reaction of both Mn^{++} and of MnO_2 with pinacol precludes an accurate determination of the induction factor, and the question of the oxidation states of chromium in the reaction pathway had best be left for further investigation.

Acknowledgment.—The authors wish to express their appreciation to the Petroleum Research Fund and the Eugene Higgins Trust for support of this investigation.

CAMBRIDGE 38, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

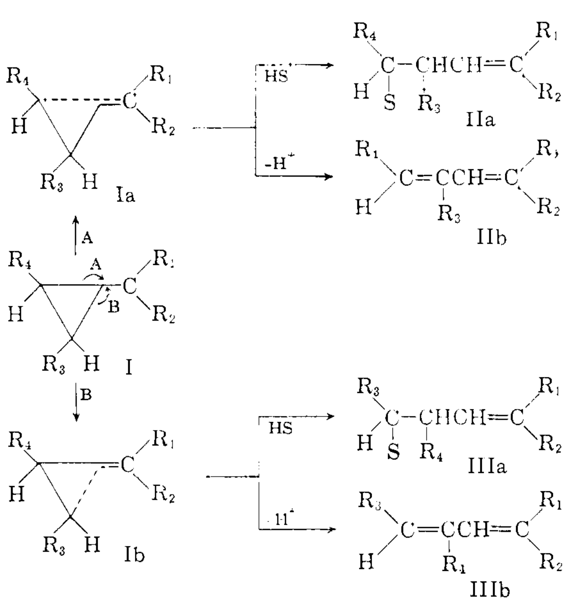
Cyclopropanes. V.[1] The Cyclopropylcarbinyl Rearrangement[2]

BY H. M. WALBORSKY AND J. F. PENDLETON[3]

RECEIVED JULY 8, 1959

The direction of cyclopropane ring opening is studied by the dehydration of a series of ring-substituted cyclopropylcarbinols. Dehydration of I (R_4 = C_6H_5, $C_6H_5CH{=}CH$ and $C_6H_5CH{=}CHCH{=}CH$; R_3 = H; R_2 = R_1 = C_6H_5 or H) affords IIb. That carbethoxymethylene adds in a terminal fashion was demonstrated by its addition to the terminal double bond of 1-phenylhexatriene. This terminal addition permitted the extension of unsaturation and thus styrene was converted to 1-phenylbutadiene; 1-phenylbutadiene to 1-phenylhexatriene; and finally 1-phenylhexatriene to 1-phenyloctatetraene. The assignment of an all-*trans* configuration to the hydrocarbons IIb by means of their ultraviolet absorption spectra is discussed.

There are numerous examples of cyclopropane ring opening caused by the generation of a positive charge on a carbon adjacent to a cyclopropane ring; *viz.*, a cyclopropylcarbinyl cation I. However, in unsubstituted cyclopropylcarbinyl systems,[4-8] and carbinyl carbon substituted cyclopropylcarbinyl systems[9-14] ring opening can lead to only one product since the two bonds in the ring which can open are equivalent. Ring-substituted cyclopropylcarbinyl cations I on the other hand can give rise to two possible products on ring opening. The cyclopropane ring in I can open at A or B leading to the possible transition states or intermediates Ia or Ib, respectively. Ring opening should occur in such a manner that *that bond will break which leaves the positive charge on the carbon atom which can best delocalize this charge.* Thus, the products obtained will depend on the relative positive charge-delocalizing ability of R_3 and R_4. If R_4 is more capable of delocalizing a positive charge than R_3, then the intermediate Ia will be of lower energy, and preponderance of products arising from this intermediate should be observed (IIa and IIb). Attack of solvent or acid (HS) gives IIa, while direct loss of a proton yields IIb. Support for this hypothesis can be found in the rearrangements observed when the following carbinols are subjected to acid treatment: 2-phenyl-3-carboxycyclopropylcarbinol,[15] α-thujene,[16a] sabinene,[16b] sabinaglycerol[16c] and 2,2-diphenylcyclopropylcarbinol.[17]



The system first studied was the phenylcyclopropyl system. A mixture of *cis*- and *trans*-ethyl 2-phenylcyclopropylcarboxylate(V) had been prepared in good yield by Burger and Yost by the addition of ethyl diazoacetate to styrene.[18] Treatment of this mixture (V) with phenylmagnesium bromide afforded *cis*- and *trans*-(2-phenylcyclopropyl)-diphenylcarbinol (VIa, 20%) and (VIb, 46%), respectively. The assignment of configuration was based on the infrared adsorption data appearing in Table I. The absence of intermolecular hydrogen bonding of VIa and the observed strong intramo-

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[1] For paper IV of this series, see H. M. Walborsky and F. J. Impastato, *Chemistry & Industry*, 1690 (1958).

[2] This work was supported by grant G-3314 of the National Science Foundation, which we gratefully acknowledge.

[3] This manuscript is based on the Ph.D. thesis of J. F. Pendleton, June, 1959.

[4] J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951).

[5] C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

[6] N. J. Demjanov, *Ber.*, **40**, 4393 (1907); **40**, 4961 (1907).

[7] R. Skrabal, *Monatsh.*, **70**, 420 (1937).

[8] L. I. Smith and S. McKenzie, Jr., *J. Org. Chem.*, **15**, 74 (1950).

[9] P. Bruylants and A. Dewael, *Bull. classe Sci. Acad. roy. Belg.*, [5] **14**, 140 (1928); *Chem. Zentr.*, **89**, **II**, 2708 (1918).

[10] T. A. Favorskaya and S. A. Fridman, *J. Gen. Chem.* (*U.S.S.R.*), **15**, 421 (1945); *C. A.*, **40**, 4655 (1946).

[11] M. Doyarenko, *Ber.*, **60B**, 1536 (1927).

[12] T. A. Favorskaya and N. V. Shcherbinskaya, *Zhur. Obshchei Khim.*, **23**, 1667 (1953).

[13] T. A. Favorskaya, *et al.*, *ibid.*, **20**, 855 (1950); *C. A.*, **44**, 9353 (1950).

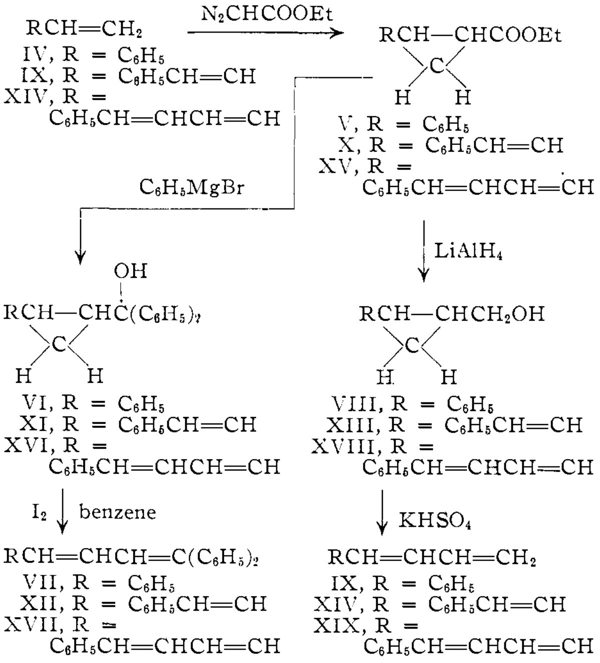
[14] P. Lipp, J. Buchkremer and H. Seeles, *Ann.*, **499**, 1 (1932).

[15] R. Stoermer, F. Schenck and E. Pansegrau, *Ber.*, **60**, 2566 (1927).

[16] (a) O. Wallach, *Ann.*, **350**, 167 (1906); (b) **357**, 65 (1907); (c) **360**, 96 (1908).

[17] H. M. Walborsky and F. M. Hornyak, THIS JOURNAL, **77**, 6396 (1955).

[18] A. Burger and W. Yost, *ibid.*, **70**, 2198 (1948).



lecular hydrogen bonding with the phenyl group[19] which can take place only if the carbinol and phenyl groups are *cis* to each other indicates a *cis* configuration for VIa.[21] Both VIa and VIb, when dehydrated with iodine in refluxing benzene rearranged to give 67% of 1,1,4-triphenylbutadiene.[22] That a carbonium ion is an intermediate in this rearrangement is indicated by the fact that iodine-catalyzed dehydrations have been shown to give the same products as acid-catalyzed dehydrations of alcohols.[23,24] (2-Phenylcyclopropyl)-carbinol (VIII) prepared by the reduction of V was dehydrated by distillation over potassium acid sulfate[25] to give a 72% yield of 1-phenylbutadiene.[26]

TABLE I

OH STRETCHING INFRARED ABSORPTION[20] OF CYCLOPROPYLDIPHENYLCARBINOLS

Compound	Intramolecular, cm.$^{-1}$ Free	Bonded	$\Delta\nu$	Intermolecular, cm.$^{-1}$
trans-2-Phenyl (VIb)	3614(s)	....		3400(v)
cis-2-Phenyl (VIa)	.....	3568(s)	(47)	.....
2,2-Diphenyl	3615(w)	3564(s)	51	.....

The second system to be studied was the (2-styrylcyclopropyl)-carbinyl species. The terminal addition of ethyl diazoacetate to phenylbutadiene was shown by von der Heide[27] in the production of ethyl 2-styrylcyclopropylcarboxylate (X). This terminal addition is not surprising if one considers the electrophilic nature of methylenes.[28-33] Addition of carbethoxymethylene to the terminal position of phenylbutadiene allows the positive charge generated to be stabilized by the conjugated styryl unit.[34]

Addition of phenylmagnesium bromide to X gave a 58% yield of (α-2-styrylcyclopropyl)-diphenylcarbinol (XI), 45% of which was isolated as the solid *trans*-carbinol (last fractions from aluminum oxide chromatography). Iodide dehydration of XI afforded 1,1,6-triphenylhexatriene (XII) in 72% yield. Ozonolysis of XII gave the required benzoic acid and benzophenone.

Lithium aluminum hydride reduction of X yielded (2-styrylcyclopropyl)-carbinol (XIII). This carbinol also was obtained partially (45%) as the solid *trans* isomer which gave benzoic acid and *trans*-cyclopropanedicarboxylic acid on oxidation. The remainder was a mixture of *cis* and *trans* isomers. Dehydration of XIII over potassium acid sulfate gave 1-phenylhexatriene[35] (XIV) in 59% yield.

Terminal addition of ethyl diazoacetate to phenylhexatriene was demonstrated in the formation of ethyl 2-phenylbutadienylcyclopropylcarboxylate (XV) in 68% yield. The homogeneity of the product was shown by the identity of the ultraviolet absorption curves of the solid *trans* ester and the remaining *cis–trans* liquid mixture. The shape of the curves was the same indicating only one unsaturated chromophore present. The *trans* isomer did have an extinction coefficient of 41,000 which was 7,000 more than that of the remaining liquid ester, but the presence of the *cis* isomer in the mixture can account for this difference.[36] Terminal cyclopro-

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[19] P. von E. Schleyer and R. Bacskai, THIS JOURNAL, **80**, 6691 (1958).

[20] These data were obtained on a Perkin–Elmer model 21 infrared spectrophotometer using lithium fluoride cells. The authors are indebted to P. von E. Schleyer for obtaining these results.

[21] This is further supported by the fact that very similar absorption in this region is obtained in the 2,2-diphenyl analog, in which one ring phenyl group must by necessity be *cis* to the diphenylcarbinol group. That two phenyl groups on the carbinyl carbon are not sufficient hindrance to cause the loss of intermolecular hydrogen bonding, is seen in the absorption of the *trans*-carbinol VIb where the normal absorption of an alcohol is observed (free and intermolecular bonded OH stretching absorption). The less hindered configuration of VIb was demonstrated also by the fact that the *trans*-carbinol was obtained from the last fractions of the chromatographic separation, indicating that VIb was the alcohol most strongly bound to the alumina.

[22] S. Israelashvili and F. Bergmann, *J. Chem. Soc.*, 1070 (1953).

[23] J. Wibaut, *et al.*, *Rec. trav. chim.*, **58**, 329 (1939).

[24] J. Church, F. Whitmore and R. McGrew, THIS JOURNAL, **56**, 180 (1934).

[25] In all the dehydrations attempted in this research potassium acid sulfate was used as a catalyst for the primary carbinols. Iodine was used for the tertiary carbinols, since these are diphenyl substituted and therefore easily dehydrated.

[26] O. Grummitt and E. I. Becker, *Organic Syntheses*, **30**, 75 (1900).

[27] C. von der Heide, *Ber.*, **37**, 210 (1904).

[28] M. S. Kharasch, *et al.*, *J. Org. Chem.*, **18**, 1030 (1953).

[29] D. H. Reid, *et al.*, *J. Chem. Soc.*, 1193 (1955).

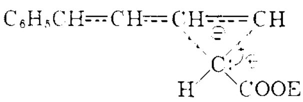
[30] G. M. Badger, *Rec. trav. chim. Pays-Bas*, **71**, 468 (1952).

[31] P. S. Skell and A. Y. Garner, THIS JOURNAL, **78**, 5430 (1956).

[32] W. von E. Doering and L. H. Knox, *ibid.*, **78**, 4947 (1956).

[33] E. Herrick and M. Orchin, *J. Org. Chem.*, **24**, 139 (1959).

[34] A concerted electrophilic attack of carbethoxymethylene at the terminal double bond of phenylbutadiene allows delocalization of the positive charge formed in the transition state (comparable to the bromonium ion) through the conjugated styryl residue.



After this initial electrophilic addition this species has a "built-in" nucleophilic center in the form of a non-bonded pair of electrons on the methylene carbon. Nucleophilic attack of these electrons coupled with the resulting localization of the electrons of the original double bond forms the remaining bonds of the cyclopropane ring.

[35] The ultraviolet absorption spectrum was identical to that of 1-phenylhexatriene prepared by H. C. Barany, E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2093 (1951), except that the extinction coefficient was 51,000 compared to Braude's value of 55,000 (see Experimental). Attempts to purify the triene further resulted in considerable loss of material and the compound was used directly from distillation.

[36] R. J. Mohrbacher and N. H. Cromwell, THIS JOURNAL, **79**, 401 (1957).

pane formation would leave the conjugated phenylbutadiene moiety intact. The ultraviolet absorption spectra of phenylbutadiene and the *trans*-ester XV can be seen in Fig. 1. The absorption of XV at longer wave lengths (11–13 mμ) is expected since in this case there is an added substituent on the butadiene system[37] and also the cyclopropane ring is capable of extending the conjugated system.[36] Besides the existence of the residual phenylbutadiene, terminal cyclopropane formation gives rise to a *disubstituted* cyclopropane derivative. Oxidation of *trans*-XV (as the carboxylic acid) with potassium permanganate gave benzoic acid and *trans*-cyclopropane-1,2-*dicarboxylic* acid.[38]

The addition of phenylmagnesium bromide to XV resulted in a carbinol XVI which could not be isolated in a pure form. The carbinol was therefore dehydrated directly from the work-up of the Grignard addition. Iodine dehydration gave 1,1,8-triphenyloctatetraene (XVII) in 59% yield based on starting ester. Ozonolysis afforded benzoic acid and benzophenone.

The primary carbinol, (2-phenylbutadienylcyclopropyl)-carbinol (XVIII), obtained from the reduction of XV was stable and as with the other series a solid isomer was obtained. This solid carbinol had an extinction coefficient at 293 mμ, 4,000 greater than the remaining mixture and was assigned the *trans* configuration. Potassium acid sulfate dehydration of XVIII resulted in only a 20% yield of 1-phenyloctatetraene (XIX).

Discussion of Results

It can be seen from the results above that in each series, phenyl, styryl and phenylbutadienylcyclopropylcarbinol, the generation of a positive charge to give the carbinyl cation has caused ring opening to occur in such a manner that the charge was delocalized by the conjugated ring substituent. All the rearrangements then are in complete agreement with the hypothesis presented. In all cases the predicted conjugated unsaturated products arose from these intermediates by loss of a proton from a methylene group adjacent to the electron-deficient carbon.

This mode of ring opening, coupled with the fact that carbethoxymethylene adds to a conjugated system at the terminal double bond, provides *a novel method of extending conjugated units in an unsaturated system.* The repetition of three reactions, addition of ethyl diazoacetate to an olefin, reduction to the carbinol and dehydrative rearrangement of the carbinol, has made possible the conversion of styrene to 1-phenylbutadiene, 1-phenylbutadiene to 1-phenylhexatriene, and finally 1-phenylhexatriene to 1-phenyloctatetraene.

Discussion of Ultraviolet Absorption Data.—The assignment of the structure of the polyenes synthesized in this research, other than those which are known compounds, was based to a large extent on their ultraviolet absorption spectra.

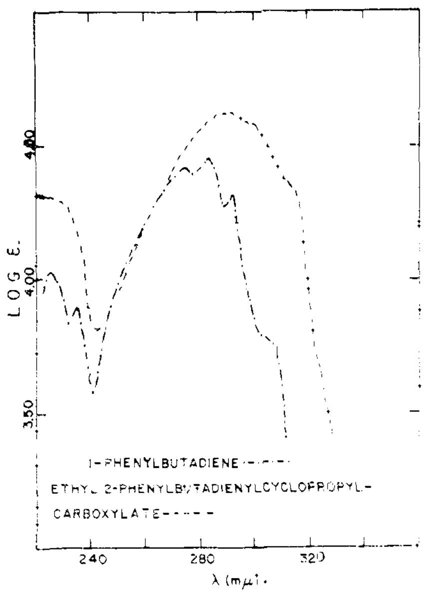


Fig. 1.—Ultraviolet absorption spectra of 1-phenylbutadiene[35] and *trans*-ethyl 2-phenylbutadienylcyclopropylcarboxylate (XV) in alcohol.

Considering first the position of main absorption, the three triphenylpolyenes seem to absorb in the expected wave length range. Their absorption occurs at longer wave lengths (3 to 9 mμ) than the corresponding all *trans*-1,ω-diphenylpolyenes prepared by Kuhn[39] (see Table II).

TABLE II

ULTRAVIOLET ABSORPTION OF PHENYLPOLYENES IN ALCOHOL

n = number of double bonds, wave length in mμ

	1,ω-Diphenyl[39]		1,1,ω-Triphenyl		1-Phenyl	
n	λ	Σ	λ	Σ	λ	Σ
1	297	27,000	301	17,000[40]	244	12,000
2	328	40,800	336	48,000[23]	282	31,000[35]
3	349	67,400	358	68,600	311	55,000[35]
4	375	84,000	378	85,000	337	85,500

As can be seen from Table II, there is a convergence of absorption position as the number of ethylene linkages (*n*) is increased. This convergence is not regular in the case of the diphenyl- and triphenylpolyenes but it does follow a regular pattern in the case of the 1-phenylpolyenes. Here, shifts in wave length of 36 and 31 mμ are observed in going from $n = 1$ to $n = 2$ and from $n = 2$ to $n = 3$, respectively. These shifts of 36 and 31 mμ indicate a convergence of 5 mμ and one would expect an additional convergence of 5 mμ or a shift of only 26 mμ in going from $n = 3$ to $n = 4$. This shift then gives a predicted value of 337 mμ for the main absorption of 1-phenyloctatetraene and the observed wave length of absorption is exactly this value.

The general shape of the absorption curves offers another means of determining structure in polyenes.

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(37) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Spectroscopy in Organic Chemistry," 2nd edition, Edward Arnold Ltd., London, 1957, p. 99.

(38) The presence of a disubstituted cyclopropane derivative was also shown by the absorption of XV in the near infrared at 1.64 μ characteristic of cyclopropane $(-CH_2-)$ (W. H. Washburn and M. J. Mahoney, THIS JOURNAL, **80**, 504 (1958) and H. M. Walborsky and F. J. Impastato, *Chemistry & Industry*, 1690 (1958)). Since terminal methylene $(=CH_2)$ also shows absorption in this region, XV was reduced with hydrogen over a palladium-on-charcoal catalyst and the identical absorption was obtained at 1.64 μ.

(39) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 87 (1927/1928).

(40) B. Arends, *Ber.*, **64B**, 1936 (1931).

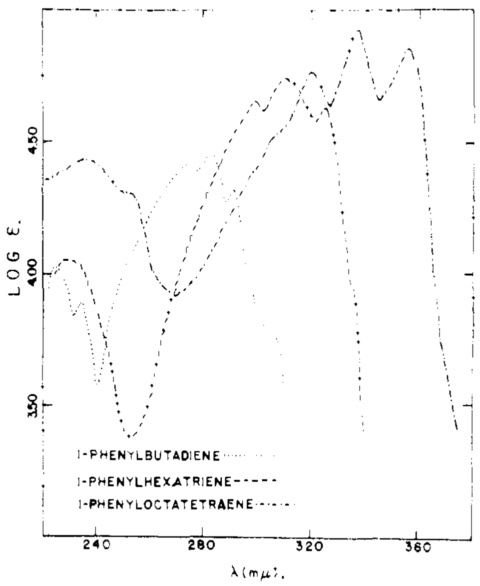

Fig. 2.—Ultraviolet absorption spectra of 1-phenylbutadiene,[35] 1-phenylhexatriene and 1-phenyloctatetraene in alcohol.

The appearance of three well-defined absorption maxima in the 1-phenylpolyenes (Fig. 2) indicates an all-*trans* configuration of these compounds.[41–44] The 1-phenylbutadiene obtained in this research has been shown to be *trans–trans*.[26]

The interpretation of the absorption spectra of the triphenylpolyenes is not as simple. The absence of fine structure in these curves (Fig. 3), would indicate that the compounds were not all *trans*, but Zechmeister[42–44] has shown that while diphenylpolyenes with an internal double bond still retain fine structure in their spectra, the presence of a *cis* terminal double bond causes the loss of most of the fine structure and shifts the position of main absorption to lower wave lengths. The lack of fine structure can be explained then without assuming the loss of an all-*trans* configuration. Since the triphenylpolyenes have a 1,1-diphenyl grouping, by necessity, one of the phenyl groups must be in a *cis*-terminal position. Furthermore the fact that these polyenes absorb at longer wave lengths than the corresponding diphenylpolyenes indicates that the all-*trans*-1,ω-diphenyl chromophore is intact since 1,1,2-triphenylethylene absorbs at longer wave lengths than *trans*-1,2-diphenylethylene and here the unsaturated center in each case is fixed *trans*.

The final proof of an all-*trans* configuration lies in an examination of the extinction coefficients of the main absorption band of these phenylpolyenes. Hausser and Kuhn[45] have shown that in the series of all-*trans*-diphenylpolyenes a plot of extinction coefficient (ε) against the number of double bonds (n) is a straight line (Fig. 4). The same relationship holds in the case of the triphenyl- and 1-phenylpolyenes isolated in this work.

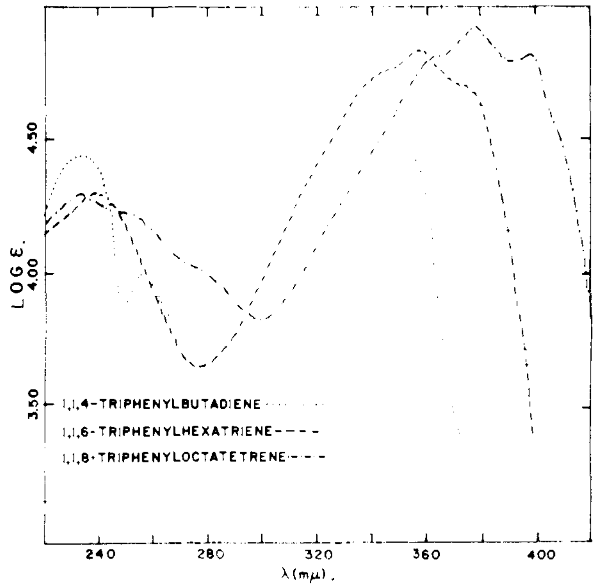

Fig. 3.—Ultraviolet absorption spectra of 1,1,4-triphenylbutadiene,[22] 1,1,6-triphenylhexatriene and 1,1,8-triphenyloctatetraene in alcohol.

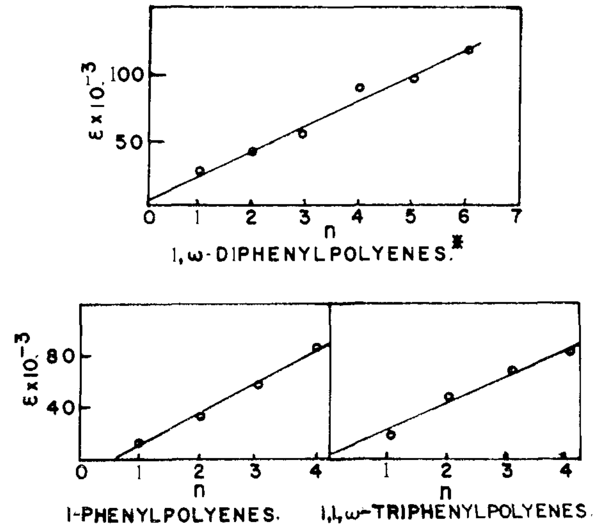

Fig. 4.—Plot of extinction coefficient (E) *vs.* number of double bond (n) for phenyl-, diphenyl- and triphenylpolyenes.

Experimental[46,47]

***cis* and *trans*-(2-Phenylcyclopropyl)-diphenylcarbinol (VI).** To 0.135 mole of phenylmagnesium bromide in 200 ml. of dry ether was added dropwise 10 g. (0.053 mole) of ethyl 2-phenylcyclopropylcarboxylate in 50 ml. of dry ether. After final addition the mixture was stirred 12 hours at room temperature. The complex was decomposed with saturated aqueous ammonium chloride. The ether solution was dried and stripped and the resulting oil was chromatographed on an alumina column (500 g. Alcoa F-20 grade alumina). A small amount of starting ester was obtained (0.50 g.) and 2.96 g. (20%) of the solid *cis*- carbinol, m.p. 82–84° from 95% ethanol.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.67; H, 6.73.

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(41) L. Zechmeister and A. Polgar, This Journal, **65**, 1522, 1940 (1943).

(42) J. Pinckard, B. Willie and L. Zechmeister, *ibid.*, **70**, 1938 (1948).

(43) K. Lunde and L. Zechmeister, *ibid.*, **76**, 2308 (1954).

(44) L. Zechmeister and J. Pinchard, *ibid.*, **76**, 4144 (1954).

(45) K. Hausser, *et al.*, *Z. physik. Chem.*, **B29**, 384 (1935).

(46) All melting points are uncorrected.

(47) Elemental analyses were performed by E. Thommen, Basel, Switzerland.

Also 6.80 g. (45.5%) of liquid *trans*-carbinol was obtained which on standing in the ice-box solidified; m.p. 68.5–70.0°.

Anal. Calcd. for $C_{22}H_{20}$: C, 87.96; H, 6.71. Found: C, 87.43; H, 6.94.

1,1,4-Triphenylbutadiene.—Using an apparatus containing a water trap 1.66 g. (0.0055 mole) of *trans*-2-phenylcyclopropyldiphenylcarbinol was refluxed in benzene containing a trace of iodine for 48 hours. The benzene solution was then extracted with aqueous thiosulfate, dried and the solvent stripped under vacuum. The resulting dark brown oil was taken up in 95% ethanol and yielded 1.04 g. (67%) of white needles, m.p. 100–102°, b.p. 197–200° (2 mm.), log ϵ_{336} 4.7, log ϵ_{235} 4.4 (Fig. 3); reported physical constants[23,48] for 1,1,4-triphenylbutadiene: m.p. 101° b.p. 210° (3 mm.), log ϵ_{336} 4.6, log ϵ_{241} 4.2. The *cis*-carbinol gave the same product in approximately the same yield (60%).

(2-Phenylcyclopropyl)-carbinol (VIII).—To a suspension of 16.8 g. (0.44 mole) of lithium aluminum hydride in one liter of dry ether was added dropwise with stirring 108 g. (0.57 mole) of ethyl 2-phenylcyclopropylcarboxylate at a rate fast enough to cause refluxing. After final addition the mixture was refluxed for 0.5 hour and then decomposed with 40% aqueous sodium hydroxide solution. The ether solution was decanted and dried over anhydrous sodium sulfate. The ether was stripped *in vacuo* and the residual oil distilled to yield 67.5 g. (80%) of product, b.p. 91–96° (0.3 mm.), n^{20}_{D} 1.5513, d^{4}_{20} 1.044.

Anal. Calcd. for $C_{10}H_{12}$: C, 81.04; H, 8.16. Found: C, 80.79; H, 8.46.

Phenylurethan of (2-Phenylcyclopropyl)-carbinol.—(2-Phenylcyclopropyl)-carbinol (0.5 g.) was heated with 1 ml. of phenyl isocyanate and on cooling a solid separated. Excess isocyanate was removed by extraction with low-boiling petroleum ether and the resulting solid was recrystallized from 95% ethanol, to yield white needles, m.p. 88.5–89°.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.37; H, 6.41; N, 5.24. Found: C, 76.89; H, 6.64; N, 5.64.

1-Phenylbutadiene.—In a 500-ml. round-bottomed flask set for distillation with a short column, were placed 62.3 g. (0.42 mole) of 2-phenylcyclopropylcarbinol and 30 g. of dry powdered potassium acid sulfate.[49] The pressure was adjusted to 15 mm. and the bath temperature was raised rapidly to 160° then gradually to 200° over the next hour at which point the last of the diene had distilled, b.p. 85–90°. The product was then dried over sodium sulfate and then distilled. Phenylbutadiene (37.7 g.) was obtained, b.p. 90–96° (15–18 mm.), n^{23}_{D} 1.6072; reported[26] values b.p. 86° (8 mm.), n^{25}_{D} 1.607–1.608. Also 2.55 g. of starting carbinol was recovered, b.p. 85–90° (1.5 mm.). The yield of 1-phenylbutadiene based on recovered carbinol was 72%.

α-(2-Styrylcyclopropyl)diphenylcarbinol (XI).—Ethyl 2-styrylcyclopropylcarboxylate (10 g., 0.046 mole) in 25 ml. of dry ether was added dropwise to a stirring solution of phenylmagnesium bromide (0.11 mole) and the mixture was stirred for 10 hours. The complex was decomposed with aqueous ammonium chloride, the ether solution decanted and concentrated to dryness. The resulting oil was chromatographed twice on an alumina column (Alcoa F-20). α-(Styrylcyclopropyl)-diphenylcarbinol was obtained, 8.4 g. (58%), of which 3.95 g. was the solid *trans*-carbinol, crystallizing as white pellets from 95% ethanol; m.p. 87–89°.

Anal. Calcd. for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.97; H, 6.84.

The remainder was a liquid, n^{23}_{D} 1.6205.

Anal. Calcd. for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.08; H, 6.79.

1,1,6-Triphenylhexatriene (XII).—Using an apparatus containing a water trap, a solution of 1.75 g. (0.0054 mole) of liquid α-(2-styrylcyclopropyl)-diphenylcarbinol in benzene was refluxed with a trace of iodine for 48 hours. The solution was then extracted twice with aqueous thiosulfate, dried, and concentrated to dryness. The resulting dark brown solid was chromatographed on an alumina column (Merck aluminum oxide) giving 1.2 g. (72%) of a yellow solid which separated from acetonitrile as fine yellow plates, m.p. 154.5–155.5°, $\epsilon_{\max}$ (357 mμ) 69,000 (Fig. 3).

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.35; H, 6.71.

Ozonolysis of 1,1,6-Triphenylhexatriene.—An ozone-oxygen mixture was passed through a solution of 500 mg. of triene in 50 ml. of ethyl acetate at 0° for 0.5 hour. The solvent was removed *in vacuo* and 15 ml. of 10% hydrogen peroxide and 0.5 ml. of concentrated sulfuric acid were added to the residue and the mixture was allowed to stand at room temperature for 12 hours. This mixture was then taken to dryness *in vacuo*. The residue was taken up in a small amount of 10% aqueous sodium hydroxide and extracted three times with ether. The ether extracts were combined, dried over sodium sulfate and stripped to dryness *in vacuo*. The residual oil refused to solidify and a 2,4-dinitrophenylhydrazone derivative was prepared, m.p. and mixed m.p. 235–237°.

The aqueous basic solution above was acidified with concentrated hydrochloric acid and extracted with ether. This was dried over anhydrous sodium sulfate and taken to dryness. The resulting solid was recrystallized from water and melted at 121–123°. The melting point when mixed with an authentic sample of benzoic acid was 121.5–123°.

(2-Styrylcyclopropyl)-carbinol (XIII).—To a suspension of 8.4 g. (0.22 mole) of lithium aluminum hydride in 600 ml. of dry ether was added dropwise with stirring 74.0 g. (0.34 mole) of ethyl 2-styrylcyclopropylcarboxylate at a rate fast enough to cause refluxing. After final addition the mixture was refluxed for one hour and then decomposed with 10% aqueous sodium hydroxide solution. The ether solution was decanted, dried over sodium sulfate, and the ether removed *in vacuo*. The residual oil was distilled yielding 50.0 g. (85%) of product, b.p. 114–117° at 0.3 mm. This product was taken in boiling low petroleum ether and yielded a solid which on repeated recrystallizations gave 20 g. (34% based on starting ester) of a white solid, transparent plates, m.p. 60–61°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.50; H, 8.19.

A liquid carbinol (23.0 g., 39%) was recovered from the above mother liquors and redistilled for analysis.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.28; H, 8.21.

Phenylurethan of Solid (2-Styrylcyclopropyl)-carbinol. (procedure identical with that for phenylcyclopropylcarbinol): white plates from 95% ethanol, m.p. 104–105°.

Anal. Calcd. for $C_{19}H_{19}O_2N$: C, 77.79; H, 6.53; N, 4.76. Found: C, 77.86; H, 6.56; N, 5.02.

Oxidation of *trans*-(2-Styrylcyclopropyl)carbinol.—The solid carbinol (2.2 g., 0.0126 mole) was placed in a round-bottom flask with 100 cc. of water and 10 drops of concentrated sulfuric acid. Potassium permanganate (8.0 g.) was added and the mixture brought to reflux and continued refluxing for 24 hours. At this point an additional 2 g. of permanganate was added and refluxing continued for 12 hours. The solution was then cooled and filtered and the manganese dioxide washed with water. The solution was neutral to litmus and on acidification a solid separated, 0.32 g., m.p. 119.5–120.5°; mixed m.p. with pure benzoic acid not depressed. The filtrate was extracted continuously with ether for 36 hours and on evaporating the ether extracts a white solid was obtained (0.95 g.), m.p. 174–176° from ether–petroleum ether, which did not depress the m.p. of *trans*-cyclopropanedicarboxylic acid.[50] The yield of benzoic acid is 63%, and of *trans*-cyclopropanedicarboxylic acid is 58% based on starting material. The yields based on recovered oxidized material (2.5 g.) were 75 and 81%, respectively.

Oxidation of the Liquid (2-Styrylcyclopropyl)-carbinol.—Liquid (2-styryl-cyclopropyl)-carbinol (2.05 g., 0.012 mole) was refluxed in water with 10 g. of potassium permanganate for 24 hours. A work-up similar to the above oxidation gave 1.5 g. of oxidized material, of which 0.9 g. was benzoic acid, m.p. and mixed m.p. 119–120°, and 0.1 g. was *trans*-cyclopropanedicarboxylic acid, m.p. and mixed m.p. 174–176°. The remainder was a wax, m.p. 139–154°.

1-Phenylhexatriene (XIV).—In a 100-ml. round-bottomed flask set for distillation with a short path distillation head

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(48) F. Bergmann, S. Israelashvili and J. Gottlieb, *J. Chem. Soc.*, 2522 (1952).

(49) The ratio of flask volume to grams of carbinol is set at ten since there is considerable foaming during the dehydration; any smaller ratio results in mechanical transfer of reactants.

(50) E. Buchner and A. Papendieck, *Ann.*, **284**, 212 (1895).

(air-cooled condensing unit), was placed 10 g. of (2-styrylcyclopropyl)-carbinol and 5 g. of dry powdered potassium acid sulfate. The pressure was adjusted to 0.2 mm. and a bath, preheated to 180°, was placed around the flask. The temperature was maintained at 180° until water vapors were exhausted and then gradually raised to 200° until all the liquid had distilled, b.p. 110–130° (2 mm.), Using the same set-up, this procedure was repeated until 69 g. (0.44 mole) of carbinol had been used.[51] Between each step the system was flushed with dry nitrogen and the distillate was kept in the solid state by intermittent cooling. Distillation of the product resulted in a liquid, b.p. 75–76° (2 mm.), which solidified, m.p. 48–51°; $\epsilon_{\max}$ 325 mμ (39,000), 311 (51,000), 299 (42,000), 242 (9,000) 236 (13,400), 228 (13,700); reported[35] values m.p. 56°, $\epsilon_{\max}$ 325 mμ (43,000), 311 (55,000), 299 (46,000), 242 (shoulder), 235 (10,700), 229 (11,400) (Fig. 2). Starting carbinol (27.2 g.) was recovered, b.p. 114–117° (0.3 mm.). The amount of triene obtained was 21 g. or 57% based on recovered carbinol.

Ethyl 2-Phenylbutadienylcyclopropylcarboxylate (XV).—1-Phenylhexatriene (20 g., 0.13 mole) and 19 g. (0.15 mole) of ethyl diazoacetate were heated together for two hours at 85–90°[52] and then for 34 hours on a steam-bath. The ethyl diazoacetate and other low boiling materials were removed *in vacuo* at 140° and the remainder chromatographed on a column of 500 g. of alumina (Alcoa F-20); 18.6 g. (59%) of product was obtained. The last fractions solidified and after recrystallization from petroleum ether gave 2.5 g. of *trans*-ethyl 2-phenylbutadienylcyclopropylcarboxylate, white plates, m.p. 81.5–82.5°.

Anal. Calcd. for $C_{16}H_{1}\,O_2$: C, 79.31; H, 7.49. Found: C, 79.35; H, 7.27.

A sample of the remaining liquid was analyzed.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.22; H, 7.48.

Another run of 20 g. (0.13 mole) of triene and 19 g. (0.15 mole) of ethyl diazoacetate was carried out as above, but the product was distilled with the use of a Newman molecular still and a 68% yield of product was obtained.

2-Phenylbutadienylcyclopropylcarboxylic Acid.—A solution of 2.2 g. (0.0091 mole) of solid ethyl 2-phenylbutadienylcyclopropylcarboxylate and 2 g. of potassium hydroxide in 100 ml. of 95% ethanol was refluxed for several hours. Flaky crystals appeared on cooling and 1.7 g. of the potassium salt was isolated. Acidification resulted in a yellow solid which after sublimation and recrystallization from methanol–water gave a white flaky solid, m.p. 154–157°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.17; H, 6.51.

Oxidation of 2-Phenylbutadienylcyclopropylcarboxylic Acid.—A mixture of 0.55 g. (0.0026 mole) of acid and 2.2 g. of potassium permanganate in 75 ml. of water was refluxed for four hours, and finally an additional 1 g. of permanganate was added and the mixture refluxed for 8 hours more. The manganese dioxide was filtered and washed several times with water and the combined filtrates were evaporated to dryness, and the residue taken up in hot water yielding 172 mg. (55%) of benzoic acid, m.p. and mixed m.p. 121.5–122.5°. Continuous ether extraction of the filtrate yielded a white solid which was precipitated from ether by petroleum ether; 150 mg. (45%), m.p. 175°. This solid did not depress the m.p. of pure *trans*-cyclopropanedicarboxylic acid.

1,1,8-Triphenyloctatetraene (XVII).—Ethyl 2-phenylbutadienylcyclopropylcarboxylate (2.0 g., 0.0083 mole) in 30 ml. of dry ether was added dropwise to a stirring mixture of phenylmagnesium bromide (0.017 mole) in 50 ml. of dry ether. After final addition the mixture was stirred for 18 hours and then decomposed with saturated aqueous ammonium chloride. The ether layer was dried over anhydrous sodium sulfate, filtered and the solvent removed *in vacuo*. The resulting yellow oil was immediately placed in 100 ml. of benzene containing a trace of iodine and the mixture refluxed with the water being collected in a Dean–Stark trap. After refluxing for 48 hours, the solution was cooled and treated with aqueous sodium thiosulfate. The red-brown benzene layer was dried and the solvent removed *in vacuo*. The resulting solid was taken in petroleum ether–benzene and placed on a Florisil column made with petroleum ether. A bright yellow solid was eluted with petroleum ether and this was taken in acetonitrile and precipitated in the cold giving 1.60 g. of a bright yellow powder (59% based on starting ester), m.p. 135–138°, $\epsilon_{\max}$ (378 mμ) 85,000 (Fig. 3).

Anal. Calcd. for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.16; H, 6.73.

Ozonolysis of 1,1,8-**triphenyloctatetraene** was performed exactly as with the ozonolysis of 1,1,6-triphenylhexatriene above.

The 2,4-dinitrophenylhydrazone of the neutral fraction melted at 234–236°. When mixed with authentic benzophenone 2,4-dinitrophenylhydrazone, it melted at 234–236.5°; the solid from the acid fraction melted at 120.5–121.5° and when mixed with pure benzoic acid, the melting point was 121–123°.

(2-Phenylbutadienylcyclopropyl)-carbinol (XVII).—Ethyl 2-phenylbutadienylcyclopropylcarboxylate (40.6 g., 0.168 mole) was added neat to a stirring mixture of 4.6 g. (0.12 mole) of lithium aluminum hydride in 350 ml. of dry ether. The mixture was allowed to stir for two hours after the addition and the complex was decomposed with 10% aqueous sodium hydroxide. The ether solution was decanted, dried and the solvent removed *in vacuo*. The resulting oil was distilled using a Newman molecular still giving a colorless oil, bath temperature 140–150°, pressure 0.1 mm., $\epsilon_{\max}$ (293 mμ) 32,000, n^{23}D 1.6360, yield 28.80 g., 85%.

Anal. Calcd. for $C_{14}H_{160}$: C, 83.96; H, 8.05. Found: C, 83.72; H, 8.27.

A small amount of this liquid was taken in low-boiling petroleum ether and on cooling a white flaky solid crystallized, which after four recrystallizations from low petroleum ether, melted at 97.98.5°, $\epsilon_{\max}$ (293 mμ) 35,000.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.91; H, 8.35.

1-Phenyloctatetraene (XIX).—2-Phenylbutadienylcyclopropylcarbinol (9.8 g., 0.049 mole) and 4.0 g. of powdered potassium acid sulfate were placed in a 50-ml. short-path solid distillation apparatus and the pressure was adjusted to 0.5 mm. An oil-bath preheated to 170° was raised around the boiling flask and after initial foaming and exhaustion of water vapors, a small amount (3.0 g.) of a yellow-orange liquid came over at 120–130° and solidified in the receiver. The bulk of the reaction mixture charred in the boiling flask. The solid distillate was eluted rapidly through a short alumina column with low petroleum ether. The resulting white powder was recrystallized several times from low petroleum ether and gave 1.8 g. (20%) of phenyloctatetraene, a white fluffy solid, m.p. 127–128.5°; $\epsilon_{\max}$ (320 mμ) 59,100, $\epsilon_{\max}$ (337 mμ) 85,500, $\epsilon_{\max}$ (356 mμ) 72,300 (Fig. 2).

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 91.09; H, 7.63.

A second analysis was performed after the sample vial had been opened for several hours and the results (C, 90.51; H, 7.68) indicate that the compound is very sensitive to oxygen.

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(51) Attempts to dehydrate large batches of carbinol resulted in low yields.

(52) Caution—induction period.