TABLE IX

COMPETITIVE REACTIONS AT 0° AND 50°[a]

		Sulfur dioxide		Solvent		Vapor phase	Products			
							II		III	
Expt.	t, °C.	G.	Mole	G.	Mole	SO_2, mole	G.	Mole	G.	Mole
					In chloroform					
44	0	2.70	0.0422	54.05	0.453	0.0017	7.11	0.0395	0.155	0.00106
45	0	2.80	.0437	52.95	.444	.0017	7.13	.0396	.170	.00116
46	50	2.70	.0422	52.60	.4405	.0032	7.22	.0400	.254	.001735
47	50	2.80	.0437	52.75	.442	.0033	7.20	.0399	.247	.00169
					In tetrahydrofuran					
48	0	14.15	0.221	24.1	0.334	0.0072	6.87	0.0382	0.128	0.000875
49	0	14.60	.228	23.65	.328	.0080	6.86	.0381	.133	.000913
50	50	14.35	.224	23.7	.329	.0152	6.82	.0378	.505	.00345
51	50	14.75	.230	23.4	.3245	.0156	6.80	.0377	.510	.00348

[a] Taken: 3.55 g. (0.0433 mole) of I and 4.25 g. (0.0434 mole) of maleic anhydride.

(2) From a solution of 5.140 g. of II, 0.517 g. of III, *ca.* 0.5 g. of maleic anhydride in 28 g. of benzene, the solvent was removed, etc.; found: 5.10 g. of II and 0.511 g. of III.

(3) From a mixture of 4.473 g. of II, 1.004 g. of III, 0.111 g. of polysulfone (a possible by-product), 0.7785 g. of maleic anhydride, and 32 g. of chloroethyl ether, the polysulfone was removed by filtration. The solvent was removed, etc.; found: 4.37 g. of II and 0.966 g. of III.

Before calculating the ratio of rate constants and dielectric constants, sulfur dioxide in the vapor phase was estimated by equation 7, and the amount subtracted from total sulfur dioxide. The dielectric constant D was calculated for ideal solutions

$$D = \Sigma X_i \cdot D_i \qquad (8)$$

where X_i is the mole fraction of the i'th component and D_i is its dielectric constant. The following dielectric constant data were used: I, 2.102 at 25°[21]; maleic anhydride, 50.0 at 60°[22]; sulfur dioxide, 14.3 at 14.5°, 13.3 at 32°,[23] and 13.6 at 27° by interpolation; chloroform, 4.806 at 20°[24]; benzene, 2.284 at 20°[25]; bis-(β-chloroethyl) ether, 21.2 at 20°[26]; tetrahydrofuran, 7.39 at 25°[27]; mesitylene, 2.356 at 20°.[28]

Stability of III.—An approximately one molar aqueous solution of III was refluxed for one hour. No sulfur dioxide was detected in the solution or vapor by litmus paper or odor.

Compound III, 1.1 g., and maleic anhydride, 0.8 g., dissolved in 14.7 g. of tetrahydrofuran, were allowed to stand for 6 weeks at room temperature. The solution was evaporated and the residue dissolved in 15 ml. of 10% sodium hydroxide. Cooling, filtering and washing gave 0.8 g. of III, m.p. 129–131°. When the alkaline filtrate was acidified with hydrochloric acid, no precipitate of IV formed.

In a second experiment, 1.0 g. of III, 4.0 g. of maleic anhydride and 37 ml. of chloroethyl ether were allowed to stand for 6 days at room temperature. The solution was distilled *in vacuo*, the residue was treated with 15 ml. of hot, 10% sodium hydroxide. After cooling and extraction with 50 ml. of benzene, distillation of the benzene gave 1.0 g. of III as the residue, m.p. 131.5–133.5°. The alkaline filtrate gave no precipitate on acidifying.

In a third experiment, 1.0 g. of III, 4.0 g. of maleic anhydride and 37 ml. of benzene were allowed to stand for 6 days at room temperature. Separating this mixture as before gave 0.93 g. of III, m.p. 125–128°, while the alkaline filtrate gave no precipitate on acidifying.

Competitive Reactions at 0° and 50°.—Calculations and experimental procedure were the same as for the room temperature reactions, except that 200-ml. pressure bottles were used at 50 ± 0.5° (Tables V and IX).

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[21] E. H. Farmer and F. L. Warren, *J. Chem. Soc.*, 1300 (1933).

[22] P. Walden, *Z. physik. Chem.*, **46**, 174 (1903).

[23] P. Eversheim, *Ann. Phys.*, [4] **8**, 539 (1902).

[24] A. Weissberger, ed., "Technique of Organic Chemistry," Vol. VII, "Organic Solvents," 2nd ed. rev., Interscience Publishers, Inc., New York, N. Y., 1955, p. 193.

[25] Reference 24, p. 72.

[26] Reference 24, p. 256.

[27] F. E. Critchfield, J. A. Gibson and J. L. Hall, THIS JOURNAL, **75**, 6044 (1953).

[28] T. W. Richards and J. W. Hipley, *ibid.*, **41**, 2010 (1919).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

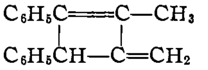
Cyclobutane Diolefins. 1,2-Diphenyldimethylenecyclobutane[1,2]

BY A. T. BLOMQUIST AND YVONNE C. MEINWALD

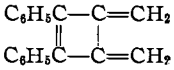
RECEIVED DECEMBER 3, 1959

Thermal decomposition of 1,2-bis-(dimethylaminomethyl)-3,4-diphenylcyclobutane dioxide affords a 1:1 mixture of isomeric dienes, 1,2-diphenyldimethylenecyclobutane (III) and 3-methylene-1,4-diphenyl-2-methylcyclobutene (I). The completely exocyclic conjugated diene III undergoes normal 1,4-Diels–Alder addition reactions with both maleic anhydride and tetracyanoethylene.

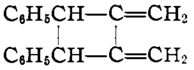
The unusual formation of spiro compounds *via* 1,2-cycloaddition of tetracyanoethylene (TCNE) to certain conjugated cyclobutane polyolefins, such as I and II, was described in earlier papers.[2a,c] Subsequently, J. K. Williams also observed similar addition reactions for other derivatives of methylenecyclobutane.[3] On the basis of pertinent studies reported to date, the facile 1,2-cycloaddition of TCNE to 1,3-conjugated dienes appears to be limited to dienes which possess a rigid transoid arrangement of the double bonds and hence are



I



II



III

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[1] This study was supported by the National Science Foundation, Grants NSF-G2922 and NSF-G5923.

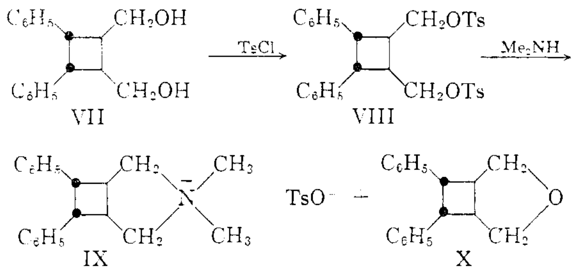
[2] For preceding related papers see A. T. Blomquist and Y. C. Meinwald: (a) THIS JOURNAL, **79**, 5316 (1957); (b) **79**, 5317 (1957); (c) **81**, 667 (1959).

[3] J. K. Williams, *ibid.*, **81**, 4013 (1959).

unable to form normal 1,4-Diels–Alder adducts. It was of interest, nevertheless, to examine the behavior of TCNE with 1,2-dimethylenecyclobutane systems in order to ascertain whether only normal Diels–Alder additions would result or whether spiro products from 1,2-addition would occur also. For this reason, synthesis of the exocyclic conjugated diene 1,2-diphenyldimethylenecyclobutane (III) was undertaken.

The diene III could not be isolated as a pure hydrocarbon free of the isomeric diene I. Pyrolysis of 1,2-bis-(dimethylaminomethyl)-3,4-diphenylcyclobutane dioxide (VI) gave a 1:1 mixture of the two dienes. Fortunately, however, diene III proved to be much more reactive than diene I toward TCNE; this rate difference permitted the isolation of a pure adduct derived from III from the mixture of dienes. Also, reaction of the diene mixture with maleic anhydride was completely selective, since diene I is inert toward this reagent.

Synthesis of 1,2-bis-(dimethylaminomethyl)-3,4-diphenylcyclobutane (V), required as an intermediate for the amine oxide VI, was first attempted by a route which involved displacement of the tosyl groups in 1,2-bis-(hydroxymethyl)-3,4-diphenylcyclobutane ditosylate (VIII) with dimethylamine. However, reaction of the tosylate VIII with dimethylamine under a variety of conditions gave only the cyclic quaternary ammonium tosylate IX together with a small amount of the related cyclic ether X.[4] Similarly, aminolysis of the dibromide XI gave the quaternary ammonium bromide XII as the sole product of reaction. The two quaternary salts, IX and XII, gave, as expected, the same picrate derivative.



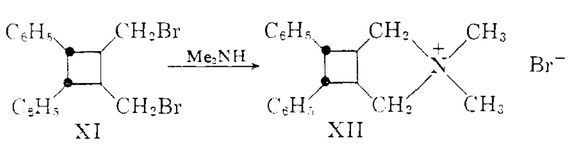
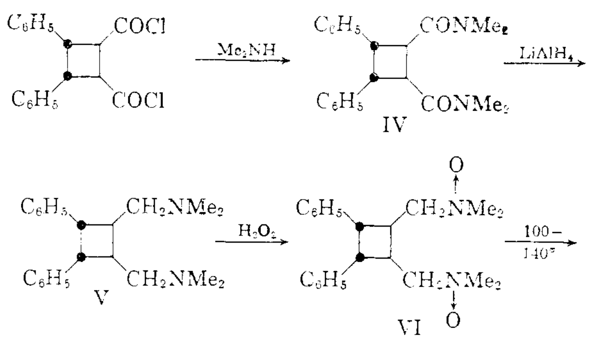
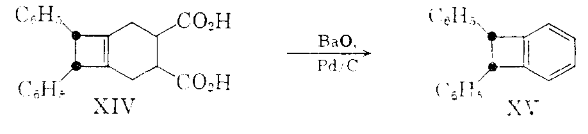


Chart A



mixture of dienes I and III

A successful route to the amine V was realized in the lithium aluminum hydride reduction of the substituted β-truxinamide IV as outlined in chart A. Treatment of the amine V with hydrogen peroxide effected a smooth conversion to the amine oxide VI. Thermal decomposition of the oxide at 100–140° and 0.5–1.5 mm. gave a colorless oil (65–70% yield) whose infrared spectrum resembled that of the diene I but which also showed an additional strong absorption band at 11.30 μ.[2c] Thus, the liquid pyrolysate appeared to be a mixture of dienes I and III. This mixture could not be resolved by chromatography because of the tendency for the dienes to polymerize. However, treatment of the diene mixture with maleic anhydride gave a crystalline adduct XIII (35%) derived from diene III together with pure unreacted diene I (35%). The anhydride adduct XIII was not isolated directly but was obtained as the related dicarboxylic acid XIV, m.p. 172–184°. The broad m.p. range of the acid XIV is probably a consequence of its comprising a mixture of stereoisomers. Several recrystallizations of this mixture of acids gave one pure isomer of XIV which showed m.p. 198–199°. The ultraviolet spectrum of the acid adduct XIV showed only unconjugated benzenoid absorption. The stereoisomeric mixture of acids was heated with an intimate mixture of barium oxide and 10% palladium-*on*-carbon with the hope of effecting decarboxylation and aromatization to form 1,2-diphenylbenzocyclobutene (XV).[6] A mixture of hydrocarbons was obtained (76% yield) which could be resolved by chromatography into two components. The two hydrocarbons, obtained in approximately a 1:5 ratio, proved to be 9-phenylanthracene and *o*-dibenzylbenzene. The identity of each hydrocarbon was established by direct comparison of its properties with those of an authentic specimen of the known compound.[7]



The transformation of the acid-adduct XIV to 9-phenyl anthracene was unexpected and merits brief comment. It seems plausible that at the high temperature required for the decarboxylation and dehydrogenation of XIV to XV the cyclobutene ring of diphenylbenzocyclobutene would open to the diphenyl derivative of *o*-quinonedimethane (XVI). This quinonoid hydrocarbon could readily cyclize to a dihydroanthracene derivative as shown in chart B. Further dehydrogenation would then give 9-phenylanthracene. Support for the above is given by the recent work of Jensen and Coleman[6] who showed that the hydrocarbon XV reacted with sulfur dioxide to give a Diels–Alder sulfone-adduct derived from the quinonoid hydrocarbon XVI.

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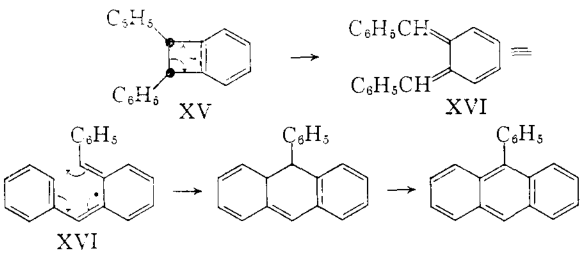
(4) An interesting example of a similar formation of a tetrahydrofuran derivative was encountered by Stork, *et al.*, in the total synthesis of cantharadin.[5]

(5) G. Stork, E. E. van Tamelen, L. J. Friedman and A. W. Burgstahler, This Journal, **75**, 384 (1953).

(6) F. R. Jensen and W. E. Coleman, *ibid.*, **80**, 6149 (1958).

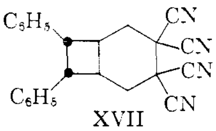
(7) R. Adams and M. H. Gold, *ibid*,. **62**, 56 (1940).

CHART B

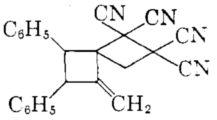


The sulfone-adduct gave 9-phenyl-9,10-dihydroanthracene when heated to its m.p.

Addition of TCNE to the mixture of dienes I and III in benzene solution and at room temperature gave rapidly a crystalline, sharp melting adduct derived from diene III. The infrared spectrum of the adduct is in accord with structure XVII and not with XVIII. It is thus apparent that the 1,2-dimethylenecyclobutane system perfers to add TCNE in the normal Diels–Alder fashion. In this context, the formation of a spiro product from the triene II with TCNE[2a,c] reflects a striking change in the mode of addition brought about by the additional endocyclic double bond.



XVII



XVIII

Experimental Part[8]

1,2 - Bis - (hydroxymethyl) - 3,4 - diphenylcyclobutane Ditosylate (VIII).—The glycol VII, m.p. 108–110°,[2c] (10.72 g., 0.04 mole) was treated with 22.8 g. (0.12 mole) of tosyl chloride in 150 ml. of pyridine at ice-bath temperature overnight. The cold reaction mixture was diluted with 100 ml. of water and extracted with benzene. The benzene solution was washed successively with cold dil. hydrochloric acid, 10% sodium carbonate solution and satd. salt solution. Evaporation of the solvent gave a colorless, viscous residue which solidified upon the addition of 50% ether–petroleum ether. The solid tosylate VIII (21.3 g. 94.5%) after recrystallization from benzene–ether was obtained as colorless needles, m.p. 113–115°.

Anal Calcd. for $C_{30}H_{32}O_6S_2$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.75; H, 5.80; S, 11.32.

Reaction of the Ditosylate VIII with Dimethylamine.—A mixture of 12.2 g. of the tosylate VIII, 20 ml. of dimethylamine and 2 ml. of benzene contained in a sealed Pyrex bomb was heated at 45–50° for 24 hr., during which time crystals separated. After evaporation of the dimethylamine, the cooled mixture was diluted with water and extracted with ether. From the dried ether solution there was isolated 1.6 g. of 6,7-diphenyl-3-oxabicyclo[3.2.0]heptane (X), m.p. 66–70°. After recrystallization from ether–petroleum ether the oxide X appeared as hard needles, m.p. 74–75°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.27; H, 7.34.

Extraction of the aqueous layer with ethyl acetate or chloroform, after drying and evaporation of the organic solvent, gave 5.5 g. of the quaternary ammonium tosylate IX as soft needles, m.p. 168–170°. The compound IX, N-methyl 6,7-diphenyl-3-azabicyclo[3.2.0]heptane methotosylate, had m.p. 169–170° after recrystallization from benzene.

Anal. Calcd. for $C_{27}H_{31}NSO_3$: C, 72.12; H, 6.95; N, 3.16; S, 7.13. Found: C, 71.71; H, 7.16; N, 3.18; S, 8.19.

A sample of the quaternary compound IX in ethanol was treated with a saturated solution of picric acid. The **picrate derivative** of IX, recrystallized from ether–ethanol, showed m.p. 85–86°. Upon continued heating the derivative resolidified and then showed m.p. 135–136° dec.

Anal. Calcd. for $C_{26}H_{26}N_4O_7$: C, 61.65; H, 5.17; N, 11.06. Found: C, 62.05; H, 5.47; N, 10.74.

Reaction of 1,2-Bis-(bromomethyl)-3,4-diphenylcyclobutane (XI) with Dimethylamine.—A mixture of 7.88 g. of the dibromide XI[2c] and 20 ml. of dimethylamine in a sealed Pyrex tube was kept at room temperature for 4 hr. and at 40° overnight, whereupon the entire mixture solidified. After evaporation of the excess dimethylamine the quaternary ammonium bromide XII, N-methyl-6,7-diphenyl-3-azabicyclo[3.2.0]heptane methobromide, m.p. 258° dec., was obtained in quantitative yield.

Anal. Calcd. for $C_{20}H_{24}NBr$: C, 67.04; H, 6.75; N, 3.96; Br, 22.30. Found: C, 67.14; H, 6.98; N, 3.70; Br, 22.52.

The picrate derivative of XII, prepared as described above, showed m.p.'s 85–86° and 135–136° and did not depress the m.p. of the picrate derivative obtained from IX.

N,N,N′,N′-Tetramethyl β-Truxinamide (IV).—β-Truxinoyl chloride[9] was prepared by reaction of 18.8 g. (0.0635 mole) of β-truxinic acid with 27 g. (0.13 mole) of phosphorus pentachloride in benzene at room temperature overnight. After removal of the solvent and phosphorus oxychloride *in vacuo* at 50°, the acid chloride obtained, m.p. 95–96°, was dissolved in 60 ml. of anhydrous benzene. Dimethylamine was bubbled into this solution for 40 min., with the mixture cooled occasionally by an ice–water-bath. After the mixture had stood at room temperature for another 40 min., it was filtered and the collected solid washed with water to remove dimethylammonium chloride. There was obtained 14.2 g. of the amide IV, m.p. 159–161°. An additional 2.2 g. of the amide was isolated from the benzene filtrate to give a total yield of IV of 74%.

Anal. Calcd. for $C_{22}H_{26}O_2N_2$: C, 75.40; H, 7.48; N, 7.99. Found: C, 76.15; H, 7.63; N, 8.07.

1,2-Bis-(dimethylaminomethyl)-3,4-diphenylcyclobutane (IV).—A solution of 18 g. of the amide IV in 300 ml. of anhydrous benzene was added with stirring to a suspension of 4 g. of lithium aluminum hydride in 300 ml. of anhydrous ether. This mixture was stirred at 60° for 4 days and then treated with water. The usual isolation procedure gave 15.3 g. (94%) of the diamine V as a colorless liquid, b.p. 152–154° (0.35 mm.).

Anal. Calcd. for $C_{22}H_{30}N_2$: C, 81.93; H, 9.38; N, 8.69. Found: C, 81.83; H, 9.56; N, 8.94.

The dipicrate derivative of V was prepared and was isolated in two polymorphic modifications which had m.p.'s 145° and 198°.

Anal. Calcd. for $C_{34}H_{36}O_{14}N_8$: C, 52.30; H, 4.65; N, 14.35. Found: C, 52.30; H, 4.73; N, 14.22.

1,2-Bis-(dimethylaminomethyl)-3,4-diphenylcyclobutane Dioxide (VI).—To a solution of 15.3 g. (0.047 mole) of the diamine V in 5 ml. of methanol cooled in an ice-bath 35 ml. of 30–35% hydrogen peroxide solution was added slowly with shaking. After the mixture had stood in an ice-bath overnight it was stirred at room temperature for 24 hr. and at 40° for 7 days. At the end of this time the *p*H of the solution was about 7. Excess hydrogen peroxide was destroyed by stirring the mixture overnight with a small amount of 10% palladium-on-charcoal. The solution now gave a negative test for peroxides with starch–potassium iodide paper. The mixture was filtered, the palladium catalyst washed with water, and the combined filtrate and washings was made up to 50 ml. with added water. This solution of the amine oxide VI was used in the subsequent pyrolysis. **A dipicrate derivative** of the bis-amine oxide VI was prepared and, after recrystallization from ethanol, was obtained as yellow prisms, m.p. 185–186° dec.

Anal. Calcd. for $C_{34}H_{36}O_{16}N_8$: C, 50.24; H, 4.47; N, 13.79. Found: C, 50.46; H, 4.46; N, 13.52.

Pyrolysis of the Bis-amine Oxide VI.—An aqueous solution which contained 0.0025 mole of the oxide VI was placed in a vacuum sublimation apparatus and the water removed *in vacuo* at 40°. The solid, glass-like residue was then heated under 0.5 mm. pressure with an oil-bath. The temperature of the bath was gradually increased to 100°

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[8] All b.p.'s are uncorrected; all m.p.'s are corrected.

[9] R. Stoermer and E. Laage, *Ber.*, **59B**, 642 (1926).

when decomposition began. The bath temperature was kept at 120–130° until decomposition was complete. Pyrolysis at higher temperatures, >160°, resulted in the formation of undesirable tertiary amine V. The pyrolysate, a mixture of the isomeric dienes I and III, collected on the cold finger of the apparatus as a colorless, viscous liquid. The infrared spectrum of this liquid showed an absorption maximum at 11.30μ.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.00; H, 6.95.

Reaction of the Diene III with Maleic Anhydride.—The liquid mixture of isomeric dienes I and III obtained in the above pyrolysis was dissolved in benzene and immediately treated with a benzene solution of 0.25 g. of maleic anhydride and a small amount of hydroquinone. The mixture was kept under nitrogen. Although oily droplets appeared at once, the reaction mixture was kept at room temperature overnight. The benzene was then removed *in vacuo* and the residue treated with 15 ml. of 10% sodium hydroxide solution. The alkaline solution was extracted thoroughly with ether. There was obtained 0.20 g. (34%) of the diene I from the dried ether extracts. This diene I, m.p. 62–64° after one recrystallization from methanol, had infrared and ultraviolet absorption spectra which were identical with those observed for diene I previously.[2c]

Acidification of the alkaline solution followed by ether extraction gave 0.21 g. (35%) of the maleic anhydride adduct XIII as the corresponding dicarboxylic acid XIV, 7,8-diphenylbicyclo[4.2.0]-1(6)-octene-3,4-dicarboxylic acid. After one recrystallization from aqueous ethanol the dicarboxylic acid showed m.p. 172–181°. Additional recrystallizations raised the m.p. to 198–199°.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.68; H, 5.77.

Reaction of the Diene III with Tetracyanoethylene.—The mixture of dienes I and III obtained from the pyrolysis of 0.0025 mole of the bis-amine oxide VI was dissolved in benzene and added, under nitrogen, to a solution of 0.25 g. (0.002 mole) of TCNE in benzene. The mixture became dark green in color immediately. After the mixture had stood at room temperature for 1 hr., the benzene was removed *in vacuo* and the brown tarry residue extracted with boiling ether. The red ether extract was decolorized with Norite and filtered. Concentration of the ether solution gave 150 mg. of the adduct 3,3,4,4-tetracyano-7,8-diphenylbicyclo[4.2.0]-1(6)-octene (XVII) as colorless needles, m.p. 114–115° dec.

Anal. Calcd. for $C_{24}H_{16}N_4$: C, 79.98; H, 4.48; N, 15.55. Found: C, 79.71; H, 4.69; N, 15.49.

Decarboxylation and Aromatization of the Dicarboxylic Acid XIV.—The thoroughly ground mixture of 1.7 g. of the acid XIV, 3.5 g. of barium oxide and 0.5 g. of 10% palladium-on-charcoal placed in a vacuum sublimation apparatus was carefully heated with a free flame under 0.5–1.0 mm. pressure. A Wood metal-bath heated to 330–350° was used in smaller scale experiments. A hydrocarbon mixture together with some palladium-on-charcoal collected on the condenser. From time to time, flaming was discontinued, the reaction mixture cooled, the condensate dissolved in ether, and the reaction mixture residue stirred with a spatula. The foregoing operation was repeated until sublimation ceased. Evaporation of the combined, filtered ether extracts gave about 1 g. of a yellowish solid hydrocarbon mixture. This mixture was dissolved in a minimum amount of carbon tetrachloride and chromatographed on alumina (Merck, 71707) using 60 parts by weight of alumina and pentane as an eluent. The first fraction gave 0.85 g. of *o*-dibenzylbenzene, m.p. 76.5–77.5°.

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.24; H, 7.25.

An authentic sample of *o*-dibenzylbenzene, m.p. 77–78°, prepared by the catalytic reduction of *o*-dibenzoylbenzene[7] in ethanol with a 10% palladium-on-charcoal catalyst, showed no depression in m.p. upon admixture with the sample of hydrocarbon isolated above. Also, the infrared spectra of the two samples of hydrocarbon were superimposable.

The second fraction (0.15 g.) obtained in the chromatographic separation proved to be 9-phenylanthracene. It had m.p. 152° which was undepressed upon admixture with an authentic sample, prepared by the acid-catalyzed dehydration of the carbinol obtained from the addition of phenylmagnesium bromide to anthrone. Furthermore, the infrared and ultraviolet spectra of the two samples of 9-phenylanthracene were identical.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55; mol. wt., 254.31. Found: C, 94.62; H, 5.41; mol. wt., 244.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Ionic Polmerization. XV.[1] Further Molecular Terminating Agents in the Cationic Polymerization of Styrene

BY C. G. OVERBERGER AND M. G. NEWTON[2]

RECEIVED DECEMBER 4, 1959

Three polynuclear aromatic compounds and several of the polymethylbenzenes have been examined for their molecular terminating ability in the cationic polymerization of styrene by stannic chloride. The relative reactivities toward electrophilic substitution in this system were found to be: *m*-xylene > *o*-xylene; pentamethylbenzene > mesitylene; anthracene > phenanthrene > naphthalene. No molecular termination constants could be determined for durene and hexamethylbenzene.

Previous papers in this series have demonstrated the usefulness of molecular termination constants in cationic polymerization in determining the relative reactivities of various mono- and disubstituted aromatic compounds toward electrophilic substitution.[3–5] The relative reactivities of these compounds toward a carbonium ion-anion pair in the polymerization of styrene catalyzed by stannic chloride have been found to be in good agreement with their relative reactivities in other electrophilic substitution reactions.

It had been shown that the effects of compounds of this type on the number average degree of polymerization, $\bar{P}_n$, of the resulting polystyrene can be quantitatively described by the equation[3]

$$1/\bar{P}_n = 1/\bar{P}_{no} + (k_r/k_p)([R]/[M]) \qquad (1)$$

where $\bar{P}_{no}$ is the number average degree of polymerization in the absence of the terminating agent,

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(1) This is the 15th in a series of papers concerned with ionic polymerization; for the previous paper in this series see C. G. Overberger and F. Ang, THIS JOURNAL, **82**, 0000 (1960).

(2) A portion of a thesis submitted by M. G. Newton in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the graduate school of the Polytechnic Institute of Brooklyn.

(3) G. F. Endres and C. G. Overberger, THIS JOURNAL, **77**, 2201 (1955).

(4) C. G. Overberger and G. F. Endres, *J. Polymer Sci.*, **16**, 283 (1955).

(5) C. G. Overberger, G. F. Endres and A. Monaci, THIS JOURNAL, **78**, 1969 (1956).