

by weight of solvent. The catalyst was recovered from the reaction mixture, either by filtration of the latter, if liquid at room temperature, or by filtration of an ethereal solution of the reaction mixture. The reaction solvent was removed either by distillation under reduced pressure or by steam distillation, after removal of the ether. The residue from these distillations was then warmed for about fifteen minutes with an excess of 5% potassium hydroxide solution, and the undissolved material taken up in ether. Four or five extractions of the ethereal solution with alkali removed practically all of the phenanthrol. The alkaline extracts were combined with the first alkaline solution and acidified with concentrated hydrochloric acid, whereupon the phenanthrol separated in a crystalline state. From the residue of the ethereal solution the unreacted ketotetrahydrophenanthrene may be recovered as its semicarbazone. The results of some of the experiments are summarized in Table I.

1-Phenanthrol.—Pure 1-phenanthrol was obtained from the dehydrogenation product by one distillation at 1 mm., followed by sublimation; m. p. 153–154°.

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.56; H, 5.19. Found: C, 86.21; H, 5.16.

The acetate and the methyl ether melted at 134–135° and 103–104°, respectively. The melting points agree with the corresponding values given in the literature.^{2a,3a,4,6}

4-Phenanthrol.—4-Phenanthrol was purified in the same manner as the 1-isomer, and melted at 113–115°, in agreement with the value given by Mosettig and Burger.⁶

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.56; H, 5.19. Found: C, 86.44; H, 5.55.

The acetate and methyl ether melted at 58–59.5° and 67–68°, respectively, in agreement with the values given in the literature.^{2b,3b}

Summary

1- and 4-phenanthrol have been prepared in yields of 68–86% and 56–63%, respectively, by the catalytic dehydrogenation of 1- and 4-keto-1,2,3,4-tetrahydrophenanthrene.

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[CONTRIBUTION NO. 48 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Chemical Constitution of a Bituminous Coal as Revealed by its Hydrogenation Products

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In earlier contributions from this Laboratory² it was shown that both the extract and the residue from the extraction of a Pittsburgh seam coal with benzene at 260°, yielded, upon high pressure hydrogenation at 350° with a copper-calcium chromite catalyst, 80% of their carbon as petroleum ether soluble oils essentially hydrocarbon in nature. Boiling points, refractive indices and hydrogen-carbon ratios indicated that these hydrocarbons were partially hydrogenated polycyclic aromatic compounds. Because of (1) the nature of the catalyst employed, which is particularly effective in breaking cyclic and linear ether oxygen linkages, (2) the moderate temperatures used, which preclude appreciable degradation of hydrocarbon structures and (3) the large fraction of the carbon of the original coal converted, it appears that these oils properly may be regarded as fundamental units of the coal in the sense that the coal structure may be considered as built of such units combined through peripheral functional groups.

In this paper are presented the results so far obtained in the characterization of these oils.

The oils recovered from the preliminary hydrogenation with copper-calcium chromite were completely saturated by hydrogenation over Raney nickel catalyst, then fractionally distilled and the fractions characterized through their boiling points, refractive indices, molecular weights and hydrogen-carbon ratios.

Experimental.—Both the residue and the extract from the extraction of Edenborn³ coal with benzene at 260° were hydrogenated over Adkins catalyst by the stepwise procedure described by Biggs^{2b} in which hydrogenation, followed by removal of petroleum ether soluble oils, was repeated until there was practically complete conversion to oils. From 200 g. of residue there was obtained in seven steps 24.5, 21.7, 18.6, 20.4, 26.5, 12.6 and 9.2 g., or a total of 133.5 g. of petroleum ether soluble oils containing 79.7% of the carbon of the starting materials. From 100 g. of extract there was obtained in five steps 21.5, 26.7, 19.5, 12.8 and 4.7 g., or a total of 85.2 g. of petroleum ether soluble oils representing 87% of the carbon of the original extract. The accumulated products in each case were then dissolved in benzene and subjected to a final hydrogenation over Adkins catalyst at 280° for twenty-four hours. After removal of benzene the product was dissolved in cyclohexane and subjected to hydrogenation over 10% of Raney nickel catalyst at 220° and 1800 pounds (120 atm.) initial hydrogen pressure until the absorption of hydrogen had ceased. This necessitated cooling the bomb

(1) Now located at Summit, N. J., Bell Telephone Laboratories.
(2) Biggs, *This Journal*, (a) 58, 484 (1936); (b) 58, 1020 (1936).

(3) U. S. Bureau of Mines Tech. Paper No. 525 (1932).

TABLE I

COMPARISON OF THE PROPERTIES OF SOME KNOWN HYDROAROMATIC COMPOUNDS WITH VARIOUS FRACTIONS OF THE HYDROGENATION PRODUCTS OF THE RESIDUE (R) AND EXTRACT (E) FROM THE BENZENE PRESSURE EXTRACTION OF A BITUMINOUS COAL

No. ^a	Grams	Mol %	Wt. %	Initial atm. b. p., °C.	n _D ²⁰	Mol. weights ^b		Empirical formulas			H/C
						Catechol	Diphenyl	C	H	OH	
R ₁	3.0	6.9	2.2	190	1.467	122	128	8.7	15.6	0.34	1.83
R ₂	5.4	11.1	4.0	205	1.482	146	144	10.0	17.1	.33	1.74
R ₃	2.5	4.2	1.9	230	1.494	175	177	12.5	20.6	.32	1.67
R ₄	5.5	8.2	4.1	262	1.509	195	198	14.1	22.5	.29	1.61
R ₅	2.5	3.4	1.9	315	1.524	198	218	15.6	23.8	.26	1.54
R ₆	15.9	18.6	11.8	320	1.540	244	252	18.2	27.2	.30	1.51
R ₇	17.9	15.6	13.3	395	1.563	330	338	24.6	33.2	.42	1.37
R ₈	16.4	10.8	12.1	450	1.593	405	448	33	44	.42	1.35
R ₉	51.6	21.2	38.2	520	720	53	64	.75	1.21
Loss	14.3		10.6								
E ₁	10.8	26.7	13.0	220	1.498	165	170	12	19.3	.34	1.63
E ₂	7.7	14.5	9.2	315	1.533	218	224	16	24.0	.30	1.52
E ₃	16.5	23.6	19.6	385	1.567	275	295	21.5	29.7	.36	1.39
E ₄	3.0	3.5	3.6	440	1.594	377	357	26.4	35.9	.29	1.34
E ₅	10.3	10.2	12.2	460	1.613	384	427	31.4	38.1	.38	1.23
E ₆	35.7	21.5	42.5
Deca(per)hydronaphthalene				185	1.468	138		10	18	...	1.80
Tetradeca(per)hydrophenanthrene				(250) ^c	1.499	192		14	24	...	1.71
Dodecahydrophenanthrene				268	1.508	190		14	22	...	1.57
Octadeca(per)hydrochrysene				360	1.521	246		18	30	...	1.68
Hexadecahydrochrysene				(380)	1.541	244		18	28	...	1.55
Octadeca(per)hydrotriphylene				...	1.518(n _D ²⁵)	246		18	30	...	1.68
Hypothetical compound with 7 rings				400	...	320		24	34	...	1.41

^a Nos. R₁-R₆ are from the refractionation of a fraction taken off at atmospheric pressure. No. R₉ is the residue remaining in the still. No. E₆, non-distillable in the conventional apparatus, was further distilled in a molecular still, but with partial decomposition so that analytical data for this fraction are not available. ^b Reproducible to 1 part in 10. ^c Atmospheric boiling points given in brackets are estimated from values given for lower pressures.

after five hours in order to replenish the hydrogen. The total time at 220° was approximately ten hours. The oils from both the extract and the residue absorbed from 2-3 g. of hydrogen per 100 g. of oil. That hydrogen absorption had not ceased due to poisoning of the catalyst was established by the activity of the catalyst in a subsequent hydrogenation of benzene at 180°. The resulting products were freed of cyclohexane on a water-bath and then fractionally distilled at 1 mm. pressure up to a temperature of 350°.

Microanalyses for carbon and hydrogen were made on all fractions; molecular weights were determined cryoscopically in both catechol and diphenyl according to the method of Smith and Howard,⁴ and the initial atmospheric boiling points and refractive indices were noted. The presence of some oxygen in the lower boiling fractions led to the estimation of hydroxyl contents by acetylation with acetic anhydride in pyridine solution.⁵

Results and Conclusions

The properties of the various fractions of the oils obtained by hydrogenation of residue and extract are given in Table I. For the purpose of comparison the properties of some known hydro-

aromatic compounds are given at the bottom of the table. That these fractions represent a true range of building units and not various degrees of polymerization or association of some unit or units is indicated by the close agreement of the values for the molecular weights determined in catechol and in diphenyl. In the undistilled fraction, R₉, there was some divergence which would indicate that this fraction had not been depolymerized completely. However, a further hydrogenation of this fraction at 280° for forty-eight hours produced only traces of material distilling below 400°.

An interesting point is the hydroxyl content of these supposedly hydrocarbon substances. Hydroxyl oxygen accounts for from 70-90% of the "oxygen by difference." The constant molar hydroxyl content for the various fractions from both the residue and extract suggests that oxygen-containing groups have entered into the coalification process in some systematic manner. Although the replacement of hydrogen by hydroxyl in a hydrocarbon raises the refractive index

(4) Smith and Howard, *THIS JOURNAL*, **57**, 512 (1935).

(5) Freed and Wynne, *Ind. Eng. Chem., Anal. Ed.*, **8**, 278 (1936).

slightly, the hydroxyl content of this material is sufficiently small to permit the drawing of valid conclusions concerning the nature of the hydrocarbons present from a comparison with known hydrocarbons.

If properties of known hydroaromatic compounds are compared with those of the various fractions, we find that of the residue fractions, R_1 and R_2 , limpid water white liquids, correspond rather closely to decalin; R_3 and R_4 , light yellow slightly viscous liquids, correspond to dodeca- and tetradecahydrophenanthrene; and R_5 and R_6 , golden yellow very viscous liquids of marked tackiness, correspond to hexadeca- and octadecahydrochrysene. The inclusion of dodecahydrophenanthrene and hexadecahydrochrysene, compounds lacking two hydrogen atoms of complete saturation, in the list of completely saturated compounds for comparative purposes is justified because of the great difficulty of introducing these last two hydrogen atoms. Due to lack of data on known compounds of more than four condensed rings, we can only surmise from the regular increase in boiling points and refractive indices and from molecular weight and composition that fractions R_7 , R_8 and R_9 were composed of larger members of the type assigned to the lower fractions. Thus, in molecular weight and hydrogen-carbon ratio fraction R_7 and a hypothetical seven-ring compound were nearly identical.

The fractionation of the product from the extract was not so close as that of the product from the residue and consequently we find fraction E_1 , a yellow oily liquid, corresponds roughly to a mixture of decalin and the hydrophenanthrenes; fraction E_2 , a yellow very viscous tacky oil, corresponds to the hydrochrysenes; and fraction E_3 , a yellow resinous substance, corresponds to a hypothetical seven-ring compound.

Despite evident overlapping, it is concluded that the respective fractions are composed chiefly of the polycyclic hydrocarbons, and their isomers and homologs, to which they are found to correspond in the above comparison. Although chiefly hydrocarbon in nature, each fraction has a hydroxyl content equivalent on the average to one hydroxyl group per three hydrocarbon molecules. That coals of lower rank contain fundamental structural elements of a cyclic nature has been indicated by the fact that low temperature (290–400°) serial hydrogenation of a brown coal

in presence of MoS_3 was found⁶ to yield benzene and kerosene fractions consisting predominantly of aromatic and naphthenic hydrocarbons.

An approximate distribution of the various sized building units in the residue and in the extract is summarized in Table II. Although there is present in both materials upward of 50% by weight of building units of molecular weight of approximately 700, the calculated average molecular weight in both cases is about 300. This compares with the results of Smith and Howard,⁴ who found molecular weights ranging from 200–300 for humic acids prepared by the oxidation of Edenborn coal.

TABLE II
APPROXIMATE DISTRIBUTION OF BUILDING UNITS IN THE EXTRACT AND RESIDUE ACCORDING TO THE NUMBER OF CONDENSED RINGS PRESENT IN THE UNITS

No. of rings	Residue		Extract	
	Mol. %	Wt. % ^a	Mol. %	Wt. %
2	18	7		
			27	13
3	12	7		
4	22	15	15	9
5–7	16	15	27	23
?>7	32	56	32	55

^a Corrected for loss.

The agreement found for the distribution of units in residue and extract is further evidence in support of the viewpoint that the benzene insoluble and soluble parts of this coal differ more in the size of the polymeric aggregate than in essential chemical structure.^{2b}

While in this study the general constitution and distribution of the building units in this coal have been shown, further evidence as to the exact nature of these substances is extremely desirable. The catalytic dehydrogenation of these hydroaromatic oils to the corresponding aromatic compounds to permit isolation and identification through addition compounds such as picrates is being studied in this Laboratory.

Summary

By catalytic hydrogenation, first over Adkins catalyst at 350°, and then over Raney nickel catalyst at 220°, approximately 80% of the carbon of the extract and of the residue from the benzene extraction of a Pittsburgh seam coal at 260° has been converted to hydroaromatic oils which may be regarded as the hydrocarbon skeletons of the building units in the respective materials.

Fractionation of these oils followed by charac-

(6) Djakova and Lozovoi, *Compt. rend. Acad. Sci., U. R. S. S.*, **2**, 254 (1935).

terization of the fractions through their molecular weights, boiling points, refractive indices and hydrogen-carbon ratios has given an approximate

distribution of the various sized units in the extract and in the residue.

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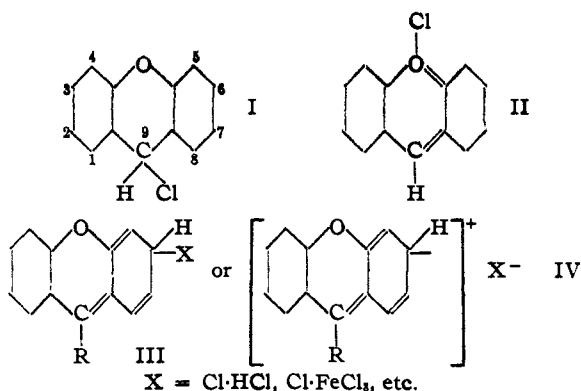
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Reaction between Triarylmethyl Halides and Phenylmagnesium Bromide. III. 9-Phenylxanthy Chloride¹

• BY C. S. SCHOEPFLE AND J. H. TRUESDAIL

In 1901, Werner² found that xanthenol gave a colored solution with hydrochloric acid and concluded that a colored xanthy chloride was formed. Since the benzenoid structure (I) would not ac-

count for the color of this salt, he accepted the oxonium structure (II) which had been assigned to such compounds the year before by Hewitt.³



count for the color of this salt, he accepted the oxonium structure (II) which had been assigned to such compounds the year before by Hewitt.³ Bünzly and Decker⁴ later prepared phenylxanthenol which likewise formed colored salts with mineral acids to which they assigned oxonium structures. Neither Werner nor Bünzly and Decker obtained the pure chlorides but they were able to isolate colored addition products with metallic salts such as ferric chloride and mercuric chloride. Xanthy chloride and phenylxanthy chloride were first prepared in pure form by Gomberg and Cone⁵ and found to be colorless. With dry hydrochloric acid gas, however, phenylxanthy chloride gave a red addition product containing one molecule of hydrogen chloride. The color observed by Werner and by Bünzly and Decker when xanthenols were treated with hydrochloric acid was, therefore, not due to the

chlorides but to the chloride-hydrochlorides which were formed.

Gomberg and Cone assigned a quinonoid structure (III) to the colored addition products of xanthy chlorides because of the close agreement in the properties of these compounds with the corresponding addition products of the triarylmethyl halides. One of the many arguments cited in favor of the quinonoid structure of the latter compounds was the fact that a bromine atom in the para position in bromotriphenylmethyl chloride is labile and is readily replaced when shaken with silver chloride in a sulfur dioxide solution,⁶ while a bromine atom in the ortho or meta position is not replaced under any conditions. The same situation was found to exist with the xanthy halides.⁵ If the bromine atom in bromophenylxanthy halides was in the 3-position, it was readily replaced by chlorine either by shaking with silver chloride in a benzene solution containing a small amount of hydrogen chloride, or merely by treating with excess of dry hydrochloric acid gas at room temperature. However, the bromine atom could not be replaced if it was in the phenyl group which is not a part of the xanthen ring, which showed that the phenyl group does not become quinonoid.

Further evidence that triarylmethyl halides can exist in two modifications was obtained from the reaction of triphenylchloromethane with phenylmagnesium bromide,⁷ where the chloride reacts partly in the benzenoid form to give tetraphenylmethane (usually 5-8% yield), and partly in the quinonoid form to give biphenyldiphenylmethane (50-80% yield).⁸ In the present paper it is shown that 9-phenylxanthy chloride likewise reacts in two forms with phenylmagnesium bromide.

(1) From the Ph.D. dissertation of J. H. Truesdail.

(2) Werner, *Ber.*, **34**, 3300 (1901).

(3) Hewitt, *Z. physik. Chem.*, **34**, 1 (1901); *Ber.*, **34**, 3819 (1901).

(4) Bünzly and Decker, *ibid.*, **37**, 2931 (1904).

(5) Gomberg and Cone, *Ann.*, **370**, 142 (1909); *ibid.*, **376**, 183 (1909).

(6) Gomberg, *Ber.*, **40**, 1861 (1907).

(7) Gilman and Jones, *This Journal*, **51**, 2840 (1929).

(8) Schoepfle and Trepp, (a) *ibid.*, **54**, 4059 (1932); (b) *ibid.*, **58**, 791 (1936).