Summary

By means of a separation of the isomeric hydrocarbons of the ethylene series of each specified carbon content into types, arbitrarily chosen upon the basis of their structural formulas, a relationship may be established between the number of structurally isomeric homologs of ethylene and the alkyl groups which may be considered to be attached to the $>C{=}C<$ grouping. Mathematical formulas of the (finite) recursion type are advanced which permit of the calculation, from their carbon content, of the number of isomers in each of these structural types. In using these recursion formulas to calculate the total number of such structurally isomeric hydrocarbons of any given carbon content, the total number of alkyl groups (*i. e.*, the total number of structurally isomeric monosubstitution products of the paraffins) of $N-2$ and all lesser carbon contents must be known.

AUSTIN, TEXAS

RECEIVED JUNE 27, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Naphthol Studies. II. The Chlorination of 1,5-Dihydroxynaphthalene

BY ALVIN S. WHEELER AND W. J. MATTOX[1]

The studies of Wheeler and Ergle[2] have shown that one, two or three atoms of bromine may be introduced into 1,5-dihydroxynaphthalene. In the present study we have prepared dichloro and trichloro derivatives but no tetrachloro compound was obtained. A similar relation was noted in the juglone studies of Wheeler and co-workers,[3,4] more bromine being taken up than chlorine. Willstätter and Schuler[5] chlorinated dihydroxynaphthalene in acetic acid solution but for the purposes of this study we found it better to chlorinate the diacetate in carbon tetrachloride. The description of our compounds C and G does not agree with that of Willstätter and Schuler. This will be re-examined. In chlorinating the diacetate at room temperature two atoms of chlorine are taken up whereas at 80° three atoms are introduced. In each case one acetyl group is hydrolyzed. We tried to prove that OH and O in compound I are ortho to each other by Dimroth's pyroboroacetate ester method. We obtained the characteristic reddish purple color but no solid product. The first two chlorine atoms are put in positions 4 and 8 and the third also in 4 since one

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[1] Extract from a thesis presented to the Faculty of the University of North Carolina by W. J. Mattox for the degree of Doctor of Philosophy in 1932.

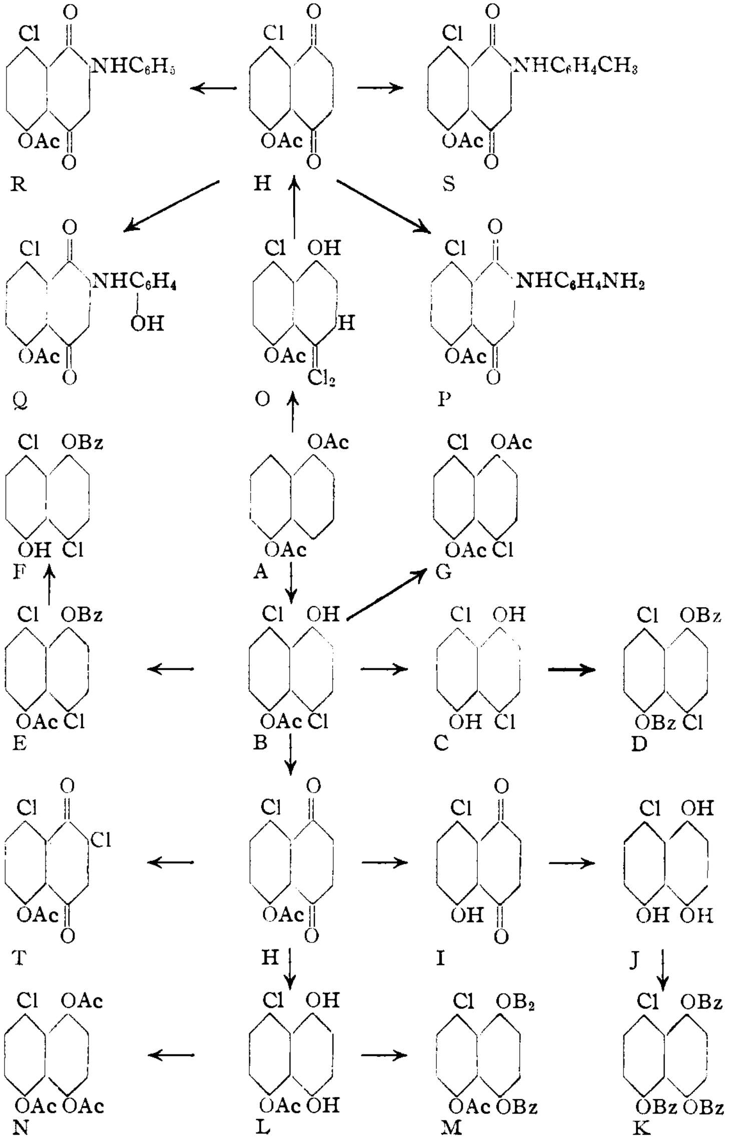
[2] Wheeler and Ergle, THIS JOURNAL, **52**, 4873 (1930).

[3] Wheeler and Scott, *ibid.*, **41**, 834 (1919).

[4] Wheeler, Dawson and McEwen, *ibid.*, **45**, 1970 (1923).

[5] Willstätter and Schuler, *Ber.*, **61**, 362 (1928).

O replaces 2Cl in the production of compound H. This is in harmony with the observed instability of compound O. Quinone H gave characteristic reactions with several aromatic amines. The nitroanilines, sulfanilic acid, *p*-aminobenzoic acid and 2,4-dichloroaniline did not react.



Experimental

4,8-Dichloro-1-hydroxy-5-acetoxynaphthalene (B).—Five grams of the diacetate of 1,5-dihydroxynaphthalene (m. p. 159°) was suspended in 40 cc. of carbon tetrachloride, a small crystal of iodine was added and a slow stream of chlorine passed at room temperature until solution took place. The solution after treatment with charcoal was reduced one-half in volume in a vacuum desiccator. Petroleum ether was then added until a cloudiness remained after stirring. The colorless needles which soon separated were recrystallized from a small amount of glacial acetic acid. On heating the substance it turned green at 158–160° and then effervesced vigorously. If recrystallized from alcohol yellow impurities clung tenaciously to the crystals. The product was soluble in acetone, chloroform and ether.

Anal. Calcd. for $C_{12}H_8O_3Cl_2$: Cl, 26.19. Found: Cl, 26.34.

4,8-Dichloro-1,5-dihydroxynaphthalene (C).—Compound B may be hydrolyzed in alkaline or acid solution, but the acid hydrolysis is to be preferred. The alkaline solution is purple in color and acidification gives a greenish product. The acid hydrolysis gives at once a white product. Two grams was dissolved in 100 cc. of warm alcohol and 30 cc. of concd. hydrochloric acid was added. The solution after standing four to five hours was poured into 200 cc. of water. The white precipitate was recrystallized from glacial acetic acid as fine, colorless needles, m. p. 194°. Willstätter and Schuler give 188–189° for a pale yellow product. The compound is soluble in alcohol, ether, chloroform, hot benzene and carbon tetrachloride. It darkens slowly on exposure to light and air.

Anal. Calcd. for $C_{10}H_6O_2Cl_2$: Cl, 31.00. Found: Cl, 30.75.

8-Chloro-5-acetoxy-1,4-naphthoquinone (H).—Two grams of B was dissolved in 40 cc. of glacial acetic acid at 50° and a solution of 4 g. of chromic acid in 10 cc. of water was added. After standing for two to three hours the solution was poured into several volumes of water. The precipitated quinone was dissolved in acetone and warmed with charcoal. The filtered solution was mixed with water, giving fine yellow needles, m. p. 143°. It can be recrystallized from alcohol in a yield 45%. This quinone was also obtained by the oxidation of the trichloro compound O. It is stable and sublimes without decomposition.

Anal. Calcd. for $C_{12}H_7O_4Cl$: Cl, 14.17. Found: Cl, 14.32.

4,4,8-Trichloro-1-hydroxy-5-acetoxynaphthalene (O).—Five grams of A was dissolved in 25 cc. of glacial acetic acid. Chlorine was passed into the solution at 50° for two and one-half hours. The solution became red and on cooling with ice the trichloro compound crystallized out. Sometimes seeding was necessary. The color of the crystals was largely removed by washing with petroleum ether. Recrystallization from hot glacial acetic acid gave colorless needles, m. p. 174°, yield 2.5 g.; soluble in acetone, hot alcohol, ether and benzene. The substance darkens in a few days when exposed to sunlight. It is readily decomposed by dilute alkali. Boiling for several hours with absolute alcohol does not remove any chlorine. Oxidation in glacial acetic acid with chromic acid gives the quinone H as does also the compound B.

Anal. Calcd. for $C_{12}H_9O_3Cl_3$: Cl, 34.75. Found: Cl, 34.72.

The dichloro compound B also takes up chlorine at 80° giving the same compound O. Analysis for Cl gave 34.69.

2,8-Dichloro-5-acetoxy-1,4-naphthoquinone (T).—One-half gram of H was dissolved in 10 cc. of glacial acetic acid and an excess of chlorine passed into the solution. Water was added until a faint cloudiness appeared. The product crystallized out on standing. It was recrystallized from alcohol as pale yellow needles, m. p. 158–159°. It is noteworthy that only one atom of chlorine is taken up.

Anal. Calcd. for $C_{12}H_6O_4Cl_2$: Cl, 24.91. Found: Cl, 24.37.

In the table other derivatives are indicated.

TABLE I

	Compound	Source	Reagent	Cryst. solvent	M. p., °C.	Solubilities			Formula	Cl, %	
						Alc.	C_6H_6	Gl. ac.		Calcd.	Found
D	4,8 - Dichloro - 1,5 - dibenzoxynaphthalene	B	PhCOCl	Acetone	179	..	..	..	$C_{19}H_{12}O_4Cl_2$	18.90	18.75
F	4,8 - Dichloro - 1 - benzoxy - 5 - hydroxynaphthalene	E	Alc. + HCl	Gl. AcOH	157–158	..	..	..	$C_{17}H_{10}O_2Cl_2$	21.14	21.32
G	4,8-Dichloro-1,5-diacetoxynaphthalene	B	CH_3COCl	Acetone	143	SS	SS	SS	$C_{14}H_{10}O_4Cl_2$	22.66	22.81
I	8 - Chloro - 5 - hydroxy - 1,4 - naphthoquinone	H	Alc. + HCl	Alc.	112	S	S	S	$C_{10}H_5O_3Cl$	17.01	16.95
J	8-Chloro-1,4,5-trihydroxynaphthalene	I	$SnCl_2$	Dil. alc.	115–120 dec.	S	S	S	$C_{10}H_7O_3Cl$	16.85	16.54
K	8-Chloro-1,4,5-benzoxynaphthalene	J	PhCOCl	Xylene	210	i	i	i	$C_{31}H_{19}O_6Cl$	6.79	6.92
L	8- Chloro - 1,4 - dihydroxy - 5 - acetoxynaphthalene	H	Zn + dil. H_2SO_4	Gl. AcOH	173 dec.	..	..	S	$C_{12}H_9O_4Cl$	14.05	13.98
M	8 - Chloro - 1,4 - dibenzoxy - 5 - acetoxynaphthalene	L	PhCOCl	Gl. AcOH	216	SS	SS	S	$C_{26}H_{17}O_6Cl$	7.70	7.56
N	8-Chloro-1,4,5-triacetoxynaphthalene	L	Ac_2O	Gl. AcOH	147	SS	S	S	$C_{16}H_{12}O_6Cl$	10.54	10.69
P	8 - Chloro - 5 - acetoxy - 1,4 - naphthoquinone-*o*-aminoanilide	H	$C_6H_4(NH_2)_2$	....	271 dec.	i	i	i	$C_{18}H_{13}O_4N_2Cl$	9.96	10.39
Q	8 - Chloro - 5 - acetoxy - 1,4 - naphthoquinone-*p*-hydroxyanilide	H	$C_6H_4OHNH_2$-*p*	....	226 dec.	S	S	S	$C_{18}H_{12}O_5NCl$	9.93	9.53
R	8 - Chloro - 5 - acetoxy - 1,4 - naphthoquinone anilide	H	$C_6H_5NH_2$	....	172	S	S	S	$C_{18}H_{12}O_4NCl$	10.33	10.45
S	8 - Chloro - 5 - acetoxy - 1,4 - naphthoquinone-*p*-methylanilide	H	$C_6H_4CH_3NH_2$-*p*	....	169	S	S	S	$C_{19}H_{14}O_4NCl$	9.98	10.06

Summary

1. 1,5-Diacetoxynaphthalene suspended in carbon tetrachloride yields with chlorine in the sunlight or with iodine as a catalyst a dichloro substitution product and at 80° a trichloro product.

2. The chloro compounds yield the same quinone when oxidized with chromic acid.

3. The quinone gave mono, di and trihydroxy naphthols.

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RECEIVED JUNE 25, 1932
PUBLISHED FEBRUARY 9, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Reaction between Alpha, Beta-Unsaturated Ketones and Organic Magnesium Compounds. Unsaturated Mesitylenic Ketones

BY E. P. KOHLER AND CARL E. BARNES

Earlier papers on this subject contain a description of the reaction between organic magnesium compounds and every member of the series of alpha, beta-unsaturated ketones which could be formed by replacing the hydrogen atoms in acrolein one by one with phenyl groups. Not one of these ketones under any conditions formed a product containing more than two phenyl groups in the beta position. In the case of tetraphenyl propenone, from which such a product was most to be expected, the reaction took an entirely unexpected direction involving addition to a phenyl group.[1]

$$(C_6H_5)_2C{=}C(C_6H_5)COC_6H_5 + C_6H_5MgBr \longrightarrow (C_6H_5)_2C{=}C(C_6H_5)COC_6H_4C_6H_5(o)$$

In view of this result it now became a matter of interest to study the reaction with unsaturated mesitylenic ketones which are so constituted that the hindrance to 1,2 addition would be prohibitive, and that any type of 1,4 addition would inevitably lead to substances with three hydrocarbon residues in the β-position. With this end in view we decided to investigate the behavior of beta phenyl benzalacetomesitylene. The reaction between phenylmagnesium bromide and this ketone had been briefly examined many years ago with negative results,[2] but with the experience gained since then in working with highly phenylated compounds this outcome no longer seemed inevitable.

We have now found that by operating under favorable conditions and with sufficient persistence it is possible to add both phenylmagnesium bromide and ethylmagnesium bromide to this ketone in ether. In the case of methylmagnesium iodide the highly colored intermediate complex product is so nearly insoluble in ether that a reaction in this solvent is impossible but even here it is possible to secure reaction by operating at a

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(1) Kohler and Nygaard, THIS JOURNAL, **52**, 4128 (1930).

(2) Kohler, *Am. Chem. J.*, **38**, 560 (1907).