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).

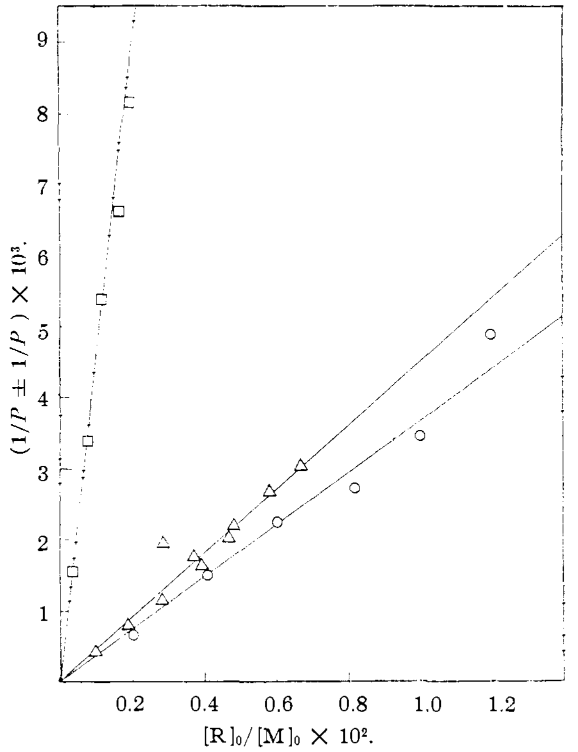

Fig. 1.—Polynuclear hydrocarbons in carbon tetrachloride–nitrobenzene solvent: □, anthracene; △, phenanthrene; ○, naphthalene.

[R]/[M] is the ratio of the molar concentration of the terminating agent to that of the monomer and k_r/k_p is the ratio of the rate constant for molecular termination to the rate constant for propagation (k_r/k_p has been called the "molecular termination constant").

In the present study molecular termination constants have been determined for three polynuclear compounds: naphthalene, phenanthrene and anthracene. In addition, several of the multimethylated benzenes were investigated, namely, *o*-, *m*- and *p*-xylene, mesitylene, durene, pentamethylbenzene and hexamethylbenzene.

Experimental

Purification of many of the materials used has been described previously.[3] All of the compounds used as molecular terminating agents were Eastman Kodak Co. materials. *o*- and *m*-xylene were redistilled, a constant boiling middle cut being retained: *o*-xylene, $n^{25}\text{D}$ 1.5011 (1.5035)[6]; *m*-xylene, $n^{25}\text{D}$ 1.4958 (1.4956).[6] They were stored over anhydrous silica gel.

Mesitylene was dissolved in two volumes of concentrated sulfuric acid, precipitated in four volumes of concentrated hydrochloric acid at 0° and washed with cold concentrated hydrochloric acid. The mesitylene sulfonic acid was decomposed by steam distillation. The separated mesitylene was dried over magnesium sulfate and distilled, a constant boiling middle cut being retained. It was stored over anhydrous silica gel, $n^{25}\text{D}$ 1.4967 (1.4967).[7] Infrared spectra of these three compounds revealed no contamination by isomers or other methylbenzenes.

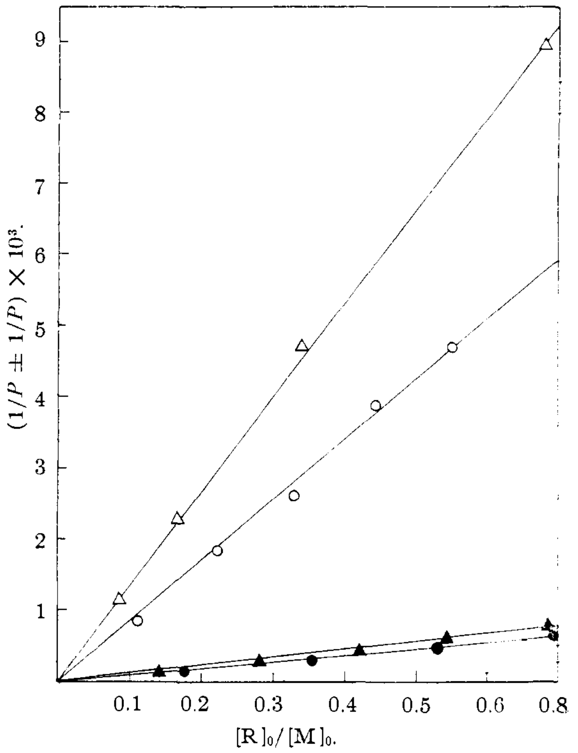

Fig. 2.—Xylenes in carbon tetrachloride–nitrobenzene solvent: △, *m*-xylene; ○, *o*-xylene; ▲, *p*-xylene; ■, toluene.

Naphthalene, phenanthrene, anthracene, durene, pentamethylbenzene and hexamethylbenzene were recrystallized from benzene: naphthalene, m.p. 81.5–82.5° (81.1°)[7]; phenanthrene, m.p. 79.3–79.7° (79.3°)[7]; pentamethylbenzene, m.p. 52.2–53.1° (54.0°)[7]; hexamethylbenzene, m.p. 164.3–164.8° (164–165°).[7] All melting points are uncorrected.

The experimental method for determining molecular termination constants has been described elsewhere.[2]

Results

The standard procedure for the polymerization of styrene by stannic chloride in carbon tetrachloride–nitrobenzene solution at 0° has been described previously.[3] The compounds to be studied were added in varying molar ratios to the monomer, replacing carbon tetrachloride. There were control polymerizations containing no added compounds for each series of determinations, and polymerizations were stopped at relatively low conversions. Table I lists, for the three polynuclear hydrocarbons, the intrinsic viscosities, the number average degrees of polymerization, the molar ratios of the additives to monomer and the k_r/k_p values calculated from eq. 1, Table II lists the data for all of the methylbenzenes.

The best values of the molecular termination constants were taken from the slopes of plots of the initial molar ratios, $[\text{R}]_0/[\text{M}]_0$, *vs.* the experimental values of $(1/\bar{P}_n - 1/\bar{P}_{n0})$. The plots for naphthalene, phenanthrene and anthracene are given in Fig. 1. Plots for *o*-xylene and *m*-xylene are given in Fig. 2, together with those for toluene[5] and *p*-xylene[3] which were previously determined. Plots for mesitylene (1,3,5-trimethylbenzene) and pentamethylbenzene are given in Fig. 3; these latter plots are atypical. The individual k_r/k_p values of mesitylene appear to be constant at the higher

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[6] "International Critical Tables," Published for the National Research Council by the McGraw-Hill Book Co., Inc., New York, N. Y., 1926–1930.

[7] E. H. Huntress and S. P. Milliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941.

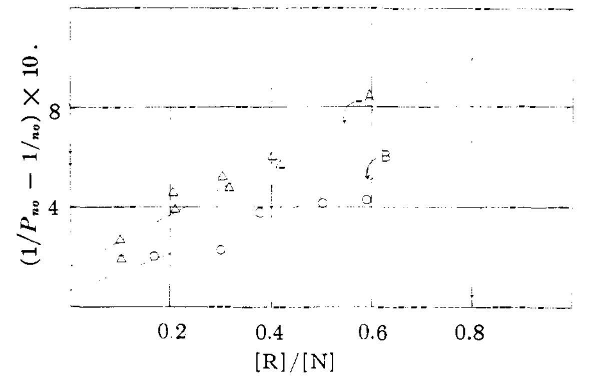


Fig. 3.—Mesitylene and Pentamethylbenzene in carbon tetrachloride—nitrobenzene solvent: A, pentamethylbenzene; B, mesitylene

concentrations of this compound; they rise with decreasing concentration and then fall off to zero at very low concentrations. The individual k_r/k_p values of pentamethylbenzene do not show a constancy at higher concentrations as those of mesitylene do, perhaps, because limited solubility prevented the investigation of sufficiently high concentrations. However, they do increase with decreasing concentration and then fall off to zero in a similar manner. The results of two runs, at higher concentrations, show the same trend but are not in complete internal agreement. For purposes of comparison only, slopes of straight lines drawn on the relatively constant positions of these plots, have been taken as tentative k_r/k_p values. Durene (1,2,4,5-tetramethylbenzene) and hexamethylbenzene, unexpectedly, increased the number average degree of polymerization slightly.

TABLE I

EFFECTS OF THE POLYNUCLEAR HYDROCARBONS ON DEGREE OF POLYMERIZATION

$[R]_0/[M]_0$	Conv., %	Time min.	$[\eta]$ (100 ml./g.)	P_n	k_r/k_p
			R = naphthalene		
0	19, 19	6, 5.5	0.223, 0.222	121, 121	....
0.0201	14	6	0.211	112	0.0338
.0406	11	6.5	.193	98	.0493
.0604	10	6.5	.188	94	.0371
.0818	9	7	.184	91	.0330
.102	8	7.5	.176	85	.0341
.122	10	8	.165	72	.0401
			R = phenanthrene		
0	16	5	0.235	132	....
0.0097	16	5.5	.227	125	.0437
.0195	15	6	.220	119	.0404
.0289	13	6.5	.202	102	.0679
.0389	15	7	.207	108	.0421
.0486	18	7.5	.199	102	.0447
.0583	16	8	.192	97	.0462
			R = anthracene		
0	14, 15	5, 6	0.233, 0.233	130, 130	....
0.0038	11	5	0.206	108	0.409
.0076	10	6	.183	91	.472
.0114	6	7.5	.164	77	.472
.0152	8	8	.155	70	.434
.0190	6	9	.145	63	.429
.0228	7	9	.127	52	.522

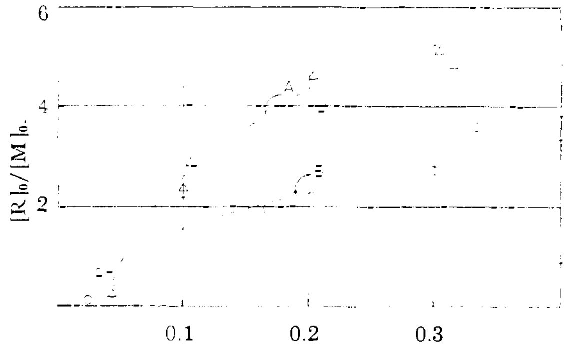
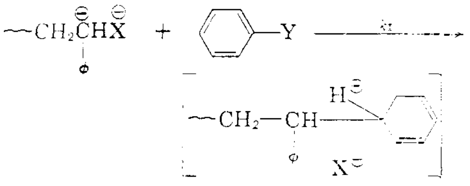


Fig. 4.—Mesitylene and pentamethylbenzene at low concentrations: A, pentamethylbenzene; B, mesitylene.

Rate studies with *p*-xylene, *p*-*t*-butyltoluene and *p*-cymene[4] over wide conversion ranges have shown that these compounds have very little effect on the over-all rate of polymerization. No rate studies were made in this investigation, but it was observed that the time required to obtain approximately 10% conversion was increased when fairly high concentrations of *o*-xylene, *m*-xylene and mesitylene were present. There was no significant rate change, however, with durene, pentamethylbenzene or hexamethylbenzene.

Discussion

The generally accepted mechanism for molecular termination by aromatic compounds in the present polymerizing[1] system is that proposed for simple nuclear alkylations of the Friedel–Crafts type[4]



As one possibility, the molecular terminator can function as a transfer agent with monomer.[4] Of the compound investigated previously, only thiophene and anisole were found to retard the over-all rate of polymerization to any significant extent. Retardation by thiophene was very much greater than retardation by anisole and was thought to be due to two unutilized pairs of electrons on the sulfur atom which might coördinate with the positive moiety of the carbonium ion–anion pair of the active centers. The retardation in the presence of *o*-xylene, *m*-xylene and mesitylene appears to be of about the same order of magnitude as that due to anisole.

Durene, at relatively high concentrations, and hexamethylbenzene, at relatively low concentrations, increase the number average degree of polymerization. The effect falls off at higher concentrations of hexamethylbenzene (Table II). No explanation of the atypical behavior of these methylbenzenes is readily apparent, but it is thought that there is a possibility that catalyst or catalyst–cocatalyst complexing with the aromatic compounds might affect the reaction when the aromatic compounds are as highly basic as these methylbenzenes.[8,13]

[8] H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3670 (1952).

TABLE II

EFFECTS OF METHYLBENZENES ON DEGREE OF POLYMERIZATION

$[R]_0/[M]_0$	Conv., %	Time, min.	$[\eta]$ (100 ml./g.)	P_n	k_r/k_p
R = *o*-xylene					
0	16, 16	6, 6	0.257, 0.249	151, 144	....
0.111	10	7.5	0.147	66	0.0783
.222	11	30	.106	41	.0830
.332	19	90	.089	31	.0783
.442	28	135	.072	22	.0870
.552	36	130	.065	19	.0849
.663	44	240	.059	17	.0808
R = *m*-xylene					
0	15	6	0.231	128	...
0.085	5	8	.128	52	0.133
.171	1 6	35	.094	33	.134
.339	88	120	.064	18	.138
.683	11	275	.044	10	.131
R = mesitylene					
0	17, 9	8, 8	0.235, 0.235	132, 132	....
0.166	3	12	0.202	105	0.0118
.333	4	30	.182	90	.0111
.500	6	60	.176	85	.0084
0	4, 5	8, 8	0.250, 0.251	145, 146	....
0.300	7	35	0.201	104	0.0090
.589	8	65	.176	85	.0082
.899	9	95	.144	63	.0100
1.198	12	125	.142	61	.0083
0	17, 11	10, 10	0.278, 0.276	170, 168	....
0.0436	9	10	0.261	154	0.0128
.0326	11	10	.260	153	.0191
.0218	11	10	.274	167	.0044
.0109	13	10	.277	169	0
.0054	11	9	.280	172	(−)
R = pentamethylbenzene					
0	5, 6	8, 8	0.268, 0.275	161, 167	....
0.100	4	9	0.219	118	0.0234
.203	4	10	.188	94	.0226
.304	5	12	.180	88	.0170
.405	6	13	.173	83	.0147
0	7	8	.232	130	....
0.106	9	10	.189	96	0.0271
.211	7	12	.177	86	.0187
.316	8	14	.169	80	.0152
.421	10	16	.170	80	.0112
0	17, 1	10, 10	0.278, 0.276	170, 166	....
0.0441	10	10	0.270	163	0.0056
.0330	10	10	.277	169	(0)[a]
.0270	11	10	.278	170	(0)[a]
.0110	10	10	.265	158	0.0381
.0055	13	10	.261	155	0.1013
R = durene					
0	17, 9	8, 8	0.235, 0.235	132, 132	....
0.122	9	9	.258	152	(−)[b]
.247	10	10	.266	159	(−)
.371	10	10	.265	158	(−)
R = hexamethylbenzene					
0	5	8	0.243	138	....
0.0333	4	9	.244	139	(0)[a]
.0667	6	9	.244	139	(0)[a]
.100	5	10	.235	131	(+)[c]
.133	5	10	.231	128	(+)[c]
0	11, 6	8, 8	0.272, 0.268	165, 161	....
0.0309	15	20	0.281	173	(−)[b]
.0627	15	20	.279	171	(−)[b]
.0931	11	20	.260	154	(+)[c]
.124	11	20	.245	141	(+)[c]

[a] The notation (0) indicates that the degree of polymerization, $\bar{P}_n$, of a sample containing R does not differ significantly from the degree of polymerization of the control, $\bar{P}_{no}$, containing no *R*. [b] The notation (−) indicates that the degree of polymerization, $\bar{P}_n$, of the sample containing R is greater than the degree of polymerization of the control, $\bar{P}_{no}$, containing no R. [c] The notation (+) indicates that the degree of polymerization, $\bar{P}_n$, of a sample containing hexamethylbenzene was lower than the degree of polymerization of the control, $\bar{P}_{no}$, containing no R.

Qualitatively, it is known that anthracene is more reactive than phenanthrene and phenanthrene is more reactive than naphthalene in electrophilic substitution reactions, but there is very little quantitative information for the comparison of their relative reactivities. Dewar and Warford[9] have studied the mononitration reactions of a number of polynuclear hydrocarbons. In competitive nitrations[10] the ratio of the reactivities of phenanthrene to naphthalene was found to be 1.2:1, in good agreement with their relative reactivities toward the polymeric carbonium ion–anion pair of the present study (Table III). Unfortunately, anthracene was not included in the group of polynuclear hydrocarbons reported. Dewar[11] has stated that the energy of activation for substitution of any particular group at any given carbon atom in an aromatic hydrocarbon should have the same relative value whether the reaction involves anionic, cationic or radical substitution. In the absence of other quantitative information, the relative reactivities of these compounds have been compared to their relative "methyl affinities" as determined by Levy and Szwarc[12] (Table III). "Methyl affinities" refer to the relative reactivities of aromatic compounds toward substitution by methyl radicals. Such common radical reactions as hydrogen extraction and combination of radicals are not included. In view of the difference in size of the methyl group and the polymeric carbonium ion, the agreement is surprisingly good.

TABLE III

RELATIVE REACTIVITIES OF THE POLYNUCLEAR HYDROCARBONS

Reagent	k_r/k_p	Rel. k_r/k_p[a]	"Methyl affinity"[b]
Naphthalene	0.0370	1	1
Phenanthrene	.0450	1.2	1.2
Anthracene	.442	12	37

[a] Relative to an assigned value of unity for naphthalene. [b] From the data of Levy and Szwarc, ref. 12.

Table IV lists the molecular termination constants of all the methylbenzenes which have been determined in this series, together with their relative reactivities based on the assigned values of unity for the reactivity of *p*-xylene. For compari-

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(9) M. J. S. Dewar and E. W. T. Warford, *J. Chem. Soc.*, 3570 (1956).

(10) M. J. S. Dewar, T. Mole and E. W. T. Warford, *ibid.*, 3581 (1956).

(11) P. M. G. Bavin and M. J. S. Dewar, *ibid.*, 164 (1956); M. J. S. Dewar, THIS JOURNAL, **74**, 3357 (1952).

(12) M. Levy and M. Szwarc, *ibid.*, **77**, 1949 (1955).

TABLE IV

RELATIVE REACTIVITIES OF THE METHYLBENZENES

Reagent	kr/kp	Rel. kr/kp[a]	Basicity[13]	Bromination[14]	Iodination[15]	Mercuration[16]
Toluene	0.00884	0.84	0.01	0.33	0.14	0.61
p-Xylene	.01055	1	1	1	1	1
o-Xylene	.083	7.9	3	2.3	1.3	2.0
m-Xylene	.134	12.8	18	7.1	23	4.2
Mesitylene	.0073	.70	1400	625	1800	26
Durene	....	...	60	65	23	3.5
Pentamethylbenzene	0.0104	.99	4300	2580	740	24
Hexamethylbenzene	....	...	445000	.....	.....	...

[a] Relative to an assigned value of unity for *p*-xylene.

son, the relative basicities as found by McCaulay and Lien,[13] the relative reactivities in bromination[14] and iodination[15] as determined by Andrews and Keefer and in mercuration as determined by Brown and McGary,[16] are also given. It is assumed that the reaction of the carbonium ion–anion pair is one of high reactivity, comparable with *t*-butylation.[17] It can be seen that, in iodination and in mercuration, mesitylene and pentamethylbenzene are in the reverse order of their basicities; both of these reactions have high steric requirements. The steric requirement for mercuration is especially large and only here do the reactivities of the more highly methylated benzenes compare even reasonably well with their reactivities toward the polymeric carbonium ion–anion pair of the present systems. This fact and the facts that the reactivities of mesitylene and pentamethylbenzene are so much smaller than their relative base strengths would appear to indicate that durene does not seem to be subject to appreciable electrophilic substitution in this system, leads to the conclusion that this polymeric carbonium ion–anion pair has a very large steric requirement, indeed.

(13) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951).

(14) R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 5623 (1956).

(15) L. J. Andrews and R. M. Keefer, *ibid.*, **78**, 4549 (1956).

(16) H. C. Brown and C. W. McGary, *ibid.*, **77**, 2310 (1955).

(17) H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

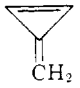
An Unusual Rearrangement in the Cyclopropene Series[1]

BY RONALD BRESLOW AND MERLE BATTISTE[2]

RECEIVED DECEMBER 9, 1959

It has been found that Δ^1-1,2-diphenylcyclopropenyldiphenylcarbinol (III) rearranges, under a variety of dehydrating conditions, to 1,2,3-triphenylazulene and 1,2,4-triphenylnaphthalene. A possible mechanism for this unusual rearrangement is discussed.

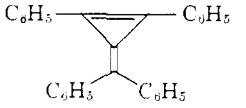
Among the compounds of theoretical interest in the cyclopropene series are the derivatives of methylenecyclopropene (I), which is related to the fulvenes. Compounds of this type are predicted to have appreciable resonance stabilization,[3] and their properties would accordingly be of great interest.



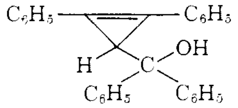
I

Although several schemes come to mind for the synthesis of such a derivative as, for instance, tetraphenylmethylenecyclopropene (II), it seemed to us that one obvious possibility was the dehydration of the carbinol III which should be readily available from the reaction of phenylmagnesium bromide with the previously described diphenylcyclopropenecarboxylic ester.[4] Unfortunately, although this type of intermediate is of course the usual one in syntheses of fulvenes[5] it has not proved useful in approaches to heptafulvenes, which are more closely related to methylenecyclopropenes; in the cyclopropenes as well as in the cycloheptatrienes, the cation, not the anion as in cyclopentadiene compounds, is the stable ion, and the dehydration requires removal of a non-acidic hydrogen in the three- and seven-membered ring cases, to form a product whose eventual polarization should be the reverse of that of the transition state for dehydration; this is again in contrast to the situation in the (successful) syntheses in the five-membered ring series. Accordingly, some difficulty was anticipated.

More seriously, the carbinol III was expected to form a carbonium ion with extraordinary ease.



II



III

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[1] These results were first reported at the Boston Meeting of the American Chemical Society, April, 1959. This work was in part supported by a grant from the National Science Foundation, which is gratefully acknowledged.

[2] American Cyanamid predoctoral fellow, 1958–1959.

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[5] E. D. Bergmann, in "Progress in Organic Chemistry," Vol. III, Academic Press, Inc., New York, N. Y., 1955, p. 81. *Cf.* also W. Doering, Sixteenth National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash., 1959.