Anal. Calcd for $C_{20}H_{24}$: C, 90.90; H, 9.09. Found: C, 90.72; H, 9.30.

Diethyl[2.2]paracyclophane was pyrolytically polymerized to give poly(ethyl-*p*-xylylene) by the general procedure described by Gorham.[4]

Registry No.—**5**, 10366-05-9; **6**, 5628-17-1; **7**, 19978-44-0; **8**, 19978-03-1; **8a**, 19978-04-2; **9**, R-CH_3, 10366-08-2; **10**, 19978-46-2; **13**, 19978-47-3; **13** methyl ester, 19978-48-4; **14**, 19978-49-5; **16**, 16070-18-1.

Bromination Reactions on Adsorbent Surfaces[1]

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Received August 26, 1968

Bromination of cyclohexene and *cis*- and *trans*-2-butenes on activated carbon is exclusively a *trans* addition. Experimental conditions and results imply that the bromination is a surface reaction. It is suggested that the exclusive *trans* product results from mobility of Br ions on the carbon surface or from the steric constraint imposed by the pores of the adsorbent. Bromination of aromatic hydrocarbons by surface reactions gives ring substitution with a distribution of isomers that depends on the polarity, but not the pore sizes, of the adsorbent. Results are interpreted in the light of steric factors governing accessibility of adsorbed bromine to the aromatic ring.

Brominated activated carbon (BAC) is known to be effective in removing ethylene from air;[2] the action is addition followed by adsorption of the adduct by the carbon.[3] BAC has been used in air purification systems to protect fruit[2] and flowers[4] against the deleterious effects of small concentrations of atmospheric ethylene. These circumstances and the thought that the reaction environment of an adsorbent surface might produce some results different from those occuring in solution led us to the present study of bromination reactions on activated carbon and other adsorbents.

Addition.—The products, kinetics, and stereochemistry of the reaction of bromine with olefins have been extensively studied,[5] and the two-step *trans*-1,2 addition in liquid phase is well known. There are reported examples of *cis* chlorination,[6] but they all involve intermediates capable of existing as stable classical carbonium ions, and probably do not involve broadside approach of the Cl_2 molecule to the double bond. Moreover, since the ability of Cl to bridge two adjacent carbon atoms is markedly less than that of Br, a chloronium ion intermediate and its stereochemical consequences ought to be less important in chlorination than the bromonium ion in bromination. If *cis* bromination were to be successful, a process involving a broadside approach of Br_2 might be promising.

We studied the stereochemical course of addition of bromine to cyclohexene and to *cis*- and *trans*-2-butenes when the reactions occurred at the surfaces of activated carbon or silica gel. For each of these olefins, *cis* and *trans* addition would give different products.

Substitution.—The reaction of bromine with alkylbenzenes uncatalyzed by Lewis acids shows a high intermolecular and intramolecular selectivity (Table I). In all cases shown, the rate of bromination of alkylbenzene is high, and *ortho/para* substitution is observed almost exclusively. Where different relative rates are shown for a particular alkylbenzene they may be attributed to different methods of measurement. Differences in product distributions may be due to different methods of analysis and/or different reaction conditions. In all cases, the attacking reagent is most likely molecular bromine and not an ionic species.

The results of studies of bromination of toluene catalyzed by Lewis acids under nonisomerizing conditions appear in Table II. Zinc chloride in acetic acid gives high intermolecular selectivity as a bromination catalyst, but isomer distribution was not reported.[7] Ferric chloride in nitromethane gives bromination with a low substrate but high positional selectivity.[8] Olah concluded that the substrate-determining step involves a transition state similar to a π complex, but the product-determining step involves σ-complex-type transition states with corresponding high *ortho/para* selectivity. The higher proportions of *ortho* substitution than those found for molecular brominations[7-9] were explained as the result of attack by the incipient bromonium ion, a group with small steric requirements compared with molecular bromine.

The increase in substrate selectivity and decrease in the *ortho/para* ratio with increasing dilution indicate that increasing solvation makes the electrophile weaker and bulkier.[8]

Complexing of either aromatic hydrocarbon[9] halogen[8,10] or attacking with the solvent decreases the *ortho/para* ratio. Adsorption of the halogen on a surface should increase its effective bulk and therefore also decrease the *ortho/para* ratio. Adsorption of the aromatic hydrocarbon, on the other hand, can either increase or decrease this ratio depending on the relative geometry between the hydrocarbon and the surface.

We studied the bromination of toluene, cumene, and *t*-butylbenzene adsorbed on alumina, silica gel, and activated carbon, to determine the resulting isomer distributions and to evaluate them in terms of steric and/or electronic factors.

Indication of Reaction at the Surface.—To support

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(1) Abstracted from the Ph.D. Thesis of S. H. S., The City University of New York, 1968.

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(3) A. Turk, J. I. Morrow, P. F. Levy, and P. Weissman, *Int. J. Air Water Pollution*, **5**, 14 (1961).

(4) C. W. Fischer, *Proc. Am. Soc. Hart. Sci.* **55**, 447 (1950).

(5) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," American Elsevier Publishing Co., New York, N. Y., 1966, Chapter 7.

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(7) L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **78**, 4549 (1956).

(8) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *ibid.*, **86**, 1039 (1964).

(9) A. Campbell and D. J. Shields, *Tetrahedron*, **21**, 211 (1965).

(10) L. M. Stock and A. Himoe, *Tetrahedron Lett.*, 9 (1960).

TABLE I
MOLECULAR BROMINATION OF BENZENE AND MONOALKYLBENZENES

Aromatic (ArH)	Reaction condition	k_{ArH}/k_B	% *ortho*	% *meta*	% *para*	Method of analysis[a]	Ref
Benzene (B)	*b*	1					
Toluene	*b*	340	31		69	id	*c*
	b	605	32.9	0.3	66.8	ir	*d*
	e		41.5		58.5	oxidn	*f*
Ethylbenzene	*b*	290					*c*
	e		18		82	oxidn	*f*
Cumene	*b*	180					*c*
	e		11		89	oxidn	*f*
t-Butylbenzene	*b*	110	8		92	id	*c*
	b	138	1.20	1.47	97.3	ir	*g*

[a] id, isotope dilution; ir, infrared analysis. [b] In 85% HOAc (aqueous), 25°. [c] P. W. Robertson, P. B. D. de la Mare, and B. E. Swedlund, *J. Chem. Soc.*, 782 (1953). [d] H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, **79**, 1421 (1957). [e] Neat in excess ArH, 45°. [f] I. N. Nazarov and A. V. Semenovskii, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 840 (1957). [g] L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, **81**, 5615 (1959).

TABLE II
LEWIS ACID CATALYZED BROMINATION OF TOLUENE

Solvent	Catalyst, concentration, *M*	Br_2, *M*	k_T/k_B[a]	% *ortho*	% *meta*	% *para*	Ref
CH_3COOH	$ZnCl_2$, 0.1	0.0019	148				*b*
CH_3NO_2	$FeCl_3$, 3.0	1.5	3.6	68.7	1.8	29.5	*c*
CH_3NO_2	$FeCl_3$, 0.1	0.05	32	58.4	~1	40.6	*c*

[a] T, toluene; B, benzene. [b] Reference 7. [c] Reference 8.

the likelihood that bromination of alkenes did occur at the surface and not during the recovery procedure, which consisted of extraction with carbon tetrachloride, the following experiments were performed.

A sample of brominated carbon was treated with a slight excess of an olefin (A) (in the case of ethylene a large excess was used). After 24 hr an equivalent quantity of a second olefin (B) was added, and the carbon was extracted with carbon tetrachloride. For each pair of olefins used, a second reaction was carried out in which the order of addition of the olefins was reversed. In this way any differences in the composition of any products formed during extraction which would be caused by differences in olefin reactivities could be assessed. The composition of the carbon tetrachloride solution was determined by gas chromatography and/or infrared (ir) spectroscopy. The results are summarized in Table III.

TABLE III
RESULTS OF SEQUENTIAL ADDITION OF OLEFINS TO BROMINATED CARBON

Starting olefins		Products	
A	B	A dibromide, %	B dibromide, %
Ethylene	*cis*-2-Butene	>99	<1
cis-2-Butene	Ethylene	99	1
cis-2-Butene	Cyclohexene	99	1
Cyclohexene	*cis*-2-Butene	99	1

If bromination of olefins is a surface reaction, the product should, in each case, be mainly or exclusively the bromination product of olefin A (A dibromide in Table III). If reaction occurs in solution during extraction, however, the olefins will compete and the products in each case will be determined by the relative reactivities of the two olefins toward bromine or, if the reaction is diffusion controlled, by the relative availabilities of the olefins. In either of these latter cases the order of addition of olefins should have no effect on product ratios.

The data in Table III indicate that reaction does occur at the surface, since the first-added olefin (A) in every case gives the predominant product.

If bromination of olefins occurred before recovery but not at the surface (that is, in the vapor phase and/or by capillary condensation of reactants), allylic and addition–elimination bromination reactions would be likely to compete with addition, as they do in vapor or liquid phase brominations without an adsorbent. While no B dibromide would be observed, such products as 1-bromo-2-butene, 3-bromo-1-butene, 2-bromo-2-butene, 1- and 3-bromocyclohexenes and their bromine addition products should also have been found. The absence of all products except those of direct bromine addition argues strongly against the occurrence of an appreciable reaction in the liquid or vapor phase in competition with reaction of adsorbed species.

Furthermore, in the case of bromination of aromatic compounds, work done on the vapor phase thermal and photochemical brominations of toluene shows mainly formation of benzyl bromide.[11] Therefore, in the present study in which nuclear bromination is observed, the reaction is a surface, not a vapor phase reaction. (The possibility of the occurrence of a competing vapor phase reaction to give benzyl bromide is not excluded, but such reaction will not interfere with the nuclear bromination at the surface.)

Experimental Section

Bromination Procedures.—Brominations were carried out in a high-vacuum system which has been previously described.[3] The following is typical of all of the brominations of aromatic compounds.

Carbon (Table IV) (55 g) was cleaned by heating *in vacuo* at 460–480°. Toluene (*ca.* 5 ml) was placed in the adjacent trap, the trap was evacuated until 4.0 ml (3.5 g, 38 mmol) of toluene remained, and the toluene vapors were allowed to diffuse onto the carbon. The glass oven containing the carbon was then sealed off and heated at 176° for 2 hr to distribute the toluene evenly over the surface; then it was cooled slowly.

Bromine (0.560 ml, 1.75 g, 10.9 mmol; stored over anhydrous potassium carbonate before use) was transferred under dry nitrogen to the reserve trap. The bromine was degassed by successively cooling (−78°), evacuating, warming, cooling, and evacuat-

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[11] H. R. Anderson, Jr., H. A. Scheraga, and E. R. van Artsdalen, *J. Chem. Phys.*, **21**, 1258 (1953).

Table IV

Properties of Carbons (Source: Coconut Shells)[a]

Manufacturer's[b] designation of carbon	Total surface area,[c] m²/g	Most[d] common pore size, Å	Pore[d] volume, cm³/g
JD-1	1000–1100		
K-3030	1000–1100	10–20	0.433
K-3031	500–600	10–15	0.335
K-3032	1600–1700	15–25	0.513

[a] A. Turk, J. I. Morrow, S. H. Stoldt, and W. Baecht, *J. Air Pollution Control Assoc.*, **16**, 383 (1966). [b] Barnebey-Cheney Co., Columbus 19, Ohio. [c] B. E. T. method. [d] By mercury porosimeter.

ing. The frozen bromine *in vacuo* was finally allowed to warm and to distil through the system into the trap (cooled to −78°) adjacent to the reaction vessel. This trap was then warmed to and held at −12°, and the bromine was allowed to diffuse slowly into the reaction vessel which had been wrapped with aluminum foil to prevent light-induced reactions. Addition of bromine required 3 hr.

After 8 days the vacuum system was flushed three times with ethylene, with intermittent evacuations, and then filled with ethylene which was added in small portions to the reaction vessel. The cycle of filling the system with ethylene and passing the ethylene into the reaction vessel was repeated until the pressure of ethylene within the system approximated atmospheric pressure. The reaction vessel was allowed to stand for 2 days to ensure complete reaction of the ethylene with any free bromine.

Most of the ethylene was desorbed *in vacuo* at room temperature into a trap cooled in liquid nitrogen. The oven was closed off and the liquid nitrogen was replaced with Dry Ice–acetone to distil the collected ethylene off through the system while retaining any higher boiling materials. The liquid nitrogen bath was then replaced, and the material in the oven was desorbed at successively increasing temperatures over various periods of time, as indicated for a typical experiment in Table V. Correspondingly higher temperatures were used when the alkylbenzene was of higher molecular weight.

Table V

Desorption Conditions after Bromination of Toluene

Minutes desorbed	Temperature, °C
15	Ambient
60	77
60	168
75	239
60	279
80	385

The liquid nitrogen was replaced with Dry Ice–acetone, and the ethylene was again distilled off. After the trap was warmed to room temperature, its contents were removed by pipet and washed twice with aqueous sodium bromide, once with 2 *M* sodium hydroxide, and twice with aqueous sodium bromide.

The organic layer was analyzed by glpc. The bromotoluene isomers were partially separated on a 12 ft × ⅛ in. neopentyl glycol succinate column (25% on 60/80 mesh Chromosorb P) at 112°, 240 cc of helium/min. Under these conditions the *o*-bromotoluene was cleanly separated from the *meta* and *para* isomers, which emerged together. Analyses of standard mixtures showed that the responses of the isomers were identical within experimental error, and therefore the relative areas were used as direct measures of isomer distribution. Infrared analysis of the product mixtures and of standard mixtures showed that in all reactions the *meta* isomer was present to the extent of less than 1%. The results are summarized in Table VI.

Reactions of bromine with olefins were conducted similarly. The olefin, if a gas, was added by the procedure described earlier for ethylene. If the olefin was a liquid, it was added as were the aromatic hydrocarbons. When it was necessary to know the exact molar quantity of gaseous olefin used, a bulb of known volume sealed onto the vacuum system was employed. Addition of bromine as described above required 4.5 hr.

The instability of vicinal dibromoalkanes compared with aryl bromides necessitated milder methods of recovery and analysis. Thus, after 2 days reaction time the carbon was transferred to a Soxhlet extractor and extracted for 7.5 hr with carbon tetrachloride. The solution was concentrated (rotary evaporator), and the residue was analyzed by ir and/or nmr spectroscopy.

Table VI

Results of Ring Bromination of Aromatic Hydrocarbons at Adsorbent Surfaces

Run no.	Adsorbent[a]	Hydrocarbon	Bromine added before or after hydrocarbon	Scavenger	% *ortho*[b]
1	C, JD-1[c]	Toluene	Before	None	64.5
2	C, JD-1	Toluene	After	Ethylene	48.8
3	C, JD-1	Toluene and benzene[d]	After	Ethylene	[e]
4	C, JD-1[f]	Toluene[g]	After	Ethylene	52.2
5	C, K-3030[c]	Toluene	After	Ethylene	52.3
6	C, K-3031[c]	Toluene	After	Ethylene	52.1
7	C, K-3032[c]	Toluene	After	Ethylene	51.8
8	S	Toluene	Before	Ethylene	36.2
9	S	Toluene	After	Ethylene	37.9
10	A	Toluene	After	Ethylene	27
11	C, JD-1	Cumene	After	Ethylene	28.2
12	C, JD-1	*t*-Butylbenzene	After	Ethylene	0

[a] C, activated carbon; S, silica gel; A, activated alumina. [b] The rest was *para*, the *meta* isomer being negligible in all cases. [c] Designation by manufacturer, Barnebey-Cheney Co., Columbus, Ohio. See Table IV for properties. [d] Competition experiment. [e] Not determined. [f] The carbon was acid washed prior to the experiment. [g] Toluene "from sulfonic acid" (Eastman-Kodak).

2-*o*-Bromophenyl-2-propanol (I).—This was prepared from 15.05 g (0.070 mol) of methyl *o*-bromobenzoate according to the method of Stiles and Sisti,[12] except that methyl iodide was used instead of methyl bromide for the Grignard reagent. Distillation under reduced pressure yielded a slightly yellow liquid: bp 68–73° (0.37 Torr). This crude alcohol was used directly in the preparation of *o*-bromocumene.

***o*-Bromocumene (II).**—Crude I was hydrogenated over 5% Pd–C in AcOH acidified with $HClO_4$.[12] After filtration and removal of acetic acid at reduced pressure, the residual oil was extracted with aqueous $NaHCO_3$ and steam distilled to give 9.5 g (68% over-all yield) of a clear, colorless oil. Distillation under reduced pressure yielded a clear colorless liquid: ir (liquid film) 3050 (w, aromatic H), 2960, 2900, 2840 (m, alkyl H), 1590, 1560 (w, aromatic), 1470 (m, methyl), 1420 (m, methine), 1370, 1350 (w, isopropyl), 756 cm^{-1} (s, *ortho*-disubstituted benzene); nmr (CCl_4) δ 1.23 (doublet, J = 7 cps, 6 H, methyl), 2.73 (septuplet, J = 7 cps, 1 H, methine proton), 6.9–7.3 (complex, 4 H, aromatic).

***m*-Bromocumene (III).**—This was prepared similarly to the *ortho* isomer[12] as a clear colorless liquid: ir (liquid film) 3030 (w, aromatic H), 2940 (s), 2910, 2850 (m, alkyl H), 1595, 1570 (m, aromatic), 1475, 1455 (m, methyl), 1418 (m, methine), 1377, 1357 (w, isopropyl), 778, 691 cm^{-1} (s, *meta*-disubstituted benzene); nmr (CCl_4) δ 1.21 (doublet, J = 7 cps, 6 H, methyl), 2.82 (septuplet, J = 7 cps, 1 H, methine proton), 6.98–7.40 (complex, 4 H, aromatic).

Results and Discussion

Olefins.—Bromination of olefins by BAC, under conditions such that the reaction occurred at the surface, led exclusively to the products formed by *trans* addition. Analysis by nmr spectroscopy, utilizing the chemical shifts of the methine protons and the splitting patterns of the methyl protons,[13] showed that *cis*-2-butene gave exclusively *dl*-2,3-dibromobutane and that *trans*-2-butene gave only the *meso* isomer. Comparison of the ir spectra of the 1,2-dibromocyclohexanes obtained in these reactions with the spectra of *cis*- and

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(12) M. Stiles and A. J. Sisti, *J. Org. Chem.*, **25**, 1691 (1960).

(13) F. A. L. Anet, *Proc. Chem. Soc.*, 327 (1959).

trans-1,2-dibromocyclohexanes[14] showed that only the *trans* isomer was produced. These results are independent of the order of addition of reactants. Variation of the bromine concentration on the charcoal between 1 and 10% by weight had no effects on the products nor, in the case of cyclohexene, did the use of silica gel in place of carbon. These reactions gave no detectable quantities of side products, in contrast to brominations in solution in which allylic substitution reactions compete with addition.[15,16]

The reason for these results is unclear. In every experiment the ratio of quantity of reactant to surface area of adsorbent was less than that required to yield a theoretical molecular monolayer, and capillary condensation with consequent liquid phase reaction was therefore unlikely. One possible mechanism involves a two-step surface process like that in solution, with formation of a bromonium (or β-bromocarbonium) ion and a bromide (or possibly tribromide) anion. Such a process would require mobility of a least one of the ions on the surface to give backside attack and over-all *trans* addition.

Alternatively, the steric constraint imposed by the pores in the adsorbent could facilitate the bridging of a series of Br_2 molecules, possibly through dipole-induced dipole interactions, around the olefin molecule until *trans* addition occurs. The involvement of a pore of an adsorbent with two sides of a molecule has recently been postulated for another reaction.[17] The large number of bromine molecules necessarily involved in such a pathway may be plausible in light of the facts that bromination of unreactive olefins in acetic acid has been shown to be third order in bromine in the region of bromine concentrations of 0.1–0.2 M[18] and that the effective concentration of bromine molecules at the adsorbent surface may be considerably greater than this value. Moreover, the mobility of the adsorbed molecules is reduced relative to the mobility of these molecules in solution. For these reasons the involvement of a large number of bromine molecules in bromination of an olefin at an adsorbent surface is not at all unlikely.

Any mechanism involving free radicals may be dismissed as highly unlikely since no products which would be associated with such a mechanism could be detected.

Aromatic Hydrocarbons.—The bromination of toluene at adsorbent surfaces, using ethylene as a scavenger, gave yields of combined bromotoluene isomers approximating 50% (based on Br_2), the remainder of the desorbate being $C_2H_4Br_2$ and unreacted toluene. With cumene, the combined yield of products from side-chain bromination, $C_6H_5C(CH_3)_2Br$ and $C_6H_5C(CH_3){=}CH_2$, was the major part of the product mixture. Table VI gives the distribution of isomers from ring bromination for different experiments.

The results or runs 1 and 2 showed that bromination of toluene at the carbon surface is not complete after 8 days. When ethylene was added (run 2) and the products were vacuum desorbed at high temperatures, significant quantities of ethylene bromide were formed, and the bromotoluenes consisted of 49% *ortho* isomer. When the carbon was vacuum desorbed after reaction without ethylene being added, the bromotoluenes consisted of 64.5% *ortho* isomer, and much benzyl bromide was formed. These data indicate that, if no ethylene is used, reaction occurs both on the surface and in the vapor phase at the high temperatures required for the vacuum desorption. The reaction in the vapor phase will lead to benzyl bromide.[11] The higher temperature reaction at the surface will of course be much more rapid and less selective, and the *ortho/para* ratio should be closer to statistical than at ambient temperatures, as is observed.

The low proportion of *meta* bromination ($<1\%$) in these and in all other brominations of alkylbenzenes studied indicates high selectivity, kinetic control, and no subsequent equilibration of products.

A sample of *p*-bromotoluene was adsorbed on activated carbon, left 8 days, and desorbed using the same procedure as was employed for the products of bromination reactions. No alteration of the sample occurred. Olah showed that *p*-bromotoluene isomerizes faster under the influence of aluminum chloride than either the *ortho* or *meta* isomer.[19] Therefore, the products obtained from the surface reactions are determined by kinetic control of the reaction and not by any secondary transformations of products.

This high selectivity is also intermolecular. A competition between equimolar quantities of benzene and toluene for a limited quantity of bromine (run 3) gave no detectable bromobenzene by gas chromatography, indicating a substrate selectivity of toluene over benzene by a factor of at least 100 since 1% of bromobenzene in the products could easily have been detected.

When a sample of carbon which has been cleaned *in vacuo* at high temperatures is mixed with water, the pH of the water rapidly rises to 10, indicating the presence of nonvolatile basic impurities on the carbon. To determine their possible effect on the course of bromination, a sample of carbon was extracted with aqueous hydrochloric acid, washed with water, dried, and cleaned *in vacuo* as usual. Use of this carbon (run 4) produced no change in the isomer distribution in the bromination of toluene.

Runs 5–7 show that different pore structures and surface areas have no effect on isomer distributions. The properties of these carbons are shown in Table IV.

In all these cases it can be seen that the *ortho/para* ratio is larger than for the uncatalyzed reaction of toluene and bromine in 85% acetic acid[8] and that it is insensitive to several variable properties of the charcoal surface.

When neutral silica gel was used as adsorbent (runs 8 and 9), the bromination of toluene appeared to resemble more closely the same reaction in solution. Thus, Brown and Stock found 33% *ortho* and 67% *para* bromination of toluene in 85% acetic acid.[8] Bromination on silica gel gave 37% *ortho* and 63% *para* substitution. These results could be caused by the more polar adsorbent (silica gel) being better able to stabilize ionic intermediates and/or by the toluene being less strongly adsorbed on the silica gel than on carbon and thus in a condition sterically resembling more

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[14] H. L. Goering, P. I. Abell, and B. F. Aycock, *J. Amer. Chem. Soc.*, **74**, 3588 (1952).

[15] C. D. Hurd and L. U. Spence, *ibid.*, **51**, 3561 (1929).

[16] J. Wolinsky and K. L. Erickson, *J. Org. Chem.*, **30**, 2208 (1965).

[17] E. J. Blanc and H. Pines, *ibid.*, **33**, 2035 (1968).

[18] B. E. Swedlund and P. W. Robertson, *J. Chem. Soc.*, 630 (1947).

[19] G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3464 (1962).

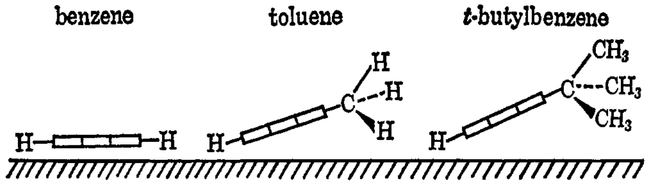

Figure 1.—Possible geometries of adsorbed aromatic hydrocarbons.

closely its condition in solution. These results also indicate the isomer composition of the bromotoluenes to be independent of the order of addition of the reactants.

Finally, bromination of toluene on neutral alumina (run 10) decreased still further the *ortho/para* ratio (27% *ortho*) probably for one or both of the reasons mentioned above for silica gel.

Cumene (run 11) gave 28.2% *ortho* bromination, also with <1% *meta* isomer. In this case side-chain bromination was actually the major process even in the dark, and large quantities of 2-bromo-2-phenylpropane and its dehydrobromination product, 2-phenylpropene, were formed. This is of course due to the α hydrogen in cumene being much more easily abstracted than those in toluene in the free-radical side-chain bromination. (This observation indicates that allylic substitution, probably *via* a free-radical mechanism, also is capable of occurring on the adsorbent surface.) With cumene, as with toluene, the *ortho/para* ratio is higher than for the same reaction in solution, in which 11% *ortho* and 89% *para* bromination are observed.[9]

t-Butylbenzene (run 12) gave completely *para* substitution. It appears that in this case the effect of the carbon surface, which is to increase *ortho* substitution in toluene and cumene, is insufficient to cause appreciable *ortho* substitution *t*-butylbenzene.

The results may be interpreted in the light of the diagrams in Figure 1 and the calculated values in Table VII.

Table VII
Derived Values from Tables I and VI

Aromatic	*ortho/para*[a] (Brown)	*ortho/para*[b]	*ortho/para*[c]
Toluene	0.49	0.71	1.1
Ethylbenzene		0.22	
Cumene		0.12	0.40
t-Butylbenzene	0.012		~0

[a] Brown. [b] Reference 9. [c] This work.

Whereas the corner-to-corner C_2 axis of the aromatic ring of benzene can be completely parallel to the axis of the pore in which it is absorbed (the pore is assumed to be approximately cylindrical), the methyl substituent in toluene can prevent the C_2 axis of this aromatic ring from attaining parallelism with the axis of the pore by preventing that end of the molecule to which it is attached from approaching the surface as closely as can the other end of the molecule. The position *para* to the methyl group in toluene can therefore approach the surface more closely than can the positions *ortho* to the methyl group. The hindrance resulting from the presence of the surface will be correspondingly greater in the *para* than in the *ortho* position. Such a situation would lead to the expectation that the *ortho/para* ratio for bromination of toluene at a surface might be greater than that in solution (neglecting solvent effects). This has been shown in the present work to be true (Table VII).

As the alkyl substitutent becomes more bulky the departure of the C_2 axis of the adsorbed aromatic ring from strict parallelism with the axis of the pore should increase. The hindrance cause by the surface at the *para* position relative to that at the *ortho* position should also increase as the C_2 axis of the aromatic compound is forced further from a geometry parallel to the axis of the pore.

Lack of a complete set of isomer distribution data for the series toluene, ethylbenzene, cumene, and *t*-butylbenzene under a uniform set of conditions makes a strict comparison of results tenuous. However, the data for toluene and cumene may be compared with the results of Nazarov and Semenovskii[9] (45°, excess aromatic hydrocarbon).

Division of the *ortho/para* ratio for bromination at the surface of activated carbon, 1.1, by the *ortho/para* ratio for liquid phase bromination at 45°,[9] 0.71, shows an increase in this ratio by a factor of 1.5. As predicted earlier, the relative increase in the *ortho/para* ratio for an alkylbenzene with a bulkier substituent than a methyl group should exceed that for toluene. For cumene, the *ortho/para* ratio at 45°[9] is 0.12. Dividing this value into the *ortho/para* ratio at activated carbon, 0.40, gives an enhancement of the *ortho/para* ratio by a factor of 3.3, more than twice the enhancement found for toluene. These results indicate the qualitative validity of the foregoing assumptions.

The data obtained for *t*-butylbenzene indicate the fraction of *ortho* substitution to be too low to make possible a similar comparison between Brown's results for toluene[8] and *t*-butylbenzene[10] and those found in the present work. Thus, *t*-butylbenzene does not follow the trend from toluene to cumene shown above. It may be that the *t*-butyl group is too bulky to allow *t*-butylbenzene to be adsorbed similarly to benzene, toluene, and cumene but with a geometry in which the C_2 axis is still further from being parallel with the axis of the pore.

Activated carbon is known to adsorb relatively nonpolar organic molecules more strongly than do the inorganic adsorbents silica gel and alumina. If an aromatic compound is less strongly adsorbed on silica gel or alumina than on activated carbon, the departure from parallel arrangements shown in Figure 1 should be lessened. Therefore the difference between the isomer distributions in bromination of toluene in solution and in the adosrbed state should also be lessened since the surfaces of silica gel and alumina will not preferentially hinder the *para* position relative to the *ortho* position as greatly as will the activated carbon surface. The *ortho/para* ratio for bromination of toluene at silica gel or alumina should therefore decrease from that for bromination at activated carbon and approach the value for the toluene molecule in solution unhindered by an adsorbent.

In addition, the presence of polar silicon–oxygen and aluminum–oxygen linkages in the inorganic adsorbents makes possible a greater stabilization of charges in adsorbed species than is found with activated carbon. Thus bromination at the surfaces of silica gel and alumina should more closely resemble reaction in acetic acid solution, in which solvent has been shown to have a stabilizing effect on the ions, than will bromination at activated carbon.

Thus, two independent considerations predict that reaction on the inorganic adsorbents will more closely resemble that in solution than will reaction on activated carbon. Such has been shown to be the case; the *ortho/para* ratios for bromination of toluene at the surfaces of activated carbon, silica gel, and alumina are 1.1, 0.59, and 0.37, respectively, compared with 0.49 in 85% acetic acid[8] and 0.71 in excess toluene.[9] Bromination at the surface of alumina actually gives a lower *ortho/para* ratio than does bromination in 85% acetic acid.

The effect of interaction between bromine and the surface on isomer distributions must also be considered.

In chlorination of toluene in various solvents the *ortho/para* ratios varied from 2.2 in trifluoroacetic acid to 0.52 in nitromethane. The *ortho/para* ratio decreased as the complexing of chlorine with solvent increased.[10]

The differential heat of adsorption of bromine is 7719 cal/mol on silica gel and 11,430 cal/mol on activated carbon; the former value is only a few hundred calories above the heat of condensation of bromine.[20] If being held more tightly on the surface would increase the selectivity of bromine for the *para* position of toluene over the *ortho* positions, than the lowest *ortho/para* ratios should be obtained on activated carbon. Since the opposite was observed, the combination of steric and electronic effects of the surface on the aromatic hydrocarbon is probably more important in determining the course of attack than are the effects of the surface on the bromine.

Registry No.—Cyclohexene, 110-83-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; cumene, 98-82-8; butylbenzene, 98-06-6; ethylene, 74-85-1.

Acknowledgment.—The work was supported by a research grant of the National Center for Air Pollution Control, U. S. Public Health Service. Stephen H. Stoldt was the recipient of an NDEA (Title IV) Fellowship, a NASA Traineeship, and City University of New York Research Assistantships.

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The Synthesis of Azulene-1-alkanoic Acids, Azulene-1,3-dialkanoic Acids, and Related Compounds. A 1,3-Bridged Azulene[1]

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Received October 31, 1968

1,3-Bis(2′,2′-dicarboxyethyl)azulene (**2**), azulyl-1,3-bis(propanoic acid) (**3**), 1,3-bis(2′-carbethoxy-3′-oxobutyl)azulene (**4**), 1,3-bis(3′-oxobutyl)azulene (**5**), diethyl azulene-1,3-dipropanoate (**6**), and 1,3-bis(3′-hydroxypropyl)azulene (**7**) have been synthesized *via* nucleophilic displacement reactions on azulyl-1,3-bis(methyltrimethylammonium) diiodide (**1**). Vilsmeier acylation reactions and reduction of the carbonyl groups in the 1-acylazulene products to methylenes by either the hydride reduction–alkylideneazulenium salt–hydride reduction method or, in one step, by diborane have been used to prepare 1-ethylazulene, ethyl 5-(1-azulyl)-5-oxopentanoate (**8a**), ethyl 5-(1-azulyl)pentanoate (**10a**), 1-(1′-oxo-4′-carbethoxybutyl)-3-(5′-chloropentyl)-azulene (**11a**), azulene-1,3-bis(hexanenitrile) (**14a**), ethyl 4-(1-azulyl)-4-oxobutanoate (**8b**), 1-(4′-chlorobutyl)-3-(1′-oxo-3′-carbethoxypropyl)azulene (**11b**), azulene-1,3-bis(pentanenitrile) (**14b**), 1,3-bis(1′-oxo-3′-carbomethoxypropyl)azulene (**16**), N,N-diethyl-10-(1-azulyl)decanamide (**21**), pentylazulene (**22**), 1,3-dipentylazulene (**23**), 1,3-dipropionylazulene (**24**), and 1,3-dipropylazulene (**25**). The principal maxima in the visible absorption spectra for the 1-alkyl- and 1,3-dialkylazulenes are compared. The diborane reduction of the acylazulenes is discussed. A high-dilution Thorpe–Ziegler ring closure of **14a** gave 1,3-(5′-cyano-6′-oxoundecamethylene)azulene (**26**), the first example of a 1,3-bridged azulene. Attempts to form 1,3-bridged products from **14b**, **21**, and **6** were unsuccessful.

In the course of studies on azulene[3] it was desired to prepare the derivatives given in the title, in part because certain of these might lead to 1,3 bridging of the nonbenzenoid azulene structure and thus provide a novel example of this type of structure. The syntheses required the formation of a saturated methylene carbon attached to the ring and a suitable functional group at the other end of the chain. This paper describes the methods found to accomplish these objectives and the preparation of the first example of a 1,3-bridged azulene.

The direct introduction of a methylene carbon onto the 1 position of azulene had been found practical as a synthetic method only for aminomethylation[4-6] and, for certain cases, the reaction with aliphatic diazo compounds.[7] The former had provided the first step in pathways to azulene-1-ethanoic acid and azulene-1-propanoic acid,[4] and the latter afforded a direct route to ethyl azulene-1-ethanoate. Since the results of an attempt to form an azulene-1,3-dialkanoic acid ester by the acid-catalyzed decomposition of an ω-diazo ester in the presence of azulene were not promising, the displacement reactions of azulyl-1,3-bis(methyltrimethylammonium) diiodide (**1**) with the anions of active methylene compounds were tried (Scheme I). From **1** and diethyl sodiomalonate was obtained, after hydroly-

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[1] Supported in part by a grant from the National Science Foundation. From the Ph.D. Thesis of R. D. Breazeale, University of Washington, 1964.

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