sodium compound, but none of these experiments were successful; a red amorphous substance apparently identical with that obtained by hydrolysis was always obtained. Tetramethylethylene dibromide was without action on the monosodium compound. Phenyl isocyanate reacted, as did benzyl chloride, but no crystalline products could be obtained.

When the methyl ether was shaken in ether with an excess of 40% sodium amalgam for about one hour the color changed from blue to green and finally to deep red-brown. Kept for several days this solution deposited dichromate-colored prisms of presumably a trisodium compound. Carbon dioxide, phenyl isocyanate and benzyl chloride gave no crystalline products. Tetramethylethylene dibromide reacted, giving deep blue solution of the monosodium compound, hydrolyzed to the red amorphous substance. Hydrolysis of the trisodium compound gave *α,γ-bisdiphenylene-β-phenylpropane* (0.6 g. from 1 g. of the methyl ether), colorless needles from acetic acid, m.p. 236–237°. The hydrocarbon was not changed when treated with an excess of sodium in boiling amyl alcohol.

Anal. Calcd, for $C_{33}H_{24}$: C, 94.3; H, 5.7. Found: C, 94.5; H, 5.7.

α,γ-Bisdiphenylene-β-phenylallyl Chloride.—A solution of 16 g. of α,γ-bisdiphenylene-β-phenylallyl alcohol in the minimum amount of hot dry benzene was cooled to 15°, a few grams of powdered calcium chloride was added, and a current of dry hydrogen chloride was led in for one hour. The mixture was filtered and distilled to a small volume under reduced pressure at a temperature not higher than 30°. The addition of ligroin caused a rapid separation of the chloride, pure enough for use directly. Recrystallization from benzene–ligroin gave bright yellow prisms that darkened at 125° and melted with blackening and gas evolution at 145–155°.

Anal. Calcd. for $C_{33}H_{21}Cl$: C, 87.7; H, 4.6; Cl, 7.8. Found: C, 88.1; H, 4.6; Cl, 7.8.

When boiled with methyl or ethyl alcohol, the chloride gave the corresponding ethers in quantitative yield. When treated with sodium in boiling ethanol, it yielded a deep blue solution, not decolorized by excess sodium; diluted with water, this solution lost its color ahd deposited a red amorphous substance. A benzene solution of the chloride gave a deep violet color with aluminum chloride.

α,γ-Bisdiphenylene-β-phenylallyl.—A suspension of 12 g. of α,γ-bisdiphenylene-β-phenylallyl chloride in 200 ml. of dry ether was shaken with 50 g. of mercury for 12 hours. The solid was then removed, washed with ether, and extracted repeatedly with hot benzene. Cooling the combined extracts gave 4.5 g. of the radical, and from the combined ether and benzene mother liquors there was obtained an additional 1.3 g. At first these operations were carried out under nitrogen, but the inert atmosphere was later found to be unnecessary.

From benzene the radical crystallized in beautiful diamond-shaped plates, green by reflected light and red-brown by transmitted light, m.p. 222–224°. These crystals contain one molecule of benzene which is given off completely only when the compound is heated at 100° for two hours under reduced pressure.

Anal. Calcd. for $C_{33}H_{21} + C_6H_6$: C, 94.6; H, 5.4; C_6H_6, 15.8. Found (sample dried at 25° under reduced pressure): C, 94.3; H, 5.5; C_6H_6 (loss at 100°), 16.5. Calcd. for $C_{33}H_{21}$: C, 94.9; H, 5.1. Found (sample dried at 100° under reduced pressure): C, 94.5; H, 5.0.

From acetic acid the radical crystallized in brown needles, m.p. 188–191°, that contained no solvent.[8]

Anal. Calcd. for $C_{33}H_{21}$: C, 94.9; H, 5.1. Found: C, 94.8; H, 5.1.

Molecular Weight (ebullioscopic).—Benzene, 19.9; $C_{33}H_{21} + C_6H_5$, 0.2782, 0.4139, 0.6277, 0.6962; Δt, 0.038, 0.056, 0.093, 0.103: *M*, 818, 827, 756, 757; mean, 790. Calcd. for $C_{66}H_{42}$: *M*, 834; α = 5.6%.

Reactions of the Radical.—The red-brown solution of the radical in acetone became deep blue when a piece of solid potassium hydroxide was added; this color was discharged by water,

A 1% ether solution of the radical became blue immediately on shaking with 1% sodium amalgam. With 40% amalgam, the solution became blue and finally red-brown, and then on hydrolysis gave α,γ-bisdiphenylene-β-phenylpropane in nearly quantitative yield. The same hydrocar-

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[5] A hydrocarbon tentatively given this structure was synthesized in a different way by L. A. Pinck and G. E. Hilbert (THIS JOURNAL, **68**, 2014 (1946)]. Repetition of their synthesis gave the product described by them and found to be identical with the substance described here (mixed m.p. and infrared spectrum), confirming the structure assigned.

[6] In view of the recent more accurate data from E. S. R. measurements (footnote 1) it is now felt that the original molecular weight determinations were in error. Resistance to oxygen is ascribed to unusual resonance stabilization of the radical.

[7] Early experiments in this direction were unsuccessful, but it now appears feasible to try again using a synthetic method discovered recently by S. Wawzonek and E. Dufek (THIS JOURNAL, **78**, 3530 (1956)).

[8] The appearance of this solvent-free material was unchanged after 23 years, but unlike the solvated radical, E.S.R. measurements by Professor Wertz showed that the old sample had lost its free radical properties.

bon was obtained by reduction of the radical with sodium and boiling amyl alcohol.

An excess of a carbon tetrachloride solution of chlorine decolorized the radical after 30 minutes; hydrogen chloride was evolved and no crystalline product could be isolated. When the radical (0.5 g.) in 20 ml. of carbon tetrachloride was mixed with 0.2 g. of bromine and allowed to stand for 12 hours, the color became noticeably lighter. Distillation of the solvent at room temperature left a brown gum which was partly dissolved by 35 ml. of boiling alcohol. Cooling this solution gave 0.15 g. of α,γ-bisdiphenylene-β-phenylallyl ethyl ether.

A solution of 0.4 g. of the radical in 25 ml. of benzene was boiled for 6 hours while a stream of oxygen was passed through. The solution was then distilled to a small volume and cooled, giving 0.1 g. of unchanged radical. No other crystalline substance could be isolated.

A hot solution of 0.5 g. of the radical in 25 ml. of acetic acid was treated with 1 g. of chromic acid in a little water. After the vigorous reaction was over the solution was boiled for five minutes. There was obtained 0.1 g. of benzoic acid and 0.3 g. of steam distilled fluorenone.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

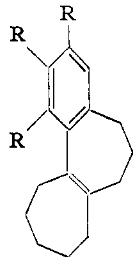
The Cyclodehydration of 2-(γ-Phenylpropyl)-cycloheptanone[1,2]

BY C. DAVID GUTSCHE, N. N. SAHA[3] AND HERBERT E. JOHNSON

RECEIVED DECEMBER 26, 1956

The cyclodehydration of 2-(γ-phenylpropyl)-cycloheptanone has been found to give, instead of the expected olefin Ia, a mixture containing 1-cyclohexyltetralin, 2-cyclohexyltetralin, 1-cyclohexylnaphthalene, 2-cyclohexylnaphthalene and other unidentified products. These materials were characterized by isolation from the cyclization mixture followed by comparison with authentic samples, the syntheses for which are described.

The work described in this communication had its inception in an attempt to synthesize octahydrodemethoxydeoxydeacetamidocolchicine (Ib)[4] by cyclization of 2-[(γ-3′,4′,5′-trimethoxyphenyl)-propyl]-cycloheptanone (IVb). The reaction, however, did not take the desired course. In the hope of elucidating the actual events, the same reaction with the un-methoxylated analog IVa was investigated in considerable detail.



Ia, R = H
Ib, R = OCH_3

The ketones IVa and IVb were prepared in 60 and 68% over-all yield, respectively, from the corresponding γ-arylbutylamines IIa and IIb by cathylation to IIIa and IIIb followed by nitrosation and treatment with cyclohexanone under the usual ring-enlargement conditions.[5] In view of the known efficacy of polyphosphoric acid as a cyclizing agent for systems containing methoxyl groups,[6] this was the reagent of choice in the case of IVb and, for comparative purposes, in the case of IVa also. In both instances, somewhat more strenuous conditions than are usually employed were necessary to effect complete disappearance of the ketone, and it is this fact which may be responsible for the wayward course of the cyclization. Ketone IVb required contact with polyphosphoric acid at 125° for 30 minutes; ketone IVa required contact with polyphosphoric acid at 100° for 24 hr. or 200° for 2.5 hr. In each case a volatile fraction (30–45%) was obtained which boiled in the range expected for the cyclodehydration product. It is these materials, principally that derived from IVa, which is the subject of this discussion.

The cyclization product from IVb consisted of an oil possessing an analysis in approximate agreement with a $C_{19}H_{26}O_3$ formula (although a methoxyl determination indicated some demethylation). The ultraviolet spectrum, however, showed strong absorption bands at 235 mμ 41,500) and 278 mμ (5000) with a minimum at 254 mμ (3580), whereas Ib has a maximum at 254 mμ (7760) and a minimum at 243 mμ (6030).[4] Similarly, the cyclization product from IVa consisted of an oil possessing an analysis in close agreement with a $C_{16}H_{20}$ formula but an ultraviolet spectrum quite different from that expected for Ia.[7]

Cyclization into the benzene nucleus was indicated by the infrared spectrum of the product from IVa which showed a pattern of bands in the 1650–2000 cm.$^{-1}$ region characteristic of 1,2-disubstituted benzenes.[8] The virtual absence of an olefinic linkage in the product was indicated by the

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[1] This work was supported, in part, by: (a) a grant-in-aid from the American Cancer Society upon recommendation of the Committee on Growth of the National Research Council, and (b) a grant-in-aid from the National Science Foundation.

[2] A preliminary account of this work was presented at the 126th Meeting of the American Chemical Society, New York, N. Y., 1954, Abstracts, p. 33-O.

[3] Postdoctoral research associate, 1955–1956.

[4] H. Rapoport, A. R. Williams, J. E. Campion and D. E. Pack, THIS JOURNAL, **76**, 3693 (1954).

[5] C. D. Gutsche, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 364.

[6] *Cf.* for example, A. Koebner and R. Robinson, *J. Chem. Soc.*, 1994 (1938); W. E. Bachmann and W. J. Horton, THIS JOURNAL, **69**, 58 (1947); R. C. Gilmore and W. J. Horton, *ibid.*, **73**, 1411 (1951); J. Koo, *ibid.*, **75**, 1891 (1953).

[7] Compounds containing a double bond in conjugation with a phenyl group ordinarily have an absorption maximum in the 245–265 mμ region. Thus, styrene has a maximum at 245 mμ (16,000)—M. Pestemer and L. Willigut, *Monatsh.*, **66**, 119 (1935); 2-phenylcyclohexene has a maximum at 247 mμ (12,000)—A. C. Cope, F. S. Fawcett and G. Munn, THIS JOURNAL, **72**, 3399 (1950); 1,2-dihydronaphthalene has a maximum at 262 mμ (10,000)—R. A. Morton and A. J. A. de Gouveia, *J. Chem. Soc.*, 916 (1934). The cyclization product from IVa has maxima at 218 mμ (13,800), 224 mμ (30,000), 268 mμ (1820) and 274 mμ (1900).

[8] C. W. Young, R. B. DuVall and N. Wright, *Anal. Chem.*, **23**, 709 (1951).