

The infrared spectrum of the polymer showed the bands previously reported.⁴ A band at 8.8 μ suggested the presence of an enol ester.¹

Saponification.—Two samples (6.706 and 8.214 g.) of the polymer were saponified with 1 *N* potassium hydroxide in ethanol (50 ml.) and excess base was titrated with 0.5 *N* hydrochloric acid to give a saponification equivalent of 296 and 295 (theoretical 294.5). The acids from the saponifications were isolated, they had a neutral equivalent of 312.5 and 314 (theoretical 313).

The ultraviolet spectrum of the acids (19.7 mg. at 100 ml., 95% ethanol) showed a maximum at 232 $m\mu$ with an absorbance of 0.83. Rearranged methyl sterculate collected from the exit of the gas chromatograph had the identical absorption with ϵ 21,000. On this basis the sterculic acid polymer contained 6.5% of rearranged sterculic acid residues as end groups.

T.l.c. of the acids and of their methyl esters showed two major spots of low R_f corresponding to hydroxy acids, a spot that developed with 2,4-DNP spray indicative of a ketone and two minor spots of high R_f corresponding to the rearranged sterculic acid residues. The methyl esters could be distilled without decomposition, b.p. 115–150° at 0.05 mm. G.l.c. of the esters showed a peak having a retention time very similar to that of methyl 9-ketostearate.

Ozonolysis.—The polymer (78 g.) in methylene chloride (750 ml.) was cooled to –35° and ozone (0.06 mole/hr.) was passed through the solution for 5 hr. Excess ozone was flushed out with nitrogen and the solution was added to 65 g. of zinc dust in 600 ml. of 50% acetic acid with vigorous stirring, after which the solution was placed on a boiling water bath for 1 hr. The aqueous portion that had steam distilled with the methylene chloride was treated with methone (10 g.) in ethanol (60 ml.) to yield 6.12 g. of the methone derivative of formaldehyde, m.p. and m.m.p. 189–190°, lit.¹² 189°, after two crystallizations from ethanol.

The residue in the flask was taken up in ether, washed with water, evaporated, and hydrolyzed with 10% potassium hydroxide in methanol (600 ml.). After addition of water, the alkaline solution was extracted with ether to yield the neutral components (12.2 g.); it was then acidified and extracted with ether to give the acid components (61 g.).

Neutral Components.—The neutral fraction was acetylated at room temperature overnight with pyridine and acetic anhydride (15 ml. each) and distilled. The first fractions (6.10 g., b.p. 103–111° at 30 mm.) contained primarily 2-decanone (4.44 g. estimated by g.l.c.); fractions 5 and 6 (1.40 g., b.p. 51–100° at 0.06 mm.) contained 2-ketodecyl acetate; and fractions 7–9 (1.97 g., b.p. 103–180° at 0.06 mm.) contained a large mixture of com-

pounds by t.l.c. 2-Decanone was converted to its 2,4-dinitrophenylhydrazone, m.p. and m.m.p. 74–75°, lit.¹³ 73–74°. 2-Ketodecyl acetate was recrystallized from methanol, m.p. 55.5–56.5°, lit.⁴ 55.5–55.8°.

Acid Components.—The acids were converted to their methyl esters with 7% boron trifluoride in methanol (500 ml.) to yield 56 g. of product which was distilled. Fractions 1–3 (5.87 g., b.p. 109–110° at 30 mm.) and fraction 4 (2.20 g., b.p. 35–38° at 0.08 mm.) contained mostly methyl pelargonate (7.63 g. estimated by g.l.c.). They were hydrolyzed to pelargonic acid which was converted to its *p*-toluidide, m.p. and m.m.p. 82–83.5°, lit.¹⁴ 84°.

Fractions 5–7 (8.46 g., b.p. 76–78° at 0.08 mm.) contained dimethyl azelate (5 g.) and an unknown ester (3.3 g.) of slightly longer retention time on g.l.c. The mixture was hydrolyzed to the acids and crystallized from 30 ml. of benzene. The crystals (2.62 g., m.p. 99–104°) were recrystallized from hot water and identified as azelaic acid, m.p. 104–106°, m.m.p. 105–107°, lit.¹⁴ 106°. The benzene filtrate was evaporated to a syrup that crystallized on standing. It was recrystallized from chloroform and then from petroleum ether (b.p. 30–40°) to yield 9-ketodecanoic acid, m.p. 47–48°, lit.¹⁵ 47.5–48.5°. The acid gave a single spot on t.l.c. (2,4-DNP spray), a positive iodoform test,¹⁴ a neutral equivalent of 180 (calcd. 186), and a semicarbazone derivative of m.p. 126–127°, lit.¹⁶ 127°, which, after recrystallization from methanol and drying *in vacuo*, melted 130–130.5°. The ethyl ester of the semicarbazone was prepared with ethanol and sulfuric acid at room temperature, m.p. 98–99°, lit.^{15,16} 97–98°. The same derivative was obtained from the ethyl ester of the acid and semicarbazine hydrochloride, m.p. 97–98°.

Fractions 8 and 9 from the distillation (21.9 g., b.p. 135–200° at 0.08 mm.) were hydrolyzed and the derived acids were crystallized from methanol three times to yield a mixture of 9-hydroxy-10-keto- and 9-keto-10-hydroxystearic acid, m.p. 62.5–66°, lit.¹⁷ 64.5–65.5°, neut. equiv. 316 (calcd. 314). A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol-benzene, m.p. 146.5–147°, lit.¹⁶ 146.5. The mixture of acids (1.24 g.) in acetic acid (10 ml.) was treated with chromic anhydride (0.25 g.) in acetic acid–water (2 ml.) on an ice bath. Water was added and the ether extract was crystallized from acetone and ethanol to yield pale yellow plates of 9,10-diketostearic acid, m.p. 84–84.5°, lit.¹⁷ 85.5°.

(13) C. Jutz, *Ber.*, **91**, 1867 (1958).

(14) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

(15) G. Barger, R. Robinson, and L. H. Smith, *J. Chem. Soc.*, 718 (1937).

(16) H. McKennis, Jr., and V. DuVigneaud, *J. Am. Chem. Soc.*, **68**, 832 (1946).

(17) G. King, *J. Chem. Soc.*, 1788 (1936).

(12) E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

Rearrangement of the Vinylog of Benzpinacol¹⁻³

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The *trans* vinylog of benzpinacol in boiling acetic acid undergoes 1,2-phenyl group migration to give the β,γ -unsaturated ketone. The *cis* isomer is first cyclodehydrated to the 2,5-dihydrofuran but is rearranged to the same ketone under more drastic acid catalysis. Rigorous proof of structure of the ketone includes degradations, reactions connecting it with a known compound, and n.m.r. spectrum of its carbinol. Lithium aluminum hydride reduction of tetraphenyl acetylene dicarbinol gives the *trans* ethylene dicarbinol and tetraphenylbutadiene, the latter seemingly by two successive conjugate ("1,4") reductions.

This investigation was suggested by the 1,2-phenyl group migration in the facile, pinacol-like rearrange-

ment of the cyclopropylog of benzpinacol, 1,2-di(di-phenylhydroxymethyl)cyclopropane.³ In an inconclusive study of the *cis* and *trans* vinylogs of pinacol (I) it had been suggested⁵ that 1,4-methyl group migration might occur and give a true vinylog of pinacolone, the

(1) (a) Supported in part by a contract with the office of Ordnance Research, U. S. Army, 1957–1958. (b) Received some support from a National Science Foundation grant, summer, 1963. (c) An important part of this work was completed by D. W. Boykin, Jr., under a University Philip Francis du Pont Fellowship, 1963–1964.

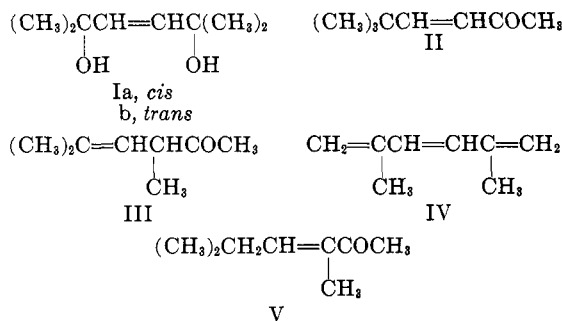
(2) (a) The larger part of this work was done in 1957 and is described in a Ph.D. Dissertation (R. G. Bass), University of Virginia, May 1961. (b) Reported in part by R. G. Bass and R. E. Lutz, Southeast Regional Meeting of the American Chemical Society, Richmond, Va., Nov., 1959; "The Bulletin" (Va. sect.), Vol. 36, 1959, abstracts, p. 197. (c) Specific mention of this work is made in ref. 4a and b.

(3) Cf. R. A. Darby and R. E. Lutz, *J. Org. Chem.*, **22**, 1353 (1957).

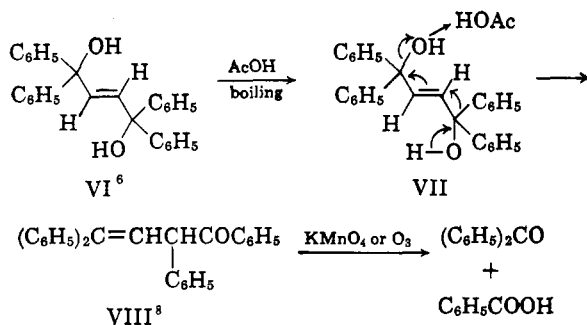
(4) Cf. (a) R. E. Lutz, J. I. Dale, and D. W. Boykin, Jr., *J. Am. Chem. Soc.*, **85**, 2340 (1963); (b) D. W. Boykin, Jr., and R. E. Lutz, *ibid.*, **86**, 5046 (1964).

(5) (a) J. R. Johnson and O. H. Johnson, *ibid.*, **64**, 2615 (1940); (b) cf. also inconclusive study of dehydration of 2-methyl-2-butene-1,4-diol, A. F. Shepard and J. R. Johnson, *ibid.*, **54**, 4385 (1932).

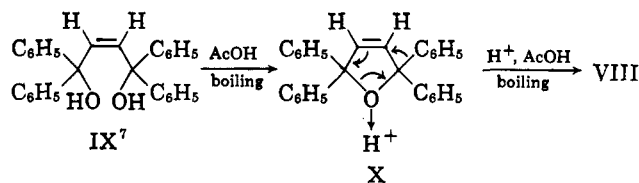
α,β -unsaturated ketone II. This would be feasible only in the *cis* isomer, however, whereas the *trans* isomer would be expected instead to undergo 1,2-methyl migration³ with considerable strain relief by destruction of both quaternary centers of the glycol and formation of the β,γ -unsaturated ketone III or its α,β -isomer V. Actually none of these rearrangement products was isolated; the *cis* dicarbinol gave only the dihydrofuran, whereas the *trans* dicarbinol apparently gave the 1,3,5-triene IV and resins.^{5a}



We have investigated the *trans* and *cis* vinylogs of benzpinacol itself (VI⁶ and IX⁷) which are incapable of dehydration to polyenes, and find that the *trans* isomer VI undergoes extraordinarily facile pinacol-like 1,2-phenyl group migration under the action of hot glacial acetic acid without added mineral acid, conditions considerably milder than those usually required for the rearrangement of pinacol itself. The product, the β,γ -unsaturated ketone VIII,⁸ was presumed to form as the result of solvent-induced ionization and concerted 2 to 3 double bond and 1 to 2 phenyl group migrations, as pictured in VII.



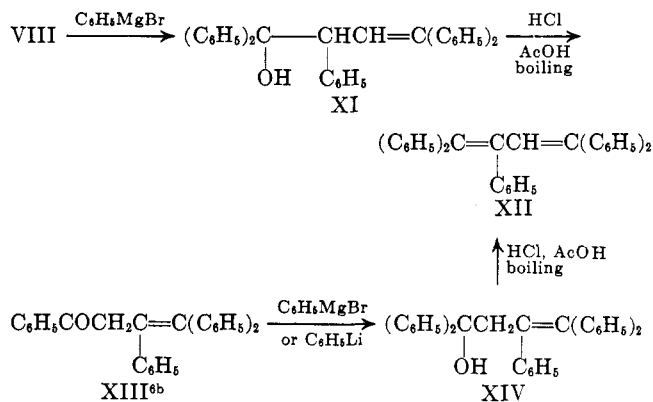
Since the steric arrangement of phenyl groups in the *cis* ethylenic dicarbinol IX would not be favorable for the type of rearrangement pictured in VII for the *trans* dicarbinol, it came as no surprise that concentrated acetic acid with or without added mineral acid caused facile cyclodehydration to the dihydrofuran X.^{6b,7b} However it seemed likely that rearrangement might occur under more drastic conditions, and a test experiment confirmed this prediction and gave the same β,γ -unsaturated ketone VIII. Phenyl group migration may take place in an intermediate allylic carbonium



ion, or directly upon protonation through a concerted process such as pictured in X.

The Structure of the β,γ -Unsaturated Ketone VIII.— This ketone, obtained first as an oil and later crystallized, was converted into a semicarbazone. Both were oxidized by permanganate to benzophenone and benzoic acid, showing that rearrangement of one of the *gem*-diphenyl groups had occurred. Ozonolysis of the ketone also gave benzophenone and indicated the β,γ -location of the double bond.⁸ Ultraviolet, infrared, and n.m.r. spectra were consistent with but did not rigorously prove this formulation.

The skeletal structure was proved by a series of reactions connecting this ketone with a known compound as follows: VIII was treated with phenylmagnesium bromide and the resulting unsaturated carbinol XI (not isolated) was dehydrated by boiling concentrated hydrochloric-acetic acid mixture to the diene XII (new). This same diene was obtained by a similar sequence of reactions from the known isomeric β,γ -unsaturated ketone XIII^{6b} by addition of phenylmagnesium bromide or phenyllithium and dehydration of the resulting isomeric unsaturated carbinol XIV (new). The diene, which involves no *cis-trans* stereoisomerism, was characterized by its ultraviolet absorption bands at 240 and 342 $m\mu$ (ϵ 24,890 and 16,950).



The ketone VIII has been related to 2,3,5,5-tetraphenyl-4,5-dihydrofuran and 1-benzoyl-1,2,2-triphenylcyclopropane from which it has been obtained upon acid-catalyzed rearrangement.^{4b} However, because of the desirability of making a still further and more rigorous check on the β,γ -location of the double bond, this ketone was reduced by lithium aluminum hydride to the unsaturated carbinol XIV in which the double bond location should not have been disturbed, an assumption confirmed by chromic acid oxidation with regeneration of the ketone (VIII). The ultraviolet absorption of this carbinol, λ_{max} 255 $m\mu$ (ϵ 16,900), strongly indicates the β,γ -location of the double bond and its α -phenylstyryl chromophore because a close model for the alternative XV, namely XVI,⁹ has its

(9) Prepared by lithium aluminum hydride reduction of 2-hydroxy-2,3,5,5-tetraphenyl-3,5-dihydrofuran^{4a}; data are to be published shortly.

(6) (a) K. Scholtis, *Ann.*, **557**, 82 (1945); (b) R. E. Lutz and C. L. Dickson, *J. Org. Chem.*, **27**, 2040 (1962).

(7) (a) P. Cadiot and W. Chodkiewicz, *Bull. soc. chim. France*, 457 (1951); (b) J. Salkind and V. Teterin, *J. prakt. Chem.*, **133**, 195 (1932).

(8) Cf. (a) relationship to cyclopropyl ketones and dihydrofurans^{4b} and (b) assignments of double bond locations in the β,γ -unsaturated ketones obtained by acid-catalyzed rearrangements of cyclopropyl ketones [H. M. Walborsky and L. Plonsker, *J. Am. Chem. Soc.*, **83**, 2138 (1961)]. (c) Ketone VIII has now been isolated (25%) from the reaction reported in ref. 4a.

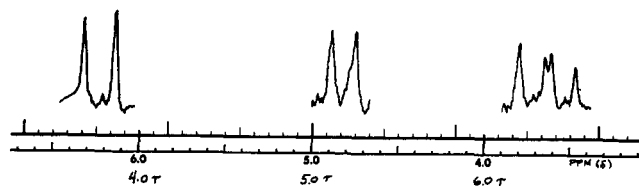
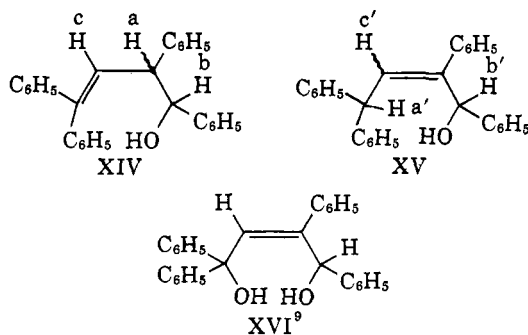


Fig. 1.—N.m.r. spectrum of 1,2,4,4-tetraphenyl-3-buten-1-ol (XIV).

styryl absorptivity at a distinctively shorter wave length, 247 $m\mu$, and a very considerably lower ϵ -value of 11,000.

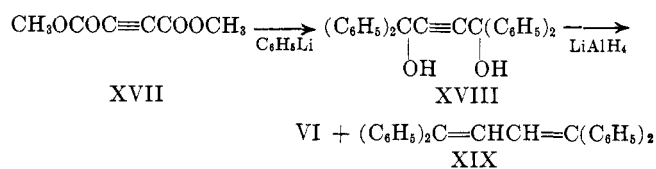


The n.m.r. spectrum for the carbinol should distinguish unequivocally between the two possibilities, XIV and XV, as it could not do for the corresponding double bond isomers of the ketone VIII. The spectrum of the carbinol, XIV (or XV), Fig. 1, includes an aromatic multiplet centered at *ca.* τ 2.8, and a singlet at 8.1 which represents the hydroxyl proton and which was identified as such by its disappearance upon deuterium exchange. The doublet centered at τ 3.75 was assigned to the vinyl proton which would exist in both XIV and XV and is marked *c* and *c'*; and the assignment was confirmed by synthesis¹⁰ of the carbinol half-deuterated at the proton *c*-position, for which this doublet was proportionally diminished in intensity. The expected splitting pattern for the protons *a*, *b*, and *c* of both XIV and XV would be two doublets and a quartet. The second doublet at τ 5.18 ($J = 9.0$ c.p.s.) must be assigned to the benzylic proton XIVb because of the large coupling constant which excludes XVb'.¹¹ The observed quartet centered at τ 6.4 is assigned to proton XIVa because it is well removed from the accepted vinylic proton region of τ 2.4–5.5,^{11b} and its coupling constant $J_{b,c} = 11.0$ c.p.s. is considerably larger than the accepted range for allylic coupling.¹¹ The compound XVI,⁹ a model for XV, showed a vinylic singlet at τ 3.45 and no evidence of coupling of the vinylic and allylic protons. The assignment of structure XIV to the carbinol and consequently the β,γ -location of the double bond in the ketone VIII are thus rigorously established.

Concerning Preparation of the *cis*-Unsaturated Dicarbinols.—In our preparation of a sample of the *cis* dicarbinol IX by catalytic reduction of the acetylenic dicarbinol XVIII following the procedure of Cadiot and Chodkiewicz,^{7a} we obtained a minor product corresponding to the one which they reported as VI and

which had a melting point close to that of the fully saturated dicarbinol. We identified our minor product as exactly that (1,1,4,4-tetraphenylbutane-1,4-diol) by comparison with an authentic sample prepared by addition of phenylmagnesium bromide to diethyl succinate.¹²

In seeking a better synthesis of the *trans* ethylenic dicarbinol VI where yields were low and separations difficult, it was noted that numerous propargyl alcohols have been reduced by lithium aluminum hydride to the corresponding allyl alcohols.¹³ For our study the acetylenic dicarbinol XVIII was prepared in a new and practical way by addition of phenyllithium to commercially available acetylene dicarbomethoxylate XVII; although the yields were low, the scheme was simple and direct.¹⁴ Lithium aluminum hydride reduced the acetylenic dicarbinol XVIII to an easily separable mixture of the *trans* ethylenic dicarbinol VI (50%) and tetraphenylbutadiene XIX (25%). The reduction to the latter is in analogy with the reduction of the 1,4-diphenylbutynediol to *trans,trans*-1,4-diphenyl-1,3-butadiene.^{13, 15a}



Mechanism of Lithium Aluminum Hydride Reduction of the Acetylene Dicarbinol XVIII.—The reduction to the *trans* ethylenic dicarbinol VI is reasonably accounted for in terms of propargyl type conjugation in the complex dianion XX and inter- or intramolecular hydride transfer to an acetylene carbon which (as compared with a corresponding ethylene carbon) is inherently though weakly electrophilic. The resulting allyloxy system, although reducible, should be somewhat more resistant toward the second hydride transfer, especially so, perhaps, if the product is stabilized in the form of a monocyclic or spiran complex,^{15c} *e.g.*, XXI.

The very interesting reductive elimination of both hydroxyl groups from the acetylene dicarbinol XVIII in one operation to produce the diene XIX can not have proceeded through the saturated 1,4-glycol followed by dehydration, because the latter glycol is known¹² and was shown in separate experiment to be stable toward the reagent under the reaction and work-up conditions—and it would be difficult to imagine reductive elimination of *both* hydroxyl groups in a mechanism involving reduction *first* of the acetylene linkage to the ethylene. The intriguing possibility of a conjugate (1,6) reductive elimination of the two hydroxyl groups to the cumulene as an intermediate, analogous to the accomplishment of just this result by the action of alcoholic sulfuric acid–potassium iodide,¹⁶

(12) S. F. Acree, *Am. Chem. J.*, **37**, 181 (1905).

(13) N. G. Gaylord, "Reductions with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 968.

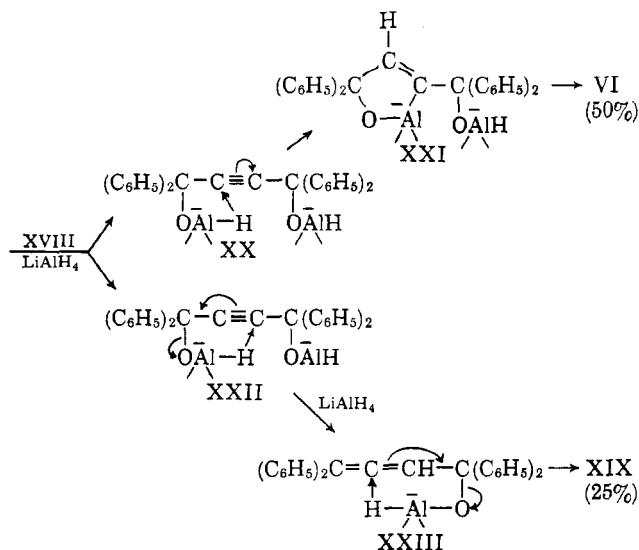
(14) *Cf.* (a) R. E. Lutz, C. L. Dickerson, W. J. Welstead, Jr., and R. G. Bass, *J. Org. Chem.*, **28**, 711 (1963); (b) G. DuPont, *Ann. chim.*, [8] **30**, 498 (1913).

(15) (a) E. B. Bates, E. R. H. Jones, and M. C. Whiting, unpublished results (ref. 13, p. 971); (b) *cf.* also *J. Chem. Soc.*, 1854 (1954); (c) F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948); (d) V. Micoev and M. Lj. Mihailovic, "Lithium Aluminum Hydride in Organic Chemistry," Izdavačko Preduzeće, Belgrade, Yugoslavia, 1955, pp. 127, 133.

(16) A. Zweig and A. K. Hoffmann, *J. Am. Chem. Soc.*, **84**, 3278 (1962).

(10) Results are to be published shortly.

(11) (a) Allylic coupling when it appears would have a relatively low J -value of *ca.* 0.5–2.0 c.p.s. (b) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.



was tested by preparing a sample of the cumulene and demonstration in an independent experiment that it is not so reduced by lithium aluminum hydride under the reaction conditions.

It appears to us that the mechanism of this remarkable reductive elimination of the hydroxyls involves two successive conjugate (1,4) reductions, the first, hydride transfer giving the allene-carbinol XXIII (e.g., XXII) [a reasonable possibility judging from the reduction of $\text{R}'\text{R}''\text{C}(\text{OH})\text{CH}=\text{CHC}\equiv\text{CH}$ to $\text{R}'\text{R}''\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{C}=\text{CH}_2$],^{15b} and the second involving the highly active central carbon of the allenic carbinol double bond (e.g., XXIII). A less likely but possible alternative second step is nonconjugate (1,2) reduction of the double bond of the allyl system^{15c} followed by dehydration. The postulation of successive conjugate reduction is supported by the striking analogy to the double addition of phenylmagnesium bromide to dibenzoylacetylene to give the unstable 1,2,3,4-tetraphenylbutadiene-1,4-diol, for which successive conjugate additions to the acetylenic ketone and intermediate allene-ketone systems have been suggested.^{14a}

Experimental

1,1,3,4-Tetraphenyl-1-buten-4-ol (VIII).^{4b,8c} **A. By Rearrangement of *trans*-1,1,4,4-Tetraphenyl-2-butene-1,4-diol (VI).**—In several runs a solution of 2.0 g. of the *trans* dicarbinol VI in 20 ml. of glacial acetic acid was refluxed for 1 min. and allowed to evaporate on a steam bath. A 20-ml. benzene solution of the resulting oil was placed on a chromatographic column filled with Florisil packed in petroleum pentane, and was eluted with 250-ml. portions of benzene-petroleum pentane of successively increasing benzene concentration (benzene added in 10% increments). The oil, obtained from the 10–50% benzene fractions, was rechromatographed and stored in a desiccator. After approximately 2 months crystals formed, and recrystallization from *n*-hexane gave 81–84% of VIII: m.p. 91.5–93°; infrared 1680 cm^{-1} ; ultraviolet λ_{max} 250 and 255 $\text{m}\mu$ (ϵ 28,000 and 26,400); n.m.r. (Varian A60) aromatic multiplet centered at *ca.* τ 2.7, doublets centered at 3.25 and 4.55; intensities 20:1:1.

Anal. Calcd. for $\text{C}_{28}\text{H}_{28}\text{O}$: C, 89.80; H, 5.92. Found: C, 89.69; H, 5.94.

B. By Acid-Catalyzed Rearrangement of 2,2,5,5-Tetraphenyl-dihydrofuran (X).—A solution of 300 mg. of the 2,5-dihydrofuran in 7 ml. of glacial acetic acid containing 3 drops of concentrated sulfuric acid was refluxed for 2 hr., poured into ice-water, and extracted with ether. The ether layer (washed with potassium carbonate solution) gave an oil which was shown to contain VIII by infrared analysis and was chromatographed over Florisil (as above). The 10–20% benzene fractions yielded 75 mg.

(25%) of starting material, m.p. 182–184, identified by mixture melting point and infrared analysis. The 40–60% benzene fractions yielded 180 mg. (80%, allowing for recovered starting material) of VIII, m.p. 92–94°, identified with the sample from VI by mixture melting point and infrared analysis.

The semicarbazone of VIII was made in absolute ethanol with pyridine and semicarbazide hydrochloride (reflux for 6 hr.). It was crystallized from a methanol-benzene mixture (with charcoal treatment): yield 55% from crude VIII (oil), m.p. 209–211° after several crystallizations from ethanol, infrared 1700 cm^{-1} , ultraviolet 254 $\text{m}\mu$ (ϵ 21,360).

Anal. Calcd. for $\text{C}_{28}\text{H}_{25}\text{N}_3\text{O}$: C, 80.71; H, 5.84. Found: C, 81.01; H, 6.14.

Permanganate oxidation of the semicarbazone of VIII in refluxing pyridine-water mixture by 6 g. of KMnO_4 (color persisting after 3 hr.) gave 60% of benzophenone and 63% of 2 equiv. of benzoic acid (identified). Oxidation of a sample of non-crystalline VIII gave similar results but lower yields.

Ozonization of VIII.—A solution of 200 mg. of pure VIII in 55 ml. of chloroform containing 1 ml. of methanol was treated with an excess of ozonized air at 0°. Evaporation, take-up in ether, washing with potassium carbonate, and acidification of the aqueous layer gave benzoic acid, 25 mg. (20%), identified by mixture melting point and infrared analysis. Evaporation of the ether layer, steam distillation, extraction of the distillate with ether, and evaporation yielded an oil which on treatment with 2,4-dinitrophenylhydrazine gave 85 mg. (44%), recrystallized from ethanol-benzene mixture, m.p. 235–238°, identified by mixture melting point and infrared analysis as benzophenone 2,4-dinitrophenylhydrazone.

1,1,3,4-Tetraphenyl-1-buten-4-ol (XIV).—A solution of 600 mg. of VIII in 25 ml. of dry ether with 60 mg. of lithium aluminum hydride was stirred for 1.5 hr. under nitrogen. Hydrolysis, acidification by 20 ml. of 15% hydrochloric acid, and washing, drying, and evaporation of the ether layer gave an oil (90–95%, infrared consistent with XIV). Purification by chromatography on Florisil produced a glassy quasi-solid XIV; attempts to crystallize it were unsuccessful; infrared (smear) 3550 and 3435 cm^{-1} ; ultraviolet 255 $\text{m}\mu$ (ϵ 16,900); n.m.r. (CDCl_3) aromatic multiplet centering at τ 2.8, olefinic doublet at 3.75, terminal benzylic CH doublet at 5.18, internal benzylic quartet at 6.4, and hydroxyl singlet at 8.1; intensities *ca.* 20:1:1:1. Shaking of the sample with D_2O caused the peak at τ 8.1 to disappear.

Anal. Calcd. for $\text{C}_{28}\text{H}_{28}\text{O}$: C, 89.32; H, 6.42. Found: C, 89.49; H, 6.41.

Chromic Acid Oxidation of XIV.—To a stirred solution of 95 mg. of XIV in 20 ml. of acetone, was added 0.1 ml. of a previously prepared solution of 10 g. of chromic oxide in 10 ml. of concentrated sulfuric acid diluted to 50 ml. Stirring for 2 min., pouring into water, and extracting with ether, drying the ether layer, and evaporating gave an oil which crystallized from *n*-hexane, 60 mg. (63%) of VIII, m.p. 90–92°, identified by mixture melting point and infrared analysis.

1,1,3,4-Tetraphenyl-1-buten-4-ol 2,4-Dinitrobenzoate.—A solution of 100 mg. of XIV and 260 mg. of 2,4-dinitrobenzoyl chloride in 3 ml. of anhydrous pyridine was refluxed for 1 hr., poured into 50 ml. of 15% hydrochloric acid, and extracted with ether. Evaporation of the ether layer and recrystallizations from ethanol-chloroform mixture (with charcoal treatment) gave 60 mg. (40%) of pure dinitrobenzoate: m.p. 156–157°, after another crystallization; infrared 1725 cm^{-1} ; ultraviolet λ_{max} 250 $\text{m}\mu$ (ϵ 26,800); n.m.r. aromatic multiplet centered at *ca.* τ 2.85, doublet at 3.7, and an overlapping quartet appearing as a triplet centered at 5.85; intensities *ca.* 24:1:1.

Anal. Calcd. for $\text{C}_{35}\text{H}_{28}\text{N}_2\text{O}_6$: C, 73.67; H, 4.59; N, 4.91. Found: C, 73.61; H, 4.31; N, 4.74.

Conversion of the Ketone VIII into 1,1,2,4,4-Pentaphenylbutadiene-1,3 (XII).—A 150-ml. absolute ether solution of a fresh sample of noncrystalline VIII prepared from 2 g. of the *trans* dicarbinol VI was treated with phenylmagnesium bromide (from 1.22 g. of Mg in 125 ml. of ether, added in portions, and refluxing for 2.5 hr.). The resulting oil (XI, not characterized) was treated with a refluxing mixture of glacial acetic acid (100 ml.) and concentrated hydrochloric acid (25 ml.) and the resulting oil, after charcoal treatment in ethanol and seeding, gave the diene XII, yield 16%, m.p. 171–173°, identified by mixture melting point and infrared analysis with the sample prepared from XIII (below).

1,1,3,4,4-Pentaphenyl-3-buten-1-ol (XIV).—A 175-ml. solution of 2 g. of the unsaturated ketone XIII^{5b} (isomeric with VIII) was added dropwise to a stirred 125-ml. ether solution of phenylmagnesium bromide (from 1.22 g. of Mg). After refluxing for 2.5 hr. and standing for 8 hr., work-up was by hydrolysis in ammonium chloride, drying the ether extract, and evaporating. The resulting solid was crystallized from ethanol (with charcoal treatment): yield 1.47 g. (61%) of XIV, needles, m.p. 177.5–178°, infrared (hydroxyl) 3500 cm.⁻¹.

Anal. Calcd. for C₃₄H₂₈O: C, 90.23; H, 6.24. Found: C, 90.20; H, 6.36.

A small sample of XIV was converted by boiling concentrated HCl–AcOH into the diene XII (identified).

1,1,2,4,4-Pentaphenylbutadiene-1,3 (XII).—The total crude solid obtained above from 2 g. of XIV was treated briefly with hot of concentrated HCl–AcOH mixture (25:100). Pouring into water, neutralizing the acid, and ether extraction, gave 1.36 g. (56%) of the diene XII, needles from absolute ethanol: m.p. 172.5–173.5°; λ_{max} (ethanol) 240 and 342 mμ (ε 24,890 and 16,950); infrared aromatic C–H band, 3170 cm.⁻¹, no absorption at 1660–2800 cm.⁻¹.

Anal. Calcd. for C₃₄H₂₈: C, 93.96; H, 6.03. Found: C, 93.79; H, 5.77.

Raney Nickel Hydrogenation of 1,1,4,4-Tetraphenylbutyne-1,4-diol^{7a} (XVIII).—In repetition of the work of Cadiot and Chodkiewicz,^{7a} 10 g. of catalyst was prepared from Raney nickel by heating (steam bath) with 100 ml. of 40% sodium hydroxide (1.5 hr.) and washing finally with absolute ethanol (ignited paper upon drying). Hydrogenation of 1 g. of XVIII in ethanol–benzene mixture (0.2 g. of catalyst) at 30 p.s.i. at 30°, and fractional crystallization of the solid products from carbon disulfide and petroleum hexane, yielded 40% of *cis* dicarbinol IX,⁷ m.p. 100.5–102° (corresponding to “α-isomer” of Cadiot and Chodkiewicz^{7a}) which showed a broad infrared hydroxyl band at 3500 and no absorption at 2880–1570 cm.⁻¹. The higher melting product, m.p. 203.5–205.5° (23%, corresponding to the “β-isomer” of Cadiot and Chodkiewicz^{7a}), was identified as the saturated 1,4-glycol, 1,1,4,4-tetraphenylbutane-1,4-diol, by mixture melting point and infrared analysis with an authentic sample prepared by addition of phenylmagnesium bromide to diethyl succinate¹² (infrared hydroxyl band at 3600 cm.⁻¹). Evidently the “β-isomer” (of Cadiot and Chodkiewicz^{7a}), supposed to be the *trans*

diol VI, is the result of completion of hydrogenation to the saturated glycol, and the supposed isomerization of the “α-isomer” (*cis* IX) is due rather to reduction by hydrogen absorbed on the catalyst.

A New Preparation of 1,1,4,4-Tetraphenylbutyne-1,4-diol (XVIII).—To phenyllithium from 9.2 g. (1.31 g.-atoms) of lithium in 150 ml. of ether, was added dropwise 10 ml. of acetylene dicarbomethoxyate in 50 ml. of ether in a Dry Ice–acetone bath. Work-up and crystallization from isopropanol (with charcoal treatment) gave a total of 8.1 g. (33%) of the glycol XVIII (identified by comparison with a sample prepared by the addition of phenyllithium to dibenzoylacetylene).^{14a}

Lithium Aluminum Hydride Reduction of Tetraphenylbutyne-1,4-diol (XVIII).—To an ether slurry of 1.52 g. (0.04 mole) of lithium aluminum hydride in 250 ml. of absolute ether was added 5 g. (0.013 mole) of XVIII portionwise over 4 min., followed by refluxing 3.5 hr. After hydrolysis and work-up the resulting solid was crystallized from ethanol, 1.13 g. (25%) of 1,1,4,4-tetraphenylbutadiene-1,3 (XII). This was identified by correspondence to known properties,¹⁷ unusual melting behavior (m.p. 195.5–197°, resolidifying, and clearing up at 203°), analysis, blue fluorescence under ultraviolet light, and λ_{max} (ethanol) 250 and 342.5 mμ (ε 22,240 and 35,550). From the filtrate from XII (above) 2.81 g. (61%) of nearly pure *trans* ethylenic glycol XI crystallized, m.p. 198–202.5° (identified by mixture melting point with an authentic sample⁶).

A similar experiment on a sample of the saturated glycol, 1,1,4,4-tetraphenylbutane-1,4-diol, involved evolution of hydrogen, but upon work-up starting material was recovered (90%, identified).

In a preliminary experiment, NaBH₄ in absolute ethanol (refluxing for 4 hr.) did not appear to reduce the acetylenic glycol XVIII.

Failure of Lithium Aluminum Hydride to Reduce Tetraphenylbutatriene (Tetraphenylcumulene).—To a solution of 322 mg. of LiAlH₄ in 50 ml. of dry ether was added 1 g. of tetraphenylcumulene¹⁶ (4-hr. reflux, under N₂). Hydrolysis and extraction by 200 ml. of ether gave 0.98 g. (98%) of starting material (m.p. 235–237°, identified).

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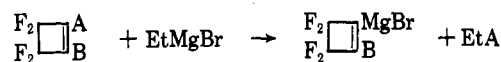
The Exchange Reactions of Fluorinated Cyclobutenes with Grignard Reagents

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Certain fluorinated cyclobutenes have been found to undergo a “halogen–metal exchange” with Grignard reagents in the following manner where A is Br and B is Cl or Br, and also where A is I and B is Br. However,



if A is bromine and B is fluorine, a competing reaction was also observed to take place. The cyclobutenyl Grignard reagent in which B is chlorine was found to undergo rearrangement. Reaction of the cyclic Grignard reagent with water and with elemental iodine gave hydrogen- and iodine-substituted cyclobutenes, respectively, in good yields. Various reaction products were isolated and identified and these products are thought to arise *via* an S_N2' reactions involving the Grignard reagent.

Only a few examples of “halogen–magnesium interchange” reactions have been reported in the literature¹ and of these only one has involved exchange of vinylic halogen. Knunyants² has shown that iodotrifluoroethylene, when treated with phenylmagnesium bromide, undergoes this type of exchange to give the vinyl Grignard reagent, CF₂=CFMgBr.

In contrast to the exchange reaction, fluoro olefins containing only fluorine or chlorine atoms at the vi-

nylic position are known to undergo a substitution reaction with Grignard reagents at the vinylic position.³ Park and Fontanelli⁴ have extended this reaction to fluorinated cyclobutene compounds.

The preparation of a fluorinated vinyl Grignard reagent was first reported by Park, Seffl, and Lacher⁵ in the reaction of CF₂=CFI with magnesium in ether. In 1956, Gray⁶ reported the reaction of CF₂=CBr₂

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