Anal. Calcd. for $C_{16}H_5N_5O_6$: C, 52.89; H, 1.38; N, 19.25. Found: C, 52.49; H, 1.56; N, 19.33.

Ultraviolet absorption spectra in dichloromethane show maxima at 365 mμ (log ε 4.38). Infrared spectra in acetonitrile and in a KBr disk showed no absorption for the cyano group.

Acid Hydrolysis of DTF.—DTF (300 mg., 0.8 × 10^{-3} mole) was suspended in 25 ml. of concentrated sulphuric acid and warmed for 20 min.; then the mixture was poured on crushed ice. The precipitate was washed free from acid and dried to give 330 mg. of white solid, m.p. 355–360° dec. A sample recrystallized from acetonitrile had m.p. 359–360° dec. and analyzed for biscarboxamidomethylene-2,4,7-trinitrofluorene.

Anal. Calcd. for $C_{16}H_9N_5O_8$: C 48.12; H, 2.27; N, 17.54. Found: C, 47.96; H, 2.28; N, 17.30.

Lithium-DTF Anion-Radical Salt.—Lithium iodide (1.8 g., 4 × 10^{-3} mole) and DTF (1.5 g., 1 × 10^{-2} mole) were each separately dissolved in 25 ml. of hot Spectrograde acetonitrile and the solutions were mixed under a nitrogen atmosphere. On cooling, the anion-radical salt separated as blue-black microcrystals (1.24 g., 75%), m.p. 290° (explodes).

Anal. Calcd. for $C_{16}H_5LiN_5O_6$: C, 51.87; H, 1.36; Li, 1.88; N, 19.92. Found: C, 51.57; H, 1.60; Li, 1.62; N, 18.57.

Electronic absorption spectra taken in acetonitrile show maxima at 740 mμ (log ε 3.21); 562 mμ (log ε 3.29); 525 mμ (log ε 324); and 425 mμ (log ε 3.20). In the infrared, relatively strong absorption at 2200 cm.$^{-1}$ for the CN group was observed. The e.s.r. signal intensities of the microcrystals corresponded to about 5 × 10^{20} spins/mole.[12]

Attempted Preparation of Et_3NH^+-$(DTF)_2^{\cdot-}$.—In a boiling solution of 0.716 g. (1.9 × 10^{-3} mole) of DTF in 40 ml. of dichloromethane was dissolved a solution of 0.10 g. (1.0 × 10^{-3} mole) of TEA in 10 ml. of the same solvent. The mixture was cooled; the solid (50 mg.) was filtered and washed with cold solvent, m.p. 185–190° dec. The analysis gave values close to 1:1 composition.

Anal. Calcd. for $C_{22}H_{20}N_6O_6$: C, 56.89; H, 4.34; N, 18.10. Found: C, 56.67; H, 4.37; N, 16.13.

The above preparation was repeated using acetonitrile and THF as solvent. The ion-radical salt was obtained after evaporation of the solvent to a small volume. The resulting paramagnetic solid did not analyze for either the 1:1 or the 1:2 complex; in every case a low nitrogen value was obtained.[13]

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(12) The e.s.r. measurements were carried out by Dr. Kedma Bar-Eli. The absorption of weighed solid samples was compared with that of solid diphenylpicryl-hydrazyl. The accuracy of the measurements is estimated to be ±25%.

(13) NOTE ADDED IN PROOF.—We have now prepared a number of salts of DTF anion radical by the metathetical reaction between the onium iodides and lithium DTF. Typical examples of the cations are triethyl methyl ammonium, N-methyl quinolinium, triphenyl methyl phosphonium, and triphenyl methyl arsonium ions. These salts have the composition $(\text{cation})^+(\text{DTF})^{\cdot-}$.

α-Myrcene (2-Methyl-6-methylene-1,7-octadiene)

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α-Myrcene (2-methyl-6-methylene-1,7-octadiene) (I) has neither been reported as found in nature nor unequivocally prepared synthetically. The only mention of I in the literature is that of G. V. Pigulevskii, *et al.*,[1] who deduced its formation in the iodine-catalyzed dehydration of linalool (II) based upon Raman spectral data. Other apparent references[2] are not pertinent, since the corresponding abstracts do not mention α-myrcene.

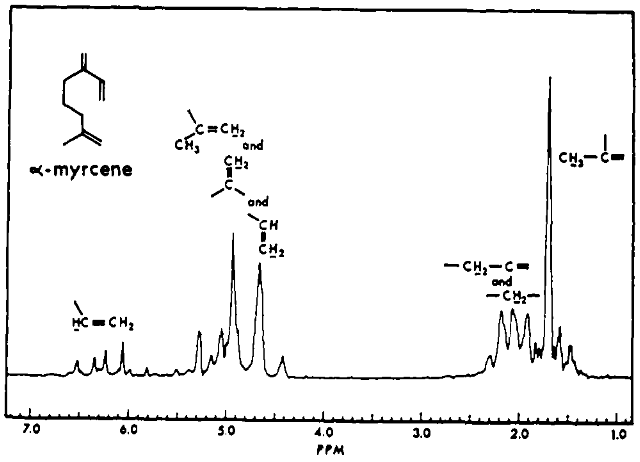


Figure 1.—N.m.r. spectrum of α-myrcene.

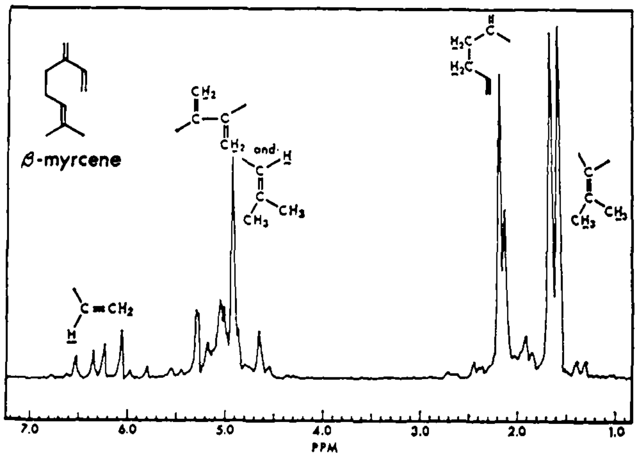
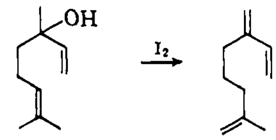
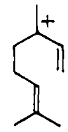


Figure 2.—N.m.r. spectrum of β-myrcene.



II I

The formation of I would not be predicted *via* a dehydration through carbonium ion III, and has not been reported as a product of such dehydration by other workers.[3,4]



III

On the other hand, *cis*- and *trans*-ocimene, β-myrcene (7-methyl-3-methylene-1,6-octadiene), and dipentene can be predicted as products and have, in fact, been so reported when using acid-type catalysts.[5,6]

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(1) G. V. Pigulevskii and N. L. Prokudina, *Dokl. Akad. Nauk SSSR*, **67**, 283 (1949).

(2) F. K. Beilstein, "Handbuch der Organischen Chemie," Vol. I, 4th Ed., 3rd Supplement, 1958, p. 1053.

(3) B. A. Arbusov and W. S. Ambramov, *Chem. Ber.*, **67**, 1942 (1934), and older references cited therein.

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(5) M. Günzl-Schumacher and U. Wicker, *Chem. Ber.*, **93**, 974 (1960).

(6) International Flavors and Fragrances, Inc., unpublished work.

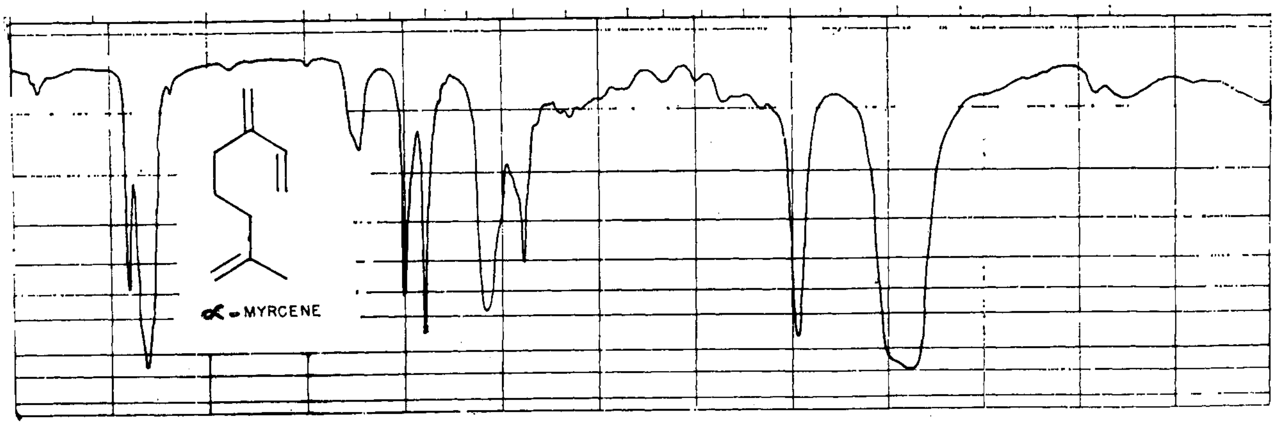


Figure 3.—Infrared spectrum of α-myrcene.

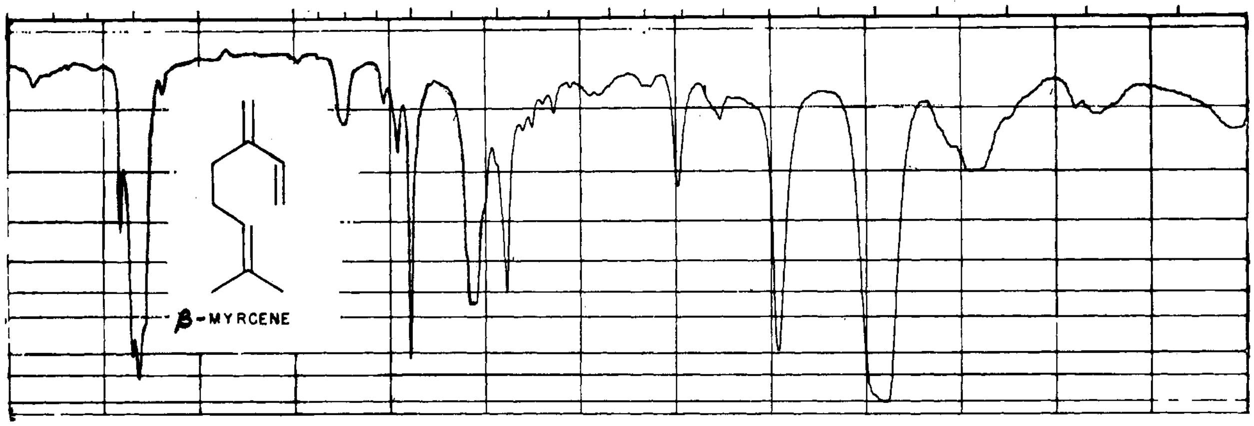
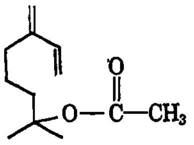


Figure 4.—Infrared spectrum of β-myrcene.

We have prepared α-myrcene by the vapor phase pyrolysis of myrcenyl acetate (IV) the mechanism for



IV

which has been reported previously.[7] This pyrolysis yields α- and β-myrcene as substantially the only products and in the statistically predicted 3:1 ratio.

We have also found α-myrcene in the pyrolysate of β-pinene.

The n.m.r. agrees precisely with the structure of α-myrcene, Figure 1. For comparison β-myrcene is included, Figure 2.

The infrared spectrum of α-myrcene,[7] Figure 3, has a very intense band at 890 cm.$^{-1}$, as expected for a compound with two vinylidene groups, and a relatively strong band at 1650 cm.$^{-1}$ attributable to the isolated vinylidene group only.[8] The shoulder at 1640 cm.$^{-1}$ and the relatively intense absorption at 1600 cm.$^{-1}$ are assigned to the conjugated dienic system.[8]

The 1650-cm.$^{-1}$ band is absent in the spectrum of β-myrcene, Figure 4, and the 1640- and 1600-cm.$^{-1}$ bands are present.

Experimental

Pyrolysis of Myrcenyl Acetate.—Myrcenyla cetate[9] (99%) was pyrolyzed at 400° in a 14 × 1 in. glass tube filled with stainless steel protruded packing at a rate of 1 g./min. using nitrogen as a carrier at 10 ml./min. flow rate. The pyrolysate from 4540 g. of the ester was washed neutral with water and sodium carbonate. The washed pyrolysate (2872 g.) was dried and distilled through a 7-ft., 1-in.-diameter column containing stainless steel protruded packing at a 20:1 reflux ratio. This fractionation effectively separated the α- and β-myrcene. A 500-g. fraction, b.p. 44° (10 mm.), was α-myrcene. The rest of the distillate consisted of a mixture of α- and β-myrcene and unchanged myrcenyl acetate. The α-myrcene cut was found to be pure by g.l.c. analysis using a 10-ft., $^{3}/_{16}$-in.-i.d., copper column filled with 10% Carbowax 20M on 60–80-mesh silane-treated Celite at a column temperature of 90° and an inlet pressure of 25-p.s.i. helium with a flow rate of 60 ml./min. The relative retention times of α- and β-myrcene on this column (β-pinene = 1.00) are 1.06 and 1.15, respectively.

The physical constants of α-myrcene are b.p. 44° (10 mm.), $n^{25}\mathrm{D}$ 1.4661, d^{25}_{25} 0.7959, $\lambda_{\max}^{\text{isooctane}}$ 224.5 mμ (ε 18,600); of β-myrcene are $\lambda_{\max}^{\text{isooctane}}$ 224.5 mμ (ε 18,600),[6] $\lambda_{\max}^{C_2H_5OH}$ 225 mμ (ε 20,130).[10]

The mass spectrum confirms the empirical structure with a strong molecular ion at $m/e = 136$.

Hydrogenation of 0.1 mole of α-myrcene, neat, at room temperature and 30-p.s.i. H_2 using 0.3% Adams PtO_2 catalyst, yielded a product whose infrared spectrum was identical with that of 2,6-dimethyloctane. Three moles of hydrogen/mole of terpene were absorbed.

β-Pinene Pyrolysate.—A preparative gas chromatograph containing a 10-ft., $^{7}/_{16}$-in.-i.d. copper column packed with 20% Carbowax 20M on 60–80-mesh Chromosorb P was used. β-Pinene pyrolysate (200 ml.) prepared by the procedure of Goldblatt and Palkin[11] from 99% β-pinene was injected in 1-ml. por-

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[7] B. M. Mitzner, E. T. Theimer, and S. Lemberg, *Can. J. Chem.*, **41**, 2097 (1963).

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34.

[9] J. H. Blumenthal, U. S. Patent 3,075,003 (Jan. 22, 1963).

[10] H. Farnow, *Dragoco Rept.*, **7**, 124 (1958).

[11] L. A. Goldblatt and S. Palkin, *J. Am. Chem. Soc.*, **63**, 3517 (1941).

tions at 100° and 30-p.s.i. helium inlet pressure at a flow rate of 200 ml./min. Only the front half of the myrcene peak was trapped, and 5 ml. of material was thus collected which contained approximately 60% α-myrcene, and 40% β-myrcene. Retrapping of this material in the same manner yielded α-myrcene which was 90% pure by analytical g.l.c.

Acknowledgment.—The authors are grateful to Dr. S. Lemberg and Mr. M. Jacobs for interpreting the n.m.r. data.

Attempted Synthesis of Hexaphenylcyclopropane

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Korshak[1] has reported the synthesis of polydiphenylmethylene. The polymer was derived by a polyrecombination reaction in which diphenylmethane was treated with a stoichiometric amount of *t*-butyl peroxide, and was reported to have molecular weights of from 10,000 to 900,000. The high degree of steric hindrance in the chain and the possibility of hydrogen abstraction from the benzene ring during synthesis suggest that structures other than a linear one may be formed, although infrared spectra did not indicate the presence of any disubstituted benzene rings. To study this question, an attempt was made to prepare the polymer by an alternate route.

It has been reported that cyclopropanes can be polymerized either by heat and pressure[2] or by titanium coordination catalysts.[3] The results suggested that, if hexaphenylcyclopropane could be prepared, it might undergo ring opening to form polydiphenylmethylene.

The synthesis of hexaphenylcyclopropane was attempted by two techniques. One was the addition of diphenylmethylene to tetraphenylethylene; the other, the synthesis of hexaphenyl-1,3-propylene glycol.

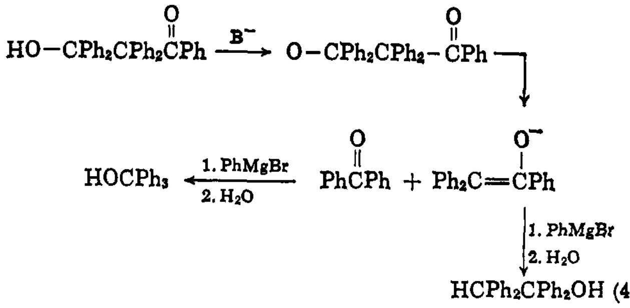
In planning the addition reaction, the series of tri-, tetra-, and pentaphenylcyclopropanes leading up to hexaphenylcyclopropanes were tried as models. The tri- and tetrasubstituted compounds, 1,1,2,2-tetraphenylcyclopropane and 1,1,2-triphenylcyclopropane, were made, but both the penta- and hexasubstituted ones failed. Only hexaphenylpyrazoline was isolated in the latter case.

The other planned route to hexaphenylcyclopropane is shown by eq. 1–3. However, our first step to hexaphenylpropylene glycol failed. Instead, 2-benzoyl-1,1,2,2-tetraphenylethanol was isolated. When this compound was treated further with phenylmagnesium bromide, the products isolated were triphenylmethanol, tetraphenylethanol, and biphenyl. These products correspond to a decomposition by the mechanism shown in eq. 4. The biphenyl is believed to be a by-product from the Grignard reagent and not a decomposition product of 2-benzyl-1,1,2,2-tetraphenylethanol.

$$\mathrm{Ph_2C(COOC_2H_5)_2 \xrightarrow[2.\ H_2O]{1.\ PhMgBr} HO[Ph_2]_3OH} \qquad (1)$$

$$\mathrm{HO[CPh_2]_3OH \xrightarrow{PBr_3} Br[CPh_2]_3Br} \qquad (2)$$

$$\mathrm{Br[CPh_2]_3Br \xrightarrow{Zn} C_3Ph_6} \qquad (3)$$



$$\mathrm{HO{-}CPh_2CPh_2\overset{\overset{O}{\|}}{C}Ph \xrightarrow{B^-} {}^-O{-}CPh_2CPh_2{-}\overset{\overset{O}{\|}}{C}Ph \longrightarrow Ph\overset{\overset{O}{\|}}{C}Ph + Ph_2C{=}\overset{\overset{O^-}{|}}{C}Ph}$$

$$\mathrm{Ph\overset{\overset{O}{\|}}{C}Ph \xrightarrow[2.\ H_2O]{1.\ PhMgBr} HOCPh_3 \qquad Ph_2C{=}\overset{\overset{O^-}{|}}{C}Ph \xrightarrow[2.\ H_2O]{1.\ PhMgBr} HCPh_2CPh_2OH} \qquad (4)$$

Experimental

1,1,2-Triphenylcyclopropane.—A solution of 0.033 mole of diphenyldiazomethane[4] in 6 ml. of ethyl ether was added to 25 ml. of styrene. After the solution was irradiated for 2 hr. with a G. E. ultraviolet sun lamp (RS275-R-40), the red color of the diphenyldiazomethane was discharged and a yellow color had formed.

The solution was diluted with *ca.* 500 ml. of petroleum ether. A precipitate of polystyrene was filtered off and discarded. The petroleum ether filtrate was evaporated under vacuum to an oil which was diluted with methanol. Some more polystyrene precipitated and was filtered off. The filtrate was once again evaporated to an oil and allowed to stand for several days. Crystals formed which were soluble in petroleum ether and moderately soluble in methanol. Recrystallization from methanol gave about 4 g. of white needles, m.p. 51–52°.

Anal. Calcd. for $C_{21}H_{18}$: C, 93.37; H, 6.63. Found: C, 93.39; H, 6.75.

The infrared spectrum of the compound (KBr pellet) shows peaks at 2.90 (s), 3.30 (s), 6.23 (s), 6.68 (s), 6.90 (s), 9.27 (m), 9.67 (m), 10.3 (m), 12.8 (s), 13.05 (s), 13.3 (m), 13.55 (m), and 14.2–14.4 (broad, strong) μ.

The n.m.r. spectrum of the sample in CCl_4 (Varian S-60A, 60 Mc., with tetramethylsilane as standard) was more complex than expected. The aromatic frequency was split unequally to −420 and −429 c.p.s. in ratio of 2:1, respectively. The $H\alpha$ line was split twice equally to −175, −168, −166, and −159 c.p.s. as expected. However, $H\beta^1$ and $H\beta^2$ showed seven lines instead of the expected eight: −120, −114, −115, −109, −104, −100, and −95 c.p.s. The ratio of the sum of areas of $H\alpha$, $H\beta^1$, and $H\beta^2$ to the aromatic hydrogen was 1:5 as expected. No propene structure was present.

1,1,2,2-Tetraphenylcyclopropane.—Approximately 0.05 mole of solid diphenyldiazomethane was prepared by evaporation of a petroleum ether solution under vacuum (see above). The solid was dissolved in 100 g. of 1,1-diphenylethylene[5] and the mixture was irradiated under a G.E. ultraviolet sun lamp for 2 days. The white crystals which formed were filtered off and washed with small amounts of petroleum ether to give about 8 g. of a product with m.p. 167–170°. Skell[6] has reported the reaction of diphenyldiazomethane with 1,1-diphenylethylene, but no details or properties of the product were given.

Anal. Calcd. for $C_{27}H_{22}$: C, 93.65; H, 6.35. Found: C, 93.65; H, 6.48.

The infrared spectrum (in KBr) was 2.95 (s), 3.30 (s), 6.25 (s), 6.70 (s), 6.90 (s), 9.25 (m), 9.65 (m), 9.85 (m), 10.95 (m), 12.52 (s), 13.2 (s), 13.9 (s), and 14.3 (s) μ.

The n.m.r. spectrum of the sample (as above) had one peak at −417 and one at −148 c.p.s.; the ratio of their areas was

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[1] (a) V. V. Korshak, S. L. Sosin, *Proc. Acad. Sci. USSR, Chem. Sec., Eng. Transl.*, **132**, 517 (1960); (b) V. V. Korshak, S. L. Sosin, *Vysokomolekul. Soedin.*, **3**, 1332 (1961).

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