[CONTRIBUTIONS FROM SINCLAIR RESEARCH LABORATORIES, INC.]

Alkylation of Benzene and Homologs with Methylcyclohexenes[1]

BY B. S. FRIEDMAN, F. L. MORRITZ AND C. J. MORRISSEY

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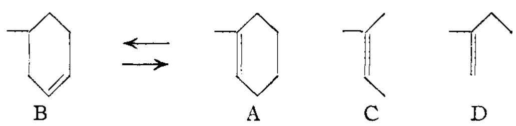
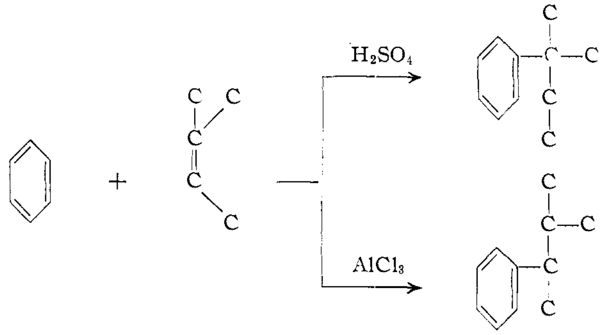
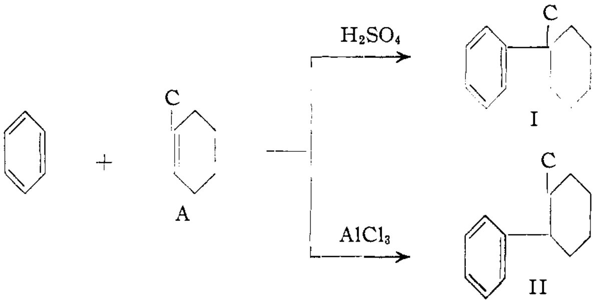
The alkylation of benzene with 1-methylcyclohexene (A) or with 4-methylcyclohexene (B), in the presence of sulfuric acid or hydrogen fluoride at 0 to 25°, gives, as previously reported, the tertiary alkylate, 1-methyl-1-phenylcyclohexane. However, when these reactions are carried out with aluminum chloride or hydrogen fluoride/boron trifluoride as catalysts, considerable amounts of secondary alkylates (2-, 3- and 4-methyl-1-phenylcyclohexanes) are formed. These results are consistent with those obtained earlier with non-cyclic olefins. At −20° benzene is not alkylated with B in the presence of aluminum chloride; however, toluene at −50° gives fair yields of monoalkylate, chiefly tertiary from A and secondary from B. *p*-Xylene is resistant to alkylation with B in the presence of sulfuric acid, even though it is readily alkylated by cyclohexene. In the presence of aluminum chloride or hydrogen fluoride *p*-xylene reacts readily with A or B to form secondary alkylates. *p*-Cymene reacts with B in the presence of sulfuric acid to form a tricyclic product considered to be 1,3,3,-6-tetramethyl-1,2-tetramethylene-indane.

The alkylation of benzene with "isomeric methylcyclohexenes" or with 4-methylcyclohexene (B), in the presence of hydrogen fluoride, has been shown[2a] to yield the tertiary alkylate 1-methyl-1-phenylcyclohexane (I). Linsk[2b] obtained I by alkylation of benzene with either 1-methylcyclohexene (A) or B in the presence of sulfuric acid. He also reported that alkylation with the carbinols corresponding to A and B produced I, and suggested that these reactions proceed by prior formation of the same tertiary carbonium ion formed either directly from 1-methylcyclohexene or by rearrangement from the 3- and 4-methylcyclohexene isomers.

In view of the structural resemblance of the methylcyclohexene (A) to the isoamylenes (C and D), as well as the facile isomerization[2] of B to A, it was anticipated that some of the unusual features[3-5] in alkylations of benzene with these alkenes, *e.g.* might occur in alkylations with the cyclic olefins







We therefore conducted a study of the effect of catalyst, temperature and structure on the reaction of A and B with benzene and some of its homologs.

(A) Benzene and Toluene.—The alkylation of benzene in the presence of sulfuric acid with 4-methylcyclohexene (B) or with 4-methylcyclohexanol yielded (expts. 8, 9; see Table I) only the tertiary monoalkylate (I) as reported by Linsk.[2b] When aluminum chloride was used, however, B yielded (expt. 2) a monoalkylate containing not more than about 7% of I, the balance consisting of the secondary alkylates, 2-methyl-1-phenylcyclohexanes (II), 3-methyl-1-phenylcyclohexane (III) and 4-methyl-1-phenylcyclohexane (IV). Even less (<3%, expt. 1) tertiary alkylate was formed from 1-methylcyclohexene (A), which is in accord with the results obtained by Schmerling, *et al.*,[6a] from the corresponding halide, 1-chloro-1-methylcyclohexane, and with those reported by Schmerling, *et al.*,[6b] and Kennedy and Schneider,[7] in reactions involving a methylcyclohexyl cation derived from methylcyclohexane *via* hydrogen transfer.

As in the case of alkylations with isoamylene, lower temperatures (0°, expt. 3) favor the production of the tertiary alkylate, but if the temperature is further decreased (−20°, expt. 4), only a negligible amount of monoalkylate is formed from B.

When a benzene solution of 1,4-di-(1-methylcyclohexyl)-benzene was stirred with aluminum chloride at 30° (expt. 5), monoalkylate was formed in 24% yield. This fraction consisted chiefly of the

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[1] Presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

[2] (a) V. N. Ipatieff, E. E. Meisinger and H. Pines, THIS JOURNAL, **72**, 2772 (1950); (b) J. Linsk, *ibid.*, **72**, 4257 (1950).

[3] M. Inatome, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **74**, 292 (1952).

[4] L. Schmerling and J. P. West, *ibid.*, **76**, 1917 (1954).

[5] B. S. Friedman and F. L. Morritz, *ibid.*, **78**, 2000 (1956).

[6] (a) L. Schmerling, J. P. Luvisi and R. W. Welch, *ibid.*, **77**, 1774 (1955), reported that the alkylation of benzene with 1-chloro-1-methylcyclohexane in the presence of aluminum chloride produced what was apparently III, or IV, or a mixture of these rather than I; (b) L. Schmerling, R. W. Welch and J. P. West, Am. Chem. Soc., Dallas, Texas, April 8–13, 1956.

[7] R. M. Kennedy and A. Schneider, U. S. Patent 2,626,966.

TABLE I

ALKYLATION OF AROMATICS WITH METHYLCYCLOHEXENES

Expt.	Moles[c] aromatic	Methylcyclohexene[d]	Catalyst	g.	Promoter	Temp., °C.	Duration, minutes	Yield,[e] %	Monoalkylate Composition[a] I	II	III	IV	Anal. method[b]
1	10 benzene	1-	$AlCl_3$	27	HCl	25	67	44	3	19	49	26	B
2	6 benzene	4-	$AlCl_3$	27	HCl	20	87	45	7	28	40	16	B
3	5 benzene[f]	4-	$AlCl_3$	27	HCl	0	46	30	44	Tr.	55	10	B
4	5 benzene[f]	4-	$AlCl_3$	27	HCl	−20	57	Tr.					
5[h]	6 benzene	[g]	$AlCl_3$		HCl	30	180	24	10	Tr.	68	13	B
6	5 benzene[f]	4-	HF BF_3	103 [i]		2	33	42	63	<5	30		B
7[w]	5 benzene	4-	HF BF_3	80 132		25	25	Tr.[k]					
8	5 benzene	4-	H_2SO_4	367		6	72	28[t]	100				A
9	5 benzene	[s]	H_2SO_4	1230		6	70	16	100				A
10	5 toluene	1-	$AlCl_3$	27	HCl	−50	30	19	90[l]				B
11	5 toluene	4-	$AlCl_3$	27	HCl	−50	39	28	37[l]				B
12	5 toluene	4-	HF	100		5	50	89	90[l]				B
13	5 *p*-xylene	1-	$AlCl_3$[m]	27	HCl	25	66	Low[u]					
14	5 *p*-xylene[f]	1-	$AlCl_3$	13	HCl	0	45	54	Tr.				B
15	2 *p*-xylene[n]	4-	$AlCl_3$	13	HCl	0	45	35	<5[o]				B
16	5 *p*-xylene[f]	1-	HF	100		4	50	76	<5[o]				B
17	2 *p*-xylene[n]	4-	H_2SO_4	184		0	50	<5					
18	2 *p*-xylene[p]	[q]	H_2SO_4	184		0	49	34					
19	2 *p*-cymene	4-	H_2SO_4	235		5	60	13[r]					
20	3 *p*-cymene	4-	$AlCl_3$	27	HCl	20	35	<3					

[a] Tr = trace. [b] A = infrared analysis of alkylate; B = infrared and mass spectrometer inspection of dehydrogenated alkylate. [c] Moles indicated per mole of olefin. [d] One mole unless otherwise indicated. [e] Yield based on alkylating agent charged. [f] *n*-Heptane as solvent. [g] 1,4-Di-(1-methylcyclohexyl)-benzene. [h] Catalyst and benzene saturated with HCl. Add the dialkylated benzene and stir. [i] Saturated with BF_3. [j] Balance consists of isomers of I. [k] Product an intractable mixture. [l] Probably 1-methyl-1-tolylcyclohexanes (balance consists of secondary isomers). [m] Nitromethane, 100 g. [n] Methylcyclohexane as solvent. [o] Probably 1-methyl-1-*p*-xylylcyclohexane[12] (balance consists of secondary isomers). [p] Cyclohexane as solvent. [q] Cyclohexene. [r] Probably 1,3,3,6-tetramethyl-1,2-tetramethylene-indane. [s] 4-Methylcyclohexanol. [t] Plus 41% of dialkylate.[g] [u] A mixture of alkylate (mass 202) and dimer (mass 192). [v] Procedure 1 (described in ref. 5) used except where noted; no solvent employed unless so indicated. [w] Procedure 4 (ref. 5).

secondary alkylates III and IV (68 and 13%, resp.); compound II was present only in trace amounts. This result is in accord with the work of Schmerling and West[4] who converted a di-*t*-hexylbenzene, 1,4-bis-(1,1,2-trimethyl-propyl)-benzene, into a secondary monoalkylate, 2-phenyl-3,3-dimethylbutane. The mechanism for these disproportionation reactions (*e.g.*, an SN′ mechanism in which the migrating group forms a carbonium ion intermediate or a bimolecular (SN2) displacement[8] of an arene by another arene followed by isomerization of the resulting monoalkylate) is not known with certainty; however, these results do show that the tertiary cycloalkyl structure will not long survive treatment with aluminum chloride at room temperature.

Boron fluoride/hydrogen fluoride proved, as in the alkylation with 3-methyl-1-butene,[5] to be too vigorous a catalyst at 25° (expt. 7) for the alkylation of benzene with B. The product contained only traces of monoalkylate; the balance consisted of an intractable mixture of dialkylate, polymer and trialkylate.[9] At a lower temperature and with a lower ratio of boron fluoride in the catalyst the yield (expt. 6) of monoalkylate was 42% and the ratio of *t*-cycloalkylate (I) to secondary alkylate was approximately 63/37.

The effect of alkylation at lower temperatures was studied with toluene since it is a more reactive nucleus. Alkylation with B at −50° (expt. 11) in the presence of aluminum chloride/hydrogen chloride yielded 28% of monoalkylate containing only about 37 parts of the *t*-alkylate (probably 1-methyl-1-tolylcyclohexane), the balance consisting of isomeric methylcyclohexyltoluenes. This is somewhat in contrast to the results obtained (expt. 10) with A which yielded 19% of monoalkylate containing about 90 parts of the *t*-cycloalkyl derivatives. Apparently at the low temperature, double-bond migration is strongly retarded, while alkylation is still a rapid reaction.

Alkylation of toluene with B at 0–5° in the presence of hydrogen fluoride yielded (expt. 12) a mixture of tertiary cycloalkylates accompanied by a small amount (<10%) of secondary cycloalkylates.

(B) *p*-Xylene.—The literature contains references[10,11] to the reaction of *p*-xylene with B in the presence of hydrogen fluoride or aluminum chloride; however, the structure of the alkylate has not been established. In our studies of this reaction with concentrated sulfuric acid as catalyst, the yield of monoalkylate was very low, yet with cyclohexene itself a 34% yield of monoalkylate was obtained (expts. 17, 18). Apparently the rate of isomerization of the intermediate secondary carbonium ion (formed from B) to the *t*-carbonium ion is

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(8) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **75**, 2411 (1953).

(9) This resembles McCaulay and Lien's[8] results with *t*-butylbenzene at 45°.

(10) H. Pines, D. R. Strehlau and V. N. Ipatieff, using hydrogen fluoride, THIS JOURNAL, **71**, 3534 (1949).

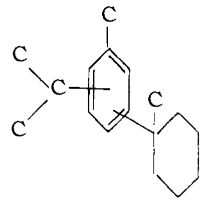
(11) Daniel Bodroux, using $AlCl_3$, *Ann. chim.*, [10] **11**, 511 (1929); *C. A.*, **23**, 4937c (1929).

much faster than the rate of alkylation of *p*-xylene by the secondary carbonium ion. Because of steric hindrance the tertiary carbonium ion apparently reacts very slowly, if at all, with *p*-xylene and instead forms polymer or is converted by hydrogen transfer reactions to acid-soluble products.

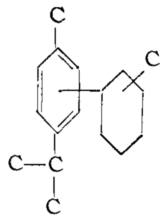
With aluminum chloride as catalyst, the yield of monoalkylate was 35% (expt. 15). This product was shown, by dehydrogenation experiments and mass spectrometer analyses, to consist of less than 5% of tertiary cycloalkylates (probably 1-methyl-1-*p*-xylylcyclohexane)[12]; the balance consisted of secondary cycloalkylates which yielded trimethyldiphenyl derivatives upon dehydrogenation. The alkylation with A also proceeded satisfactorily in the presence of aluminum chloride (expt. 14). Here again secondary cycloalkylates predominated. Complexing the catalyst with nitromethane resulted (expt. 13) in a much lower yield of monoalkylate (contaminated with polymer).

The monoalkylate produced from *p*-xylene and A in the presence of hydrogen fluoride was substantially all secondary (expt. 16). This demonstrates again[5] the ability of hydrogen fluoride to effect secondary alkylation with olefins of the type $R_2C{=}CHR$ where steric effects retard tertiary alkylation—normally the exclusive reaction at these temperatures.

(C) **p-Cymene.**—Ipatieff, Pines and co-workers[13,14] have reported the alkylation of various cymenes with B in the presence of hydrogen fluoride or sulfuric acid. They obtained much lower yields of monoalkylate from *p*- than from *m*- and *o*-cymene (8.5, 40 and 71%, resp.). Very probably the products obtained from *o*- and *m*-cymene are actually tertiary methylcyclohexyl alkylates (V).



V



VI

However, we believe that the product from *p*-cymene is not, as suggested by these authors, a methylcyclohexyl-*p*-cymene. A tertiary alkylate, *e.g.*, 1-methyl-1-*p*-cymylcyclohexane, is considered very unlikely because of the general steric hindrance to *o*-*t*-alkylation. Secondary alkylates, *e.g.*, VI, would be unlikely for the sulfuric acid-catalyzed reaction product since this catalyst yields only *t*-cycloalkyl derivatives with benzene and but traces of any alkylate whatsoever with *p*-xylene. Structure VI may also be ruled out (1) on the basis of the main parent mass value (228) which is 2 units too low for the alkylate and (2) on the basis of failure of the compound to undergo dehydrogenation to substantial degree (to diphenyl derivatives) characteristic of 1,2- 1,3- and 1,4-aryl, methyl-disubstituted cyclohexanes.

Our work indicates that the C_{17}-product is probably the tricyclic derivative VII (1,3,3,6-tetramethyl-1,2-tetramethylene-indane[15]) of mass 228, contaminated with less than about 10% of an alkylate mass 230. Based on Schlatter's mechanism[16] for indane formation in the reaction of *p*-cymene with branched olefins, compound VII might be formed *via*

TABLE II

PHYSICAL PROPERTIES OF MONOALKYLATES BEFORE AND AFTER DEHYDROGENATION

Expt.	Boiling range, °C.	$n^{20}D$ Before	$n^{20}D$ After	Mass spectrograph relative peak heights m/e	Before	After
1	243–249	1.5178–149	1.5962	174[a]	82	6
				168[b]	0	681
2	238–242	1.5171–134	1.5936	174[a]	77	8
				168[b]	0	593
3	241–244	1.5203–179	1.5700	174[a]	293	
				168[b]	4	
5	237–244	1.5180–140	1.5907	174[a]		
				168[b]		
6	243–253	1.5252–227	1.5356	174[a]	152	141
				168[b]	0	157
10	253–260	1.5263	1.5309	188[a]	272	51
				182[c]	0	6
				180[d]	0	6
11	252–260	1.5206–194	1.5686	188[a]	231	18
				182[c]	0	126
				180[d]	0	0
12	265	1.5250–256	1.5324	188[a]	158	50
				182[c]	0	15
				180[d]	0	2
14	260–279	1.5213–315	1.5571	202[a]	65	0
				200[e]	23	59
				196[f]	0	125
15	251–284	1.5160–203	1.5749	202[a]	220	4
				200[e]	22	14
				196[f]	0	138
				194[g]	0	47
16	266–276	1.5230–240	1.5682	202[a]	80	4
				200[e]	14	13
				196[f]	0	96
				194[g]	0	13
19	288	1.5298–304	1.5373	230[a]	10	2
				228[h]	94	150
				224[i]	0	12
				194[j]	0	5

[a] Alkylate. [b] Methylbiphenyls. [c] Dimethylbiphenyls. [d] $C_{14}H_{12}$ (methylfluorene?). [e] Probably an indan, possibly 1,6-dimethyl-1,2-tetramethylene-indan also designated 4a,-6-dimethyl-1,2,3,4-tetrahydrofluorene. [f] Trimethylbiphenyls. [g] $C_{15}H_{14}$ (dimethylfluorene?). [h] Indan, VII. [i] Biphenyl derivative. [j] Dimethylfluorene?.

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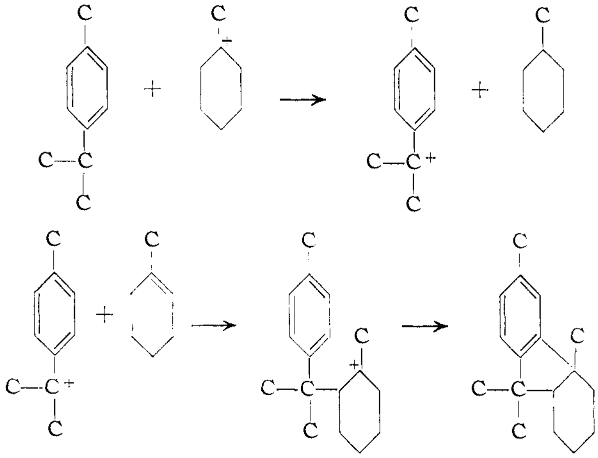
(12) The available evidence does not eliminate the possibility that dimethylcyclopentyl derivatives of *p*-xylene may be present. Steric retardation of the alkylation might provide an opportunity for isomerization of the methylcyclohexyl cation into a dimethylcyclopentyl cation prior to alkylation.

(13) V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **70**, 2123 (1948).

(14) H. Pines, D. R. Strehlau and V. N. Ipatieff, *ibid.*, **72**, 5521 (1950).

(15) 4a,6,9,9-Tetramethyl-1,2,3,4-tetrahydrofluorene.

(16) M. J. Schlatter, Division of Petroleum Chemistry, Am. Chem. Soc., Chicago, Ill., September 6–11, 1953, Abstracts p. 82, and Dallas, Texas, April, 8–13, 1956, Abstracts p. 77.



VII

Methylcyclohexane required by the mechanism was isolated in 48% yield; 1,3,3,6-tetramethyl-1-*p*-tolyl-indan[17] also was produced (expt. 19).

Additional studies of the alkylation of *p*-substituted benzenes will be reported in the future.

Experimental

Acknowledgment is due Dr. F. L. Voelz, Mr. F. L. Boys and Mr. R. Wertzler for interpretation of the infrared spectrograms and Mr. J. F. Kinder and F. L. Boys for the mass spectrometric analyses.

Alkylation Procedures.—Those previously described[5] were used (see Table I).

Identification.—The infrared absorption spectrogram of 1-methyl-1-phenylcyclohexane was identical to that previously reported.[2a] 1,4-Di-(1′-methylcyclohexyl)-benzene was prepared as described by Linsk.[2b]

In most instances the *t/s* ratio (ratio of tertiary to secondary cycloalkylation) was determined by dehydrogenating[18] the monoalkylate and examining the product by infrared and/or by mass spectrometry. For example, the monoalkylate of benzene was passed over a 0.5% platinum-on-alumina catalyst[19] or a 10% platinum-on-carbon[19] at 300–310° until the index of refraction remained fairly constant (usually 3 passes). The product was analyzed by comparison to infrared standards for compound I, biphenyl, 2-methylbiphenyl,[20] 3-methylbiphenyl[20] and 4-methylbiphenyl (synthesized[21] by diazotization of *p*-toluidine followed by condensation with benzene).

The *t/s* ratio for alkylates of benzene, toluene and *p*-xylene was estimated by noting the amount of biphenyls formed (from secondary alkylates) during dehydrogenation and noting the peak intensity of the parent mass of the tertiary alkylate surviving dehydrogenation (Table II).

The methylcyclohexyl derivative of *p*-cymene was assigned the indane structure VII on the basis of the following evidence:

MCH derivative of	n^{20}_D	d^{20}_4	C, %	H, %	Parent mass
o-Cymene[14]	1.5230	0.9318	88.86	11.19	. .
o-Cymene[14]	1.5170	.9213	88.92	11.38	. .
p-Cymene[13]	1.5305	.9581	89.40	10.68	. .
p-Cymene (VII)	1.5301	.9564	89.11	10.64	228
Calcd. for true alkylate ($C_{17}H_{26}$)			88.62	11.37	230
Calcd. for indan ($C_{17}H_{24}$)			89.40	10.60	228

The higher refractive index and greater density bespeak a tricyclic structure, as do the carbon, hydrogen and parent mass values. However, the data in Table II (Expt. 19) do indicate the presence of about 10% of true alkylate, mass 230, as an impurity.

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(17) Formation of this indan is accompanied by production of methylcyclohexane.[13]

(18) V. N. Ipatieff and H. Pines, THIS JOURNAL, **58**, 1056 (1936).

(19) Baker & Company, Inc., Newark, N. J.

(20) We are grateful to Addison M. Rothrock, National Advisory Committee for Aeronautics, Washington, D. C., for making available to us these standards previously described by K. T. Serijan, I. A. Goodman and W. J. Yankauskas, National Advisory Committee Aeronautics Technical Note No. 2557 (1951).

(21) "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1945, p. 247.

HARVEY, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Synthesis of 2,4,9-Trichloro-3-phenanthrol

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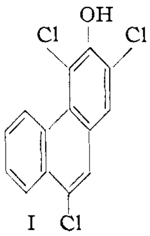
In order to obtain further evidence concerning a compound believed to be 2,4,9-trichloro-3-phenanthrol (I), 2,4-dichloro-3-methoxyphenanthrene (X) was synthesized by the general method of Pschorr. The 2,5-dichlorohomoanisic acid (VI) required in the Pschorr synthesis was synthesized in 65% yield in a five-step reaction sequence starting with ethyl 3,5-dichloro-4-hydroxybenzoate. Cleavage of the ether linkage of X, and chlorination of the resulting phenanthrol XI, afforded I.

In connection with the study of the chlorination of 3-phenanthrol[2] we prepared a new trichlorophenanthrol which, on the basis of further reactions, was believed to be 2,4,9-trichloro-3-phenanthrol (I). Prior to the completion of that study, but after the location of one chlorine at position 9 had been definitely established, it had seemed desirable to undertake the synthesis of I by a method which would afford unequivocal evidence concerning the position of the chlorine atoms believed to be at positions 2 and 4. It seemed likely that this might be achieved by the synthesis of 2,4-dichloro-3-methoxyphenanthrene by the general method of Pschorr, followed by chlorination at the 9-position of the phenanthrene ring.



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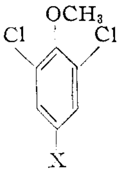

II, X = $COOCH_3$
III, X = CH_2OH
IV, X = CH_2Br
V, X = CH_2CN
VI, X = CH_2COOH

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(1) Allied Chemical and Dye Corporation Fellow 1953–1954. Taken in part from the thesis submitted by P. H. Leake in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Duke University, 1954. This work was supported in part by the Chemical Corps, Fort Detrick, Md., under contract with Duke University.

(2) C. K. Bradsher, F. C. Brown and P. H. Leake, THIS JOURNAL, **78**, 4400 (1956).