TABLE II

COLOR TESTS ON VARIOUS HYDROCARBON SAMPLES

Compound	H_2SO_4		H_2SO_4-HNO_3[a]	H_2SO_4-40% Formalin[a]
	Cold	Warm		
Phenanthrene				
(1) Crude	Yellow	Dark yellow	Red-black	Blue crystals (tan soln.)
(2) Sample (A)	None	Very pale blue	Clear red	Blue crystals (colorless soln.)
(3) (A) treated with Se				
(4) Commercial[b]				
Anthracene[c]	Yellow	Black		Dark brown-black soln.
Fluorene[b]	None	None	Pale yellow	Deep purple soln. (5 min.)

[a] The hydrocarbon was suspended in sulfuric acid and one drop of the second reagent was added.

[b] Gesellschaft für Teerverwertung.

[c] Martin, THIS JOURNAL, **58**, 1438 (1936).

solution in 200 cc. of alcohol was treated with 7.5 g. of zinc dust at 50–60° for twelve hours, the reaction mixture filtered while hot, evaporated to 50–60 cc. and set aside to crystallize. The yield was 4.6 g. (90%) of colorless plates melting at 99–99.5° after one recrystallization.

A portion of this material was heated with selenium to 300–320° for eight hours, distilled under diminished pressure and twice recrystallized from alcohol to give a sample melting at 99.5–100°.

Summary

Phenanthrene of a high degree of purity may be obtained by conversion to the dibromide followed by regeneration of the hydrocarbon on treatment with zinc dust.

Phenanthrene which has been treated with selenium apparently contains an impurity inhibiting the photochemical addition of bromine.

Anthracene has been found to catalyze an equimolecular but not a chain addition of bromine to phenanthrene in the dark.

URBANA, ILLINOIS RECEIVED JULY 1, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A Chemically-Catalyzed cis-trans Isomerization

BY CHARLES C. PRICE AND RALPH S. THORPE

The anthracene-catalyzed bromination of dioxane[1] can be accounted for only by assuming that the reaction between bromine and anthracene produces active bromine. Since many photochemical reactions of bromine presumably proceed through active bromine atoms produced by the dissociation of a bromine molecule on absorption of light, and since the same intermediate has been proposed for several reactions of hydrogen bromide in the presence of peroxides,[2] it was proposed to use one of these reactions to test the possibility that the active bromine produced by the anthracene–bromine reaction in the dark might behave in a similar manner.

The particular reaction studied was the conversion of a maleic ester to the corresponding fumaric ester. Wachholtz and Schmidt[3] have reported previously the photochemical isomerization of the ethyl and methyl esters, respectively, in the presence of bromine. Both investigators agree that the mechanism must be a chain reaction with a length of several hundred, initiated by the photochemical dissociation of bromine molecules to atoms. They represent the course of the reaction as

$$Br_2 + h\nu \longrightarrow 2Br$$
$$M + Br \longrightarrow (MBr) \longrightarrow F + Br$$

More recently Kharasch[2] has proposed a bromine atom intermediate for the peroxide-catalyzed rearrangement of isostilbene to stilbene in the presence of hydrogen bromide, and, on this basis, has extended this proposal of a bromine atom mechanism to the well-known effect of peroxides in reversing the usual mode of addition of hydrogen bromide to many olefinic double bonds.

The investigation reported herein is on the conversion of ethyl maleate to ethyl fumarate by bromine and anthracene in carbon tetrachloride solution.

Experimental.—The reactions were all carried out in purified carbon tetrachloride solution.

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(1) Price and Weaver, unpublished work.

(2) Kharasch, Mansfield and Mayo, THIS JOURNAL, **59**, 1155 (1937).

(3) (a) Wachholtz, *Z. physik. Chem.*, **125**, 1 (1929); (b) Schmidt, *ibid.*, **B1**, 205 (1930).

Ethyl maleate was prepared from the anhydride according to the directions of Wachholtz.[3a] Bromine and anthracene were added to a solution of 1 cc. of the ester in 2.5 cc. of carbon tetrachloride in a painted flask. The bromine color had always faded completely at the end of the reaction so the mixture of the two isomeric esters was obtained by fractional distillation under diminished pressure. The effective removal of carbon tetrachloride was demonstrated by the index of refraction of the ester mixture. Analysis for the percentage conversion was most convenient according to the method developed by Kistiakowsky and Smith[4] with the modification that no special apparatus was necessary for the determination. The production of cloudiness in the clear solution of 0.4 cc. of ester mixture in 0.6 cc. of liquid petroleum could be reproduced readily to within 0.5° using only the naked eye in ordinary daylight. Analysis by this method was accurate to within 1% and scarcely more difficult than an ordinary melting point determination. The results of these various determinations are summarized in Table I.

TABLE I

CONVERSION OF ETHYL MALEATE TO ETHYL FUMARATE BY BROMINE AND ANTHRACENE IN CARBON TETRACHLORIDE

Expt.	Mole % $C_{14}H_{10}$	Mole % Br_2	Time, hours	% ethyl fumarate
9	...	...	48	1
6	...	2.6	312	2
18	...	1.3	27	1
5[a]	...	2.6	288	100
19[a]	...	1.3	26	100
2	5.2	2.6	91	97.5
7	5.2	2.6	24	100
8	2.6	1.3	27	91
10	2.6	1.3	16	81
12	2.6	1.3	5	93
13	2.6	1.3	1	75
14	2.6	1.3	0.5	68
15	2.6	1.3	.25	77
20	2.6	1.3	.08	70
16, 17[b]	2.6	1.3	.5	18, 22

[a] These experiments were exposed to light. [b] In these experiments the bromine-anthracene reaction was completed *before* the ester was added.

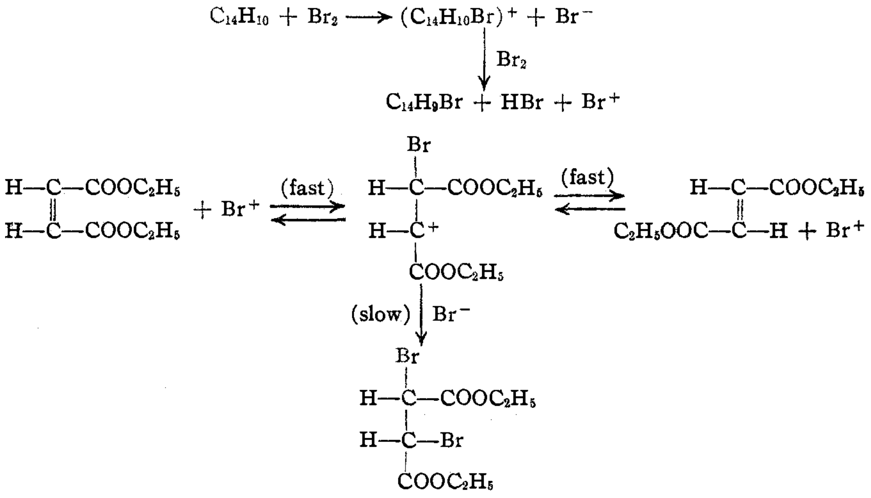
Discussion of Results.—Inspection of this table shows that ethyl maleate was converted rapidly in good yield to ethyl fumarate by the combined action of bromine and anthracene in carbon tetrachloride solution with light rigorously excluded. That the isomerization was indeed due to the combined effect of bromine and anthracene is demonstrated by Experiments 6 and 18 in which bromine alone caused no isomerization in the dark, even after a week, while the reaction in the presence of anthracene requires at most but a few minutes. The photochemical reaction reported by Wachholtz and Schmidt was observed in Experiments 5 and 19 in which bromine alone, exposed to sunlight, caused complete isomerization.

The small proportion of anthracene (1.3%) which was capable of isomerizing a large portion of the maleate is indicative of a fairly long chain mechanism for the conversion in agreement with the previous reports for the photochemical reaction.[3]

Two mechanisms appear plausible for this *cis–trans* isomerization. A bromine atom, as in the photochemical reaction, may be the active intermediate. If such were the only alternative, anthracene must react with bromine in the dark to produce bromine atoms.

$$C_{14}H_{10} + Br_2 \longrightarrow C_{14}H_{10}Br + Br$$

An alternative mechanism, however, involves a bromine cation as active intermediate. In this regard, it may be mentioned that the bromination of dioxane in the presence of anthracene may be best accounted for on the basis of the production



$$\begin{tikzcd} C_{14}H_{10} + Br_2 \arrow[r] & (C_{14}H_{10}Br)^+ + Br^- \arrow[d, "Br_2"] \\ & C_{14}H_9Br + HBr + Br^+ \end{tikzcd}$$

$$\begin{array}{c}H-C-COOC_2H_5\\ \| \\ H-C-COOC_2H_5\end{array} + Br^+ \overset{\text{(fast)}}{\rightleftharpoons} \begin{array}{c} Br\\ | \\ H-C-COOC_2H_5 \\ | \\ H-C^+ \\ | \\ COOC_2H_5\end{array} \overset{\text{(fast)}}{\rightleftharpoons} \begin{array}{c} H-C-COOC_2H_5 \\ \| \\ C_2H_5OOC-C-H\end{array} + Br^+$$

$$\xrightarrow[\text{(slow)}]{Br^-} \begin{array}{c} Br \\ | \\ H-C-COOC_2H_5 \\ | \\ H-C-Br \\ | \\ COOC_2H_5\end{array}$$

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(4) Kistiakowsky and Smith, THIS JOURNAL, **56**, 638 (1934).

of an active bromine cation by the reactions between anthracene and bromine in the dark. On this basis, the conversion of *cis* to *trans* isomers in the dark might then be represented by the series of reactions shown.

The isomerization would thus be a true chain reaction since the bromine cation is constantly regenerated after each conversion.

These results indicate that bromine cations, as well as bromine atoms, may cause rapid isomerization about an olefinic bond. This latter reaction, therefore, must be applied with reservation as a criterion for the presence of bromine atoms.

Summary

The reaction of bromine with anthracene in the dark has been found to catalyze the isomerization of ethyl maleate to ethyl fumarate.

The mechanism of this conversion has been formulated with a positively charged bromine ion as an intermediate.

The subsequent limitation of *cis–trans* isomerization as a criterion for the presence of bromine atoms is pointed out.

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[A CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

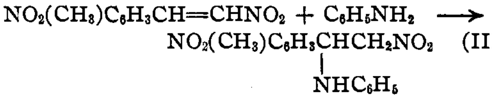
The Action of Ammonia and Aromatic Amines on 4-Methylnitrostyrene and Related Compounds

BY DAVID E. WORRALL

Nitrostyrene has been shown[1] to react with aniline in a manner characteristic of α,β-unsaturated compounds, forming ultimately a saturated β-anilino derivative. That the additive capacity of the unsaturated system toward such substances is slight became apparent when it was discovered that comparatively few reacted in this way, if at all. An attempt[2] to facilitate the reaction by working with a substance incapable of polymerization, namely, bromonitrostyrene, was fruitless as the presence of halogen promoted the formation of Schiff bases. Similar results were obtained by Musante[3] working with nitrostyrenes containing methoxy or oxymethylene groups. A study has now been made of the effect of substituents on the alkylated nitrostyrene, $CH_3C_6H_4CH{=}CHNO_2$ (I).

The ability to add organic bases is entirely lost on the introduction of a methyl group into the ring of nitrostyrene, although the tendency for polymerization or hydrolysis is not greatly changed. It is true that a condensation product of the amine and aldehyde is formed when I reacts with an alcoholic solution of phenylenediamine or benzidine, a reaction that may be interpreted as resulting from the decomposition of an intermediate addition product. Since no reaction takes place with anhydrous benzene as a solvent, it seems apparent that the product is rather the result of hydrolysis and condensation. The additive power of I is not increased by the introduction of bromine in the side chain, but the presence of a nitro group in the ring partially restores the lost reactivity. Addition compounds are formed with aniline and *p*-toluidine, but not with phenylhydrazine.

(II)



$$NO_2(CH_3)C_6H_3CH{=}CHNO_2 + C_6H_5NH_2 \longrightarrow NO_2(CH_3)C_6H_3\underset{\substack{| \\ NHC_6H_5}}{C}HCH_2NO_2$$

(III)

p-Phenylenediamine reacts in a similar manner, both functional groups being involved. With ammonia the reaction is somewhat different inasmuch as the primary addition product reacts further with a second molecule of II.

$$2NO_2(CH_3)C_6H_3CH{=}CHNO_2 + NH_3 \longrightarrow IV$$
$$(NO_2(CH_3)C_6H_3CH[CH_2NO_2])_2NH$$

The introduction of bromine into the side chain of II again cuts down the ability to form addition compounds. No reaction takes place in the absence of water and with wet reagents only unchanged components or products resulting from hydrolysis or destructive decomposition are present.

The nitrostyrene (V) obtained from nitroethane and toluic aldehyde contains an alkyl group in the side chain next to the nitro group as well as in the ring. It shows no tendency to

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[1] Worrall, THIS JOURNAL, **49**, 1598 (1927). This particular substance was first prepared, in another manner, by Tönnies, *Ber.*, **20**, 2986 (1887), although the true structure was pointed out later by Wieland, *ibid.*, **36**, 2564 (1903).

[2] Worrall, THIS JOURNAL, **43**, 919 (1921).

[3] Musante, *Gazz. chim. ital.*, **67**, 579 (1937).