benzene was refluxed for one hour. There was no evidence of reaction. One gram of aluminum ethoxide was added and reflux resumed. The theoretical quantity of methyl acetate was removed over a five-hour period. The residual liquid was distilled at reduced pressure, and upon refractionation of the distillate some methyl orthosilicate was recovered but none of the fractions decolorized bromine solution. The residue from the original distillation was a black, tarry mass with a pungent odor. Since a monomeric vinyl silicate was not isolated, the question as to whether transesterification occurred prior to or subsequent to polymerization of the vinyl groups is not answered by this experiment.

Reaction of Alkyl Borates.—The results obtained with simple alkyl borates in combination with a silicate ester (methyl orthosilicate) and with carboxylic esters (*n*-butyl acetate and methyl butyrate) are included in Table III. The reaction of butyl borate with methyl orthosilicate is noteworthy in that it provides a convenient means of preparing pure methyl borate, the direct preparation of which is troublesome because of a difficultly separable azeotropic mixture. In no case was a reaction achieved without the aid of a catalyst. Methyl borate could not be made to react with vinyl acetate under any of the conditions tried.

Acknowledgment.—The authors gratefully acknowledge a grant in aid of this work from the Pittsburgh Plate Glass Company, Columbia Chemical Division.

Summary

Transesterification reactions of alkyl silicates with each other and in combination with carboxylic esters can be effected by the use of catalysts such as aluminum chloride, aluminum ethoxide, antimony triethoxide, etc. Under equilibrium conditions mixed esters are obtained in very nearly theoretical proportions, but by continuous or intermittent removal of volatile products the reactions in most cases can be driven to completion. The carboxylic esters show large differences in reactivity, the rate of reaction with methyl orthosilicate decreasing markedly in the order ethyl formate, ethyl acetate, ethyl butyrate and ethyl carbonate. Attempts to introduce vinyloxy groups on silicon by this process are described.

CHICAGO, ILLINOIS RECEIVED AUGUST 31, 1945

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

The Action of Ultraviolet Light upon Cellulose and Cellulose Triacetate[1]

BY E. HEUSER AND GEORGE N. CHAMBERLIN[1c]

The results of previous investigations in this Laboratory on the action of ultraviolet light upon cellulose in a system in which the oxygen had been reduced to an infinitesimal quantity were interpreted as being those of an immediate photochemical reaction.[2] In the discussion which followed the presentation of the first part of this investigation,[3] it was suggested that the ultraviolet light effect might be the result of a photochemical combination of nitrogen with traces of oxygen to form nitrogen di- and tetroxides, followed by hydrolysis of cellulose by the nitrogen oxides in the presence of traces of water left in the exposed sample. A direct combination of nitrogen with oxygen within the wave length range used in these studies (the lower limit being 2300 Å.) is not very probable.[4] Moreover, the results of the second part of the investigation were obtained with nitrogen in which the oxygen had been still further reduced (to 3.4×10^{-4} as compared with $2 \times 10^{-3}\%$).

It also has been suggested that the traces of water (less than 0.02%) would alone suffice to bring about hydrolysis of the cellulose, possibly catalyzed by the ultraviolet light energy.[5] Although such an effect would seem to be possible, it would not explain the fact that irradiated cellulose undergoes the post-irradiation effect,[2] *i. e.*, continues to suffer degradation when stored in air or oxygen. The effect of a simple hydrolysis, even if catalyzed by ultraviolet light, consists of an increase in free aldehyde and hydroxyl groups. If the aldehyde groups were considered as weak spots at which the oxygen would attack in the post-irradiation step, the question arises why unirradiated cellulose, which also contains a considerable number of free aldehyde groups, remains entirely unaffected when exposed to oxygen.[2] Hence, it would appear that, even if accelerated hydrolysis took place in the presence of the traces of moisture left in the sample, it cannot be the only reaction which occurs under the action of ultraviolet light in the absence of air oxygen.

Whereas an attempt to eliminate hydrolysis entirely would have to overcome difficult obstacles, it was thought that the use of purified helium instead of nitrogen would offer a direct means of deciding whether or not the nitrogen oxide argument may be discarded.

Methods

The cotton linters, the ultraviolet lamp, the apparatus, and the techniques used for the exposure and for the puri-

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[1] (a) Prepared for the 1945 Meeting-in-Print, Division of Cellulose Chemistry, A. C. S. (b) Installments III and IV of the series "The Action of Ultraviolet Light upon Cellulose." Installments I and II appeared in THIS JOURNAL, **66**, 753 (1944). (c) The material presented in this paper constitutes a portion of a dissertation submitted by George N. Chamberlin to Lawrence College (The Institute of Paper Chemistry) in partial fulfillment of the requirements of the M.S. degree, June, 1943. Present address, U. S. Navy.

[2] Stillings and Van Nostrand, THIS JOURNAL, **66**, 753 (1944).

[3] Presented by E. Heuser before the Division of Cellulose Chemistry at the 106th Meeting of the American Chemical Society, Pittsburgh, Pa., Sept., 1943.

[4] Ellis, Wells and Heyroth, "The Chemical Action of Ultraviolet Rays," Reinhold Publishing Company, New York, 1941, pp. 324. 431–436.

[5] Montonna and Winding, *Ind. Eng. Chem.*, **35**, 782 (1943).

fication of nitrogen and helium as well as the analytical methods (unless otherwise stated) were those described previously, with only minor changes. The oxygen content of the helium after purification amounted to $4.7 \times 10^{-4}\%$. Forty-gram samples of the cotton linters material were used.

In addition to degree of polymerization (D. P.) and copper number, the carboxyl (uronic acid) content of the preparations was determined by distillation with 12% hydrochloric acid, the carbon dioxide being absorbed by ascarite, and hydrochloric acid being retained by silver phosphate in 85% phosphoric acid.

To ascertain the post-irradiation effect, the samples which had been irradiated in helium (and in nitrogen for comparison) were stored in helium, in nitrogen and in oxygen. The previously described technique was employed.

Prior to exposure to ultraviolet light, the cotton linters powder, which had been predried in a desiccator over anhydrone for eight hours, was subjected to infrared drying at 55° for sixteen hours (instead of eight and ten hours, as in the previous studies). To eliminate error in the determination of the residual moisture of the infrared-dried sample, which occurs through moisture pick-up when the sample is removed for oven drying and weighing,[3] weighed anhydrone tubes were inserted before and after the exposure chamber and were reweighed after infrared drying. This arrangement permitted the dried sample to be left in the exposure chamber and subsequent immediate exposure to the ultraviolet lamp. After the predried sample had been placed in the exposure chamber, the apparatus was alternately evacuated (25 to 50 microns reduced pressure as measured by a Pirâni gage) and flushed six times with purified nitrogen before the infrared lamp was turned on. The moisture content of the predried sample of 1.07% (originally 4.34%) was thus reduced to 0.97%. Infrared drying further reduced it to 0.012%.

Infrared drying had very little influence upon the chemical characteristics of the sample, even after forty-five hours of exposure in an atmosphere of purified nitrogen and after the infrared-dried samples had been stored in air for fifteen days. The results are shown in Table I.

TABLE I

EFFECT OF INFRARED IRRADIATION AND SUBSEQUENT STORAGE UPON THE CHEMICAL CHARACTERISTICS OF COTTON LINTERS POWDER

	Original sample	Irradiated with infrared and stored in air 14 hr.[a]	45 hr.[a]
D. P.	1300	1271 1330	1310 1307
Copper number	0.31	0.31	0.31
Uronic acid as CO_2, %	0.18	0.30	0.29

[a] Infrared irradiation.

The D. P.'s are within the limits of experimental error. The increase in acidity would seem not to be significant. When after the normal infrared drying period of sixteen hours, tank oxygen was allowed to flow through the exposure chamber for ninety-six hours but without ultraviolet irradiation, the chemical characteristics of the sample remained practically unchanged, the D. P. was 1280, the copper number 0.35 and the uronic acid acidity 0.15%.

For ultraviolet radiation, 600-watt UA-32A2 and 600-watt no. 83 Uviarc quartz tubes were used, the latter lamp yielding about twice the ultraviolet light intensity as the former. The time of exposure for all experiments was ninety-six hours and the temperature during the exposure was 55°. The cycle for evacuation and flushing with helium was the same as for nitrogen. After the final flushing, the gas was allowed to flow permanently through the exposure chamber at a rate of 50 ml. per minute. The irradiated samples were stored in purified helium and nitrogen. The effect of storage in oxygen was ascertained only for samples which had been irradiated with the stronger lamp. The storage time was fifteen to sixteen hours in all cases.

All experiments were run in duplicate, the data in the tables being the average values. As in previous studies, the deviation in D. P. for the same sample and for the duplicate sample was not more than 5%, frequently less—*i. e.*, 2 to 3%.

The results of irradiation and storage of the irradiated samples are shown in Table II. It is seen that the irradiation effect of the weak lamp was relatively small. The same lamp, when it was new, had caused a decrease in D. P. from 1250 to 823.[2] However, the results obtained with irradiation in helium were in good agreement with those obtained in nitrogen. It is also seen that the post-irradiation effect was inhibited by the use of helium to the same extent as by nitrogen, regardless of whether the nitrogen-irradiated or the helium-irradiated samples were stored in the two atmospheres. The slight decrease in D. P. and the corresponding slight increases in copper number and acidity which occurred during the storage periods were probably the result of incomplete removal of air oxygen from the storage flasks.

TABLE II

EFFECT OF ULTRAVIOLET IRRADIATION AND STORAGE IN VARIOUS ATMOSPHERES

Weak lamp	Original cotton linters	Irradiation N	Irradiation He	Storage N-irradiated N	Storage N-irradiated He	Storage He-irradiated N	Storage He-irradiated He
D. P.	1300	1180	1175	1147	1120	1130	1120
Copper number	0.31	0.61	0.62	0.80	0.81	0.80	0.80
Uronic acid, %	0.18	0.17	0.17	..	..	0.23	0.23
Strong lamp							
D. P.		1097	1058	1044	0 862	972	0 788
Copper number		0.63	0.62	0.90	1.04	0.89	1.14
Uronic acid, %		0.17	0.18	0.23	0.26	0.21	0.27

The more pronounced irradiation effects obtained with the stronger lamp, as well as the values after storage of the irradiated samples in nitrogen (see lower section of Table II), likewise show good agreement, regardless of whether irradiation took place in nitrogen or in helium. Again, the slight changes which occurred during the storage in nitrogen would seem to be explained by the effect of some residual air oxygen. When nitrogen was replaced by oxygen during storage, the post-irradiation effect was much in evidence and to the same extent, regardless of whether the nitrogen- or the helium-irradiated sample was used.

The results of these experiments would seem to rule out the assumption that the effects of ultraviolet irradiation of cellulose in a nitrogen atmosphere are caused by hydrolysis of nitrogen oxides in the presence of water.

Post-Irradiation Effects with Cellulose Triacetate

An attempt to explain the post-irradiation effect observed with cellulose[2] has been made on

TABLE III

ACTION OF ULTRAVIOLET LIGHT UPON CELLULOSE TRIACETATE AND EFFECT OF STORAGE, USING VARIOUS ATMOSPHERES

		Irradiation		Storage			
				N-irradiated		O-irradiated	
	Unexposed	N	O	N	O	N[c]	O[c]
Acetyl, %	44.8	44.7	14.1	44.2	23.5	13.9	13.1
Copper no.	2.73	2.39	11.65	2.33	4.54	11.60	17.1
Uronic acid as CO_2, %	0.145	...[a]	0.88	0.175	0.38	0.87	0.91
D. P. data	0.412	0.710	1.790	1.542	1.920	1.016	1.710
c = g./liter	.380	.609	1.930	1.501	1.980		
$\eta_{sp.}$	0.0481	0.0740	0.0808	0.1467	0.1440	0.1320	0.0615
	.0438	.0635	.0850	.1390	.1476		
D. P.[b]	234	209	90	190	150	84	72
	231	209	88	186	149		

[a] The *titratable* acidity determined by a modification of Lüdtke's calcium acetate method as used by Yackel and Kenyon [THIS JOURNAL, **64**, 121 (1942)] amounted to 0.078% carboxyl, this value being the same as for the unexposed acetate. For the sample irradiated in oxygen, the value was 0.66%. That the titratable acidity was lower than the uronic acidity is probably explained by the interlocking of carboxyl groups in the 6 positions in lactone rings which did not open completely under the conditions under which the calcium acetate method was employed. [b] The data for the D. P. of the unexposed triacetate in chloroform were as follows: c = g./liter 1.128 and 0.856; $\eta_{sp.}$ 0.1460 and 0.1075; D. P. 244 and 238. [c] For lack of material, the data refer to only one sample.

the assumption that, during irradiation, less accessible glycosidic linkages are not completely ruptured but only weakened—*i. e.*, left in a condition unstable to oxygen and even to air, no post-irradiation effect being observed where the irradiated sample is stored in nitrogen. It would seem possible that the weakening effect is exerted by hydroxyl groups modified under the action of the ultraviolet light energy, particularly those which are in neighbor positions to the glycosidic linkages. Hence, if the free hydroxyl groups in cellulose were covered by ester or ether groups, failure of the irradiated trisubstituted derivatives to undergo the post-irradiation effect would support this hypothesis, whereas a positive effect would show that the hydroxyl groups, even if modified, as they appear to be, are not essentially involved in the reaction which leaves the glycosidic linkages in a condition unstable to oxygen.

It has been known for a long time that commercial cellulose acetates suffer no loss in acetyl when exposed to ultraviolet light in the absence of oxygen, whereas their solution viscosities (and solubilities) decrease.[6] In the presence of air and particularly of oxygen, the loss in acetyl is considerable. Recent results have confirmed these earlier observations.[7]

In the present investigation, 40-g. samples of cellulose triacetate, prepared in the laboratory from the cotton linters used in the previous study (for acetyl content and other data see Table III) were exposed to the action of ultraviolet light in nitrogen and, for comparison, in oxygen and the irradiated samples were subsequently stored in nitrogen and in oxygen. The equipment and techniques used were the same as employed for cotton linters. Likewise, the times for irradiation (ninety-six hours) and for storage (fifteen to sixteen hours) were the same as before, except for the last two series of experiments. Prior to ultraviolet irradiation, the predried triacetate was subjected to infrared drying as described for the cotton linters. The original moisture content of the triacetate was 1.2%.

To remove the acetic acid which results from the loss of acetyl during exposure, the exposed and stored samples were thoroughly washed with alcohol and distilled water and finally with alcohol and ether and further dried in a vacuum oven at 60° for four hours. The specific viscosity ($\eta_{sp.}$) of the triacetate and modified preparations was determined by the cuprammonium hydroxide method. As in previous studies in this Laboratory,[8] the acetyl preparations were dissolved directly in the cuprammonium hydroxide solution, the latter acting as a saponifying agent. The viscosity measured was, thus, that of the regenerated cellulose. Because of the low D. P. range of the cellulose triacetate and the subsequent preparations, the concentrations chosen (calculated for cellulose) were higher than usually employed (see Table III). For converting the specific viscosities into molecular weights and D. P.'s, the Staudinger function and a K_m value of 5.0 × 10^{-4} were employed.[9] A check on the cuam viscosity value of the original triacetate was made by determining its specific viscosity in chloroform solution, using a K_m value[10] of 5.3 × 10^{-4}.

The uronic acid acidity of the triacetate and of the modified preparations were determined by the same method used for the cotton linters. Obviously, the presence of acetyl does not interfere with the carbon dioxide determination. In fact, the triacetate had only a slightly lower uronic acid value (0.14%) than the original cotton linters (0.18%), and the former may thus serve as a blank test. The acidity values given in Table III, however, are the uncorrected values.

The acetyl content of the triacetate and subsequent preparations was determined by the Eberstadt method as modified by Genung and Mallatt.[11] Since in this method an excess of aqueous alkali and titration of the unconsumed alkali are employed, the acetyl values include the carboxyl. However, because of the relatively low carboxyl contents of the preparations (below 1%) the error is small.

The data in Table III show that—as was to be expected—the acetyl content of the triacetate did not change on irradiation in nitrogen but did so to a considerable extent when irradiation took place in oxygen. Although the decrease in D. P. on irradiation in nitrogen was not very pronounced, it would appear, nevertheless, significant, considering the fact that the original D. P. of the triacetate was rather low and that short

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(6) See literature references cited by Heuser. "The Chemistry of Cellulose." John Wiley and Sons, Inc., New York, N. Y., 1944, p. 266.

(7) Lawton and Mason, *Ind. Eng. Chem.*, **36**, 1128 (1944).

(8) Harrison, *Paper Trade J.*, **119**, no. 5, 28 (1944).

(9) Staudinger and Reinecke, *Ann.*, **535**, 47 (1938).

(10) Staudinger and Daumiller, *ibid*, **529**, 246 (1937).

(11) Genung and Mallatt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 369 (1941).

cellulose chains are more resistant to chemical attack than longer ones. The decrease amounted to 13% as compared with a decrease of not more than 15.6% for the cotton linters when the same (strong) lamp was used (see lower section of Table II). On the other hand, the fact that the reducing power of the triacetate remained practically unchanged during irradiation in nitrogen would seem to indicate that the increase which occurs when cellulose itself is irradiated in nitrogen results not alone from the cleavage of glycosidic linkages but also from a modification of the hydroxyl groups, but that the latter is a side reaction not connected with the cleavage of glycosidic linkages. In the triacetate, the acetyl groups obviously prevented the hydroxyl groups from becoming engaged in such side reaction. The fact that the D. P. of the fully *acetylated* cellulose decreased without a corresponding increase in copper number would seem to be in agreement with general experience—*i. e.*, that the decrease in D. P. would have had to be considerably more pronounced to be reflected in a perceptible rise in reducing power. It would appear that this requirement was fulfilled by the conditions under which Montonna and Winding[5] exposed commercial secondary medium-viscosity cellulose acetate film to the action of ultraviolet light in a nitrogen atmosphere. After an exposure of thirty days, the original copper number of 2.0 had increased to 12.1.

On irradiation in oxygen, the D. P., copper number and uronic acid acidity increased considerably. Undoubtedly, the same reactions are involved as when cellulose itself is irradiated in oxygen,[2] and the increases in copper number and acidity are in part a result of the oxidation of deacetylated hydroxyl groups. The fact that uronic acid units were formed shows that at least part of the hydroxyl groups that were oxidized were in the 6 positions.

Lawton and Nason[7] are inclined to explain the decrease in viscosity which they found for their secondary acetate during irradiation in nitrogen as a result either of the action of heat (their exposure temperature was 60° for a total time of 200 to 216 hours) or of traces of oxygen left in the nitrogen-filled tubes containing the sample.

Whether or not these explanations apply in the present investigation, the irradiation effect upon our cellulose triacetate in nitrogen obviously sufficed to induce a rather pronounced post-irradiation reaction. The acetyl content decreased from 44.2 to 23.5%, the D. P. from 188 (or higher) to 150, the copper number increased to 4.54, and the acidity to 0.38%. Again, part of the copper number and acidity increases might be accounted for by oxidation of deacetylated acetyl groups.

That ultraviolet irradiation is a prerequisite for the cellulose triacetate to become attacked by oxygen either in the primary or in the post-exposure reaction, in much the same way as was found for cellulose itself,[2] is seen from the fact that oxygen alone left the triacetate unchanged. A blank test was run with tank oxygen under exactly the same conditions as when ultraviolet light was present. The data obtained are shown in Table IV.

TABLE IV

EFFECT OF OXYGEN ON CELLULOSE TRIACETATE

	Original	Oxygen blank test
D. P.	242	242
Acetyl, %	44.8	44.8
Copper number	2.73	2.5
Uronic acid as CO_2, %	0.15	0.15

The fact that cellulose triacetate was subject to the post-irradiation effect would seem to show that in cellulose itself the hydroxyl groups are not essentially involved in that particular reaction which occurs during irradiation and which weakens the glycosidic linkages to an extent that they are attacked by oxygen.

To extend the parallel with cellulose still further, samples of the triacetate which had been irradiated in an oxygen atmosphere were stored in nitrogen and in oxygen, each for twenty-eight days. The data obtained are shown in the last two columns of Table III. As would have been expected, storage in nitrogen caused practically no changes (compare columns 4 and 7). On the other hand, the only slight decrease in acetyl and D. P. and the only slight increase in acidity which occurred when the oxygen-irradiated sample was stored in oxygen (compare columns 4 and 8) would seem to show that most of the glycosidic linkages which had been weakened by the action of ultraviolet light were already ruptured by the oxygen which was present in the irradiation stage, leaving little to be accomplished during the subsequent storage in oxygen. The high copper number, however, would seem to be in disagreement with this interpretation; possibly it represents a faulty value (see footnote *c* to Table III).

Acknowledgment is due to William H. Shockley, who prepared a portion of the triacetate material and to Dr. J. A. Van den Akker, for having tested the intensity of the ultraviolet lamps and the efficiency of the Vicor-glass filters used in these studies.

Summary

1. Ultraviolet irradiation of cellulose in a helium atmosphere produces the same changes as in nitrogen, which would seem to rule out the possibility that the changes earlier observed in nitrogen resulted from the hydrolysis of cellulose by nitrogen oxides in the presence of water.

2. Samples irradiated either in nitrogen or in helium undergo the post-irradiation effect. Likewise, helium may be used instead of nitrogen for inhibiting the post-irradiation effect.

3. In contrast to cellulose, the reducing power

of cellulose triacetate is not increased by irradiation in nitrogen, and its acetyl content remains unchanged. However, on irradiation in oxygen, far-reaching deacetylation occurs and copper number and uronic acidity increase considerably. The increase of the latter shows that hydroxyl groups in the 6 positions are oxidized.

4. That cellulose triacetate irradiated in nitrogen suffers a pronounced post-irradiation effect seems to show that, in cellulose itself, the hydroxyl groups are not essentially involved in that part of the irradiation reaction which leaves the glycosidic linkages in a condition unstable to oxygen.

5. Oxygen allowed to act upon cellulose triacetate with ultraviolet light excluded produces no changes in D. P., copper number and uronic acid.

6. The behavior of cellulose triacetate which has been irradiated in an oxygen atmosphere toward storage in nitrogen and in oxygen is much the same as previously observed with cellulose itself under the same conditions.

APPLETON, WIS. RECEIVED AUGUST 20, 1945

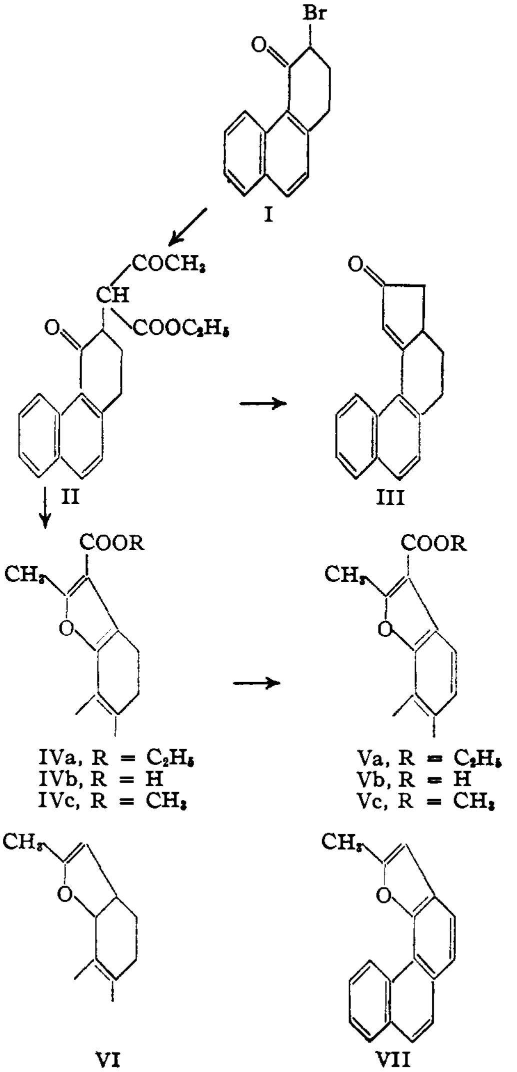
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

2'-Ketodihydro-3,4-cyclopentenophenanthrene and Derivatives of Phenanthro[4.3-*b*]furan[1]

BY A. L. WILDS AND WARREN J. CLOSE

Several years ago it was shown[2] that the diketo ester resulting from reaction of 2-bromo-1-ketotetrahydrophenanthrene with acetoacetic ester, could be cyclized in good yield either to an unsaturated ketone derived from 1,2-cyclopentenophenanthrene or to derivatives of phenanthro[1.2-*b*]furan, depending upon the reagent used. These reactions have now been found to be applicable to the corresponding compounds prepared from 3-bromo-4-ketotetrahydrophenanthrene (I) and, in an accompanying communication, from 2-bromo-1-tetralone.[3]

The bromo ketone I, obtained in 96% yield from 4-ketotetrahydrophenanthrene, was readily converted into the diketo ester II by reaction with sodio-acetoacetic ester. As anticipated, II was cyclized by the action of aqueous potassium hydroxide to $\Delta^{4,3'}$-2'-keto-1,2-dihydro-3,4-cyclopentenophenanthrene (III). However, in contrast to the isomeric ketone prepared previously, the yield of III was affected markedly by the concentration of alkali. After a considerable number of trials the optimum conditions were found to involve preliminary treatment of II with 1% potassium hydroxide (presumably resulting in cleavage to the diketone) followed by 2.5% alkali to effect ring-closure[4,3]; the yield of III was 74%.



I

II

III

IVa, R = C_2H_5
IVb, R = H
IVc, R = CH_3

Va, R = C_2H_5
Vb, R = H
Vc, R = CH_3

VI

VII

The structure of III was confirmed by Clemmensen reduction and dehydrogenation to the known 3,4-cyclopentenophenanthrene,[5] and a comparison was made with an authentic sample of the hydrocarbon kindly furnished by Dr. Bachmann. The picrate and trinitrobenzene derivative, prepared from the two samples of the

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[1] This work was supported in part by a grant from the Wisconsin Alumni Research Foundation.

[2] Wilds, THIS JOURNAL, **64**, 1421 (1942).

[3] Wilds and J. A. Johnson, *ibid.*, **68**, 86 (1946).

[4] Wilds and T. L. Johnson, *ibid.*, **67**, 288 (1945).

[5] Bachmann and Kloetzel, *ibid.*, **59**, 2212 (1937).