Using our measured heat capacities and the heat of sublimation of deuterium oxide given by Bartholomé and Clusius, we find the calorimetric entropy for $D_2O_{(g)}$ to be 45.89 E. U. at 273.10°K. and one atmosphere pressure. The entropy from spectroscopic data is 46.66 E. U., giving a discrepancy of 0.77 E. U. between the calorimetric and spectroscopic values. This is in good agreement with the theoretical discrepancy 0.806 calculated by Pauling from the assumption of random orientation of the hydrogen bonds in the crystal. This agreement, along with the similar agreement for hydrogen oxide found by Giauque and Stout, is evidence for the correctness of Pauling's theory.

BERKELEY, CALIF. RECEIVED JULY 2, 1936

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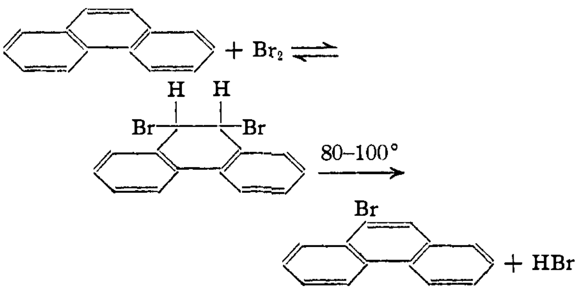
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# A Study of the Phenanthrene–Bromine Addition Reaction

BY CHARLES C. PRICE

Although it has been recognized since the discovery of phenanthrene[1] that the hydrocarbon forms a crystalline dibromide sufficiently stable to be isolated, the interesting reaction has received but little attention and the dibromide has been studied only as an incidental intermediate in the preparation of 9-bromophenanthrene,[2] loss of hydrogen bromide occurring when the substance is gently heated.



Since the reaction affords a model for the widely considered hypothesis that aromatic substitutions in general involve an addition–elimination mechanism, it was thought that a study of the kinetics of both of the above reactions in the presence and absence of halogenation catalysts might cast some light on the broad problem of substitution. That dibromides can be isolated from phenanthrene and anthracene but not from the other common aromatic hydrocarbons is no indication that these substances are different in kind from the others. It probably is merely a consequence of the greater reactivity of the central nucleus of the tricyclic hydrocarbons and of the stabilization of the dihydrobenzenoid nucleus of the addition product by the terminal, aromatic rings.

It was soon found in preliminary experiments that the reaction between phenanthrene and bromine in non-aqueous solvents is reversible, and that the position of the equilibrium and the rate of its establishment are both measurable by analytical methods. Consequently a study was made of the rate and equilibrium of the first reaction, the original problem being reserved for future investigation.

Analysis for bromine by titration was first tried and found to give approximate but unsatisfactory results, and the final measurements were made by colorimetric analysis for bromine with a Keuffel and Esser spectrophotometer. This proved to be a convenient and reliable method of attack. The experimental deviation of ±5% in the equilibrium constants determined by this method represents an error of only ±0.5% in the determination of the bromine concentration.

The phenanthrene used was a sample from coal tar (Gesellschaft für Teerverwertung) further purified by treatment with maleic anhydride,[3] distillation, and crystallization, m. p. 98.2–98.8°, corr. Pure bromine was prepared according to the directions of Scott,[4] dried over resublimed phosphorus pentoxide, and distilled. The purification of the carbon tetrachloride used as solvent was most satisfactorily accomplished by washing commercial material three times with one-tenth volume of concentrated potassium hydroxide in 50% alcohol at 60°, three times with water, three times with one-tenth volume of concentrated sulfuric acid at 25°, thorough washing with water, a

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(1) Fittig and Ostermayer, *Ber.*, **5**, 933 (1872); *Ann.*, **166**, 361 (1873); Graebe, *Ber.*, **5**, 861, 968 (1872); *Ann.*, **167**, 131 (1873).

(2) Hayduck, *Ann.*, **167**, 181 (1873); Anschütz, *Ber.*, **11**, 1217 (1878); Austin, *J. Chem. Soc.*, **93**, 1763 (1908); Sandqvist, *Ann.*, **398**, 126 (1913); Henstock, *J. Chem. Soc.*, **123**, 3097 (1923); Bachmann, THIS JOURNAL, **56**, 1365 (1934).

(3) Clar, *Ber.*, **65**, 852 (1932).

(4) Scott, *J. Chem. Soc.*, **103**, 847 (1913).

preliminary drying over calcium chloride, and distillation from phosphorus pentoxide, b. p. 76–76.5°. The use of sodium as a final drying agent, recommended by several investigators,[5] gave a product containing a slight amount of bromine-absorbing impurity (0.004–0.006%), determined by the decrease in the absorption coefficient with increasing dilution.

The rate as well as the equilibrium for the addition of bromine to phenanthrene follow quite as would be expected from the equation of the reaction

$$C_{14}H_{10} + Br_2 \underset{k_1}{\overset{k_2}{\rightleftharpoons}} C_{14}H_{10}Br_2$$

The equilibrium constant $K$ is defined as follows:

$$K = \frac{[C_{14}H_{10}Br_2]}{[C_{14}H_{10}][Br_2]} = \frac{k_2}{k_1}$$

where $k_1$ and $k_2$ represent the rate constants for the reactions as indicated.

The rate constant for the bimolecular forward reaction, $k_2$, is calculated from the expression for a bimolecular forward reaction corrected for a monomolecular back reaction

$$dx/dt = k_2(a - x)(b - x) - k_1x$$

Substitution for $k_1$ of its value as determined from the expression for the equilibrium constant, $k_1 = k_2/K$, and integration lead to the following expression for $k_2$.

$$k_2 = \frac{2.303}{t\sqrt{-q}}\left[\log\frac{2x - (a + b + 1/K) - \sqrt{-q}}{2x - (a + b + 1/K) + \sqrt{-q}} - \log\frac{-(a + b + 1/K) - \sqrt{-q}}{-(a + b + 1/K) + \sqrt{-q}}\right]$$

where $a = [Br_2]_{i\,(\text{initial})}$, $b = [C_{14}H_{10}]_i$, $x = [Br_2]_i - [Br_2]_{t\,(\text{at time t})}$, and $-q = (a+b+1/K)^2 - 4ab$.

The experimentally determined values for these constants at 15.7, 25.0 and 39.0° are shown in Tables I and II. On plotting log $K$ at these three temperatures against $1/T$, the points are observed to fall accurately on a straight line. The rate constants are all calculated from the starting time. In the determination of the rate constants for expts. 1–6 the light of the spectrophotometer was on during the entire course of the reaction, the rate constants increasing steadily due to catalysis by the light. In the remaining experiments the light was on for only about thirty seconds of every five minutes, and this seemed to have no appreciable effect on the rate of the reaction, the rate constants showing no systematic deviation either with the concentration or amount

TABLE I

EQUILIBRIUM AND RATE CONSTANTS FOR THE ADDITION OF BROMINE TO PHENANTHRENE AT 25.0°

| Expt. | $[Br_2]_i$[a] | $[C_{14}H_{10}]_i$ | $K$ | $k$ |
|---|---|---|---|---|
| 1 | 0.00696 | 0.00476 | 239 | 23–36[b] |
| 2 | .00555 | .00456 | 236 | 26[b] |
| 3 | .00555 | .00727 | 226 | 24–26[b] |
| 4 | .00699 | .00871 | 229 | . . . |
| 5 | .00699 | .00692 | 218 | 10–27[b] |
| 6 | .00699 | .01087 | 213 | 9–18[b] |
| 7 | .00845 | .00431 | 224 | 10–12.4 |
| 8 | .00845 | .01043 | 219 | 11–14 |
| 9 | .00845 | .01495 | 225 | . . . |
| 10 | .00845 | .00824 | 230 | . . . |
| 12 | .03405 | .02997 | 241 | 11–12.6 |
| 13 | .03405 | .00889 | 223 | 12–13.5 |
| 14 | .03405 | .02268 | 219 | 7–8 |
| 15 | .00655 | .01188 | 241 | 9–13.5 |
| 18 | .00655 | .00900 | 237 | . . . |
| 19[c] | .00841 | .00904 | 236 | 9–11.5 |
| 20 | .00841 | .01181 | 221 | 8–11.5 |
| 25 | .00873 | .01433 | 240 | 9–13 |
| 32 | .00542 | .01202 | 232 | 6–6.5 |
| 96[d] | .00788 | .01063 | 224 | . . . |
| 97[d] | .00782 | .00839 | 240 | . . . |
|  |  | $K_{25°}$ = | 230 |  |

[a] Concentrations expressed in moles per liter. [b] Spectrophotometer light on during entire course of experiment. [c] Oxygen removed from solvent by boiling under diminished pressure.[6] [d] Synthetic phenanthrene of Fieser and Hershberg, THIS JOURNAL, 57, 2192 (1935), used in these experiments after further selenium dehydrogenation and recrystallization, m. p. 100.7–101°, corr.

TABLE II

EQUILIBRIUM AND RATE CONSTANTS FOR THE ADDITION OF BROMINE TO PHENANTHRENE AT 39.0 AND 15.7°

| Expt. | $[Br_2]_i$ | $[C_{14}H_{10}]_i$ | $K$ | $k$ |
|---|---|---|---|---|
| 33 | 0.01042 | 0.00892 | 132 | 7–9.5 |
| 34 | .01042 | .00714 | 134.5 | 8–11 |
| 35 | .00628 | .00440 | 139 | 9.5–10.5 |
| 36 | .00628 | .01004 | 132.5 | 6.5–8 |
| 37 | .00628 | .00656 | 134.5 | 7.5–9 |
| 38 | .00628 | .00718 | 132 | 10–11 |
|  |  | $K_{39°}$ = | 134 |  |
| 39 | .00946 | .00890 | 322 | 6.5–8.5 |
| 40 | .00946 | .00648 | 358 | 8.5–9.5 |
|  |  | $K_{15.7°}$ = | 340 |  |

TABLE III

SUMMARY OF THE EQUILIBRIUM DATA FOR THE ADDITION OF BROMINE TO PHENANTHRENE

| Temp., °C. | $K$ | $-\Delta F$ (cal.) | $-\Delta H$ (cal.) | $\Delta S$ (cal./deg.) |
|---|---|---|---|---|
| 15.7 | 340 (±8) | 3350 (±10) |  |  |
| 25.0 | 230 (±6) | 3220 (±15) | 7350<br>(±250) | 13.8 |
| 39.0 | 134 (±2) | 3040 (±15) |  |  |

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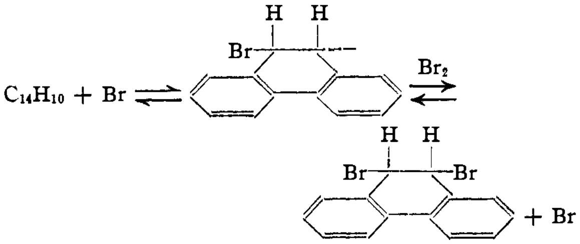
[5] Berthoud and Béraneck, *J. chim. phys.*, **24**, 213 (1927); Bauer and Daniels, THIS JOURNAL, **56**, 378 (1934).

of reaction. Table III summarizes the equilibrium data, including $\Delta F$, $\Delta H$ and $\Delta S$, for the addition of bromine to phenanthrene. The limits indicated are calculated from the average deviation of the equilibrium constants.

The inhibitory effect of oxygen noted by Bauer and Daniels[6] in a study of the addition of bromine to cinnamic acid was not noticeable in this reaction (expt. 19). Benzoyl peroxide also had no effect on either the rate or the equilibrium, nor did the antioxidant β-naphthol. It was discovered, however, that such antioxidants as diphenylamine, hydroquinone, tetrabromohydroquinone and tetrabromocatechol are very effective inhibitors of the reaction, even in relatively small amounts. It appears significant that the distinctive feature of these inhibitors is the fact that they may readily donate *atoms* of hydrogen and revert to stable compounds, namely, tetraphenylhydrazine or a quinone.

These facts all find ready explanation on the basis of a chain mechanism for the addition of bromine to phenanthrene, propagated by bromine atoms and free radicals as follows



a type of mechanism which has been proposed by several investigators studying photochemical bromination reactions.[7] It is suggested that the inhibitor functions by interaction with the bromine atoms, yielding hydrogen bromide and either tetraphenylhydrazine or a quinone. Lauer,[8] in a recent series of papers on the bromination of various aromatic hydrocarbons does not seem to consider fully the possibility of a chain mechanism in the deduction of his conclusions.

This inhibitory effect not only indicates that the reaction proceeds through a chain mechanism but makes possible an estimation of the length of the chain, a determination which usually is made only through a photochemical study of quantum yield. If, for instance, the concentration of the inhibitor is one-tenth that of the phenanthrene, it may be assumed that the chain length is approximately ten, since the chances are ten to one in favor of a bromine atom colliding with a molecule of phenanthrene, thus propagating the chain rather than hitting a molecule of inhibitor and interrupting the chain. Multiplication of the ratio of phenanthrene to inhibitor by the ratio of the uninhibited rate to inhibited rate will then give the length of the chain in the case of the uninhibited reaction. The validity of the above assumption regarding the chain length of the inhibited reaction depends chiefly on two conditions, namely, the equality of the activation energy for the reactions between bromine atoms and phenanthrene or inhibitor, and the equivalence of the steric factors involved in these two reactions. The assumption implies that the fraction of effective collisions between bromine atoms and molecules of inhibitor is the same as that for the collisions between bromine atoms and phenanthrene. The quantitative identity of the results using diphenylamine, tetrabromocatechol, and tetrabromohydroquinone seems to substantiate the validity of the assumption, and to indicate the probability that all of the above collisions result in reaction, since if either a steric effect or activation energy were a factor it would not be expected to be the same in each case.

It should be pointed out that in the determinations of the chain length by this method, the inhibitor was added in quantity sufficient so that the ordinary chain-stopping process could be neglected as compared with the interruption of the chain by the inhibitor. The results of the experiments at 25° are shown in Table IV. In each case the experiment with less inhibitor gave a lower value for the chain length, possibly due to decrease in inhibitor concentration by reaction with bromine atoms, an effect which would natu-

TABLE IV

EFFECT OF VARIOUS INHIBITORS ON THE RATE OF ADDITION OF BROMINE TO PHENANTHRENE AT 25 AND 36°

| Inhibitor | $[C_{14}H_{10}]/[\text{Inhib.}]$ | $k$ | Chain length |
|---|---|---|---|
| Diphenylamine | 38.8 | 0.18 | 2500[a] |
| Diphenylamine | 144 | .85 | 1850[a] |
| Tetrabromocatechol | 33.6 | .18 | 2050[a] |
| Tetrabromocatechol | 105 | .84 | 1400[a] |
| Tetrabromohydroquinone | 43 | .25 | 1900[a] |
| Tetrabromohydroquinone | 105 | .70 | 1650[a] |
| Tetrabromohydroquinone | 70.6 | .67 | 1000[b] |
| Tetrabromohydroquinone | 145 | 1.2 | 1200[b] |

[a] Calculated for $k_{25°} = 11$. [b] Calculated for $k_{36°} = 10$.

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[6] Bauer and Daniels, THIS JOURNAL, **56**, 2014 (1934).

[7] Berthoud and Béraneck, *J. chim. phys.*, **24**, 213 (1927); Wachholtz, *Z. physik. Chem.*, **125**, 1 (1928).

[8] Lauer, *Ber.*, **69**, 141, 146, 851, 978, 1061 (1936).

rally be increasingly noticeable with decreasing concentration of inhibitor. For this reason the higher values are perhaps the more nearly correct.

It is necessary to reconcile the interpretation of the results in terms of a chain mechanism with the observed second order kinetics. In studies of photochemical brominations,[5,7] which apparently proceed by chain reactions, the initiating reaction is the photochemical dissociation of bromine molecules to atoms, the experimentally determined rates being proportional to the first power of the bromine concentration alone. That the rate in the present case is dependent also upon the concentration of phenanthrene can be accounted for by assuming that the chain initiating reaction is

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

It is further necessary to assume that the length of the chain remains sensibly constant during the course of the reaction. A calculation of the variation of this factor with changing concentrations of the reactants was made on the basis of the following mechanism, the same as that proposed by Berthoud and by Wachholtz[7] for the addition of bromine to ethylenic double bonds, except that in the present case the chain-initiating reaction is not the photochemical dissociation of bromine.

(1) $C_{14}H_{10} + Br_2 \longrightarrow C_{14}H_{10}Br + Br$ $k_1$
(2) $C_{14}H_{10} + Br \longrightarrow C_{14}H_{10}Br$ $k_2$
(3) $C_{14}H_{10}Br + Br_2 \longrightarrow C_{14}H_{10}Br_2 + Br$ $k_3$
(4) $C_{14}H_{10}Br + Br \longrightarrow C_{14}H_{10}Br_2$ (or $C_{14}H_{10} + Br_2$) $k_4$
(5) $C_{14}H_{10}Br \longrightarrow C_{14}H_{10} + Br$ $k_5$
(6) $C_{14}H_{10}Br_2 + Br \longrightarrow C_{14}H_{10}Br + Br_2$ $k_6$
(7) $C_{14}H_{10}Br_2 + Br_2 \longrightarrow C_{14}H_{10}Br + Br_3$ (or $Br + Br_2$) $k_7$

Reaction 7 is included since a solution of phenanthrene dibromide alone is quite stable and its dissociation proceeds only on the addition of a small amount of bromine.

If now the chain length, $\alpha$, is placed equal to the ratio of the chain-propagating reactions to the chain-interrupting reactions

$$\alpha = \frac{k_2[C_{14}H_{10}][Br] + k_3[C_{14}H_{10}Br][Br_2]}{k_4[C_{14}H_{10}Br][Br]}$$

it is necessary only to obtain the concentrations of the intermediates, $C_{14}H_{10}Br$ and Br, in terms of the reactants by setting up and solving the equations of the steady state in order to obtain an expression for the chain length in terms of definitely determinable quantities. Making the one simplifying assumption that $k_6[C_{14}H_{10}Br_2]$ is negligible as compared with $k_2[C_{14}H_{10}]$, since the rate of the forward reactions must be greater than the back reactions due to the position of the equilibrium and since the concentration of the dibromide is at most equal to that of the phenanthrene at the dilution in question, the following expression can be derived:

$$\alpha^2 = 3\,\frac{k_2k_3}{k_1k_4} + \frac{k_2k_5}{k_1k_4}\,\frac{1}{[Br_2]} + \frac{k_2k_3^2}{k_1k_4}\left(\frac{[Br_2]}{k_3[Br_2] + k_5}\right)$$

A two- or three-fold change in bromine concentration, as was the case in the measurements, should have but little effect on $\alpha^2$, even less on $\alpha$ itself.

A probable reason for the lack of temperature coefficient was indicated by the results of determinations of the chain length at 36°. At this temperature the chain-initiating reaction should have approximately twice the rate at 25°, but compensating for this factor it was found that the chain length had decreased from about 2000 to 1000. The results of these experiments are shown in Table IV.

One other very interesting phenomenon discovered in the course of the work was the phenanthrene-induced bromination of dioxane, and the observations offer further support for the proposed mechanism for the initiation of the bromine–phenanthrene reaction. A solution of bromine in dioxane was found to be completely stable at room temperature or slightly above, but the addition of phenanthrene causes a rapid absorption of bromine, not only by addition to phenanthrene ($^1/_3$) but by bromination of the dioxane ($^2/_3$). The phenomenon has not been thoroughly investigated but the results suggest the following mechanism:

$$\begin{array}{rcl} C_{14}H_{10} + Br_2 & \longrightarrow & C_{14}H_{10}Br + Br \\ C_{14}H_{10}Br + Br_2 & \longrightarrow & C_{14}H_{10}Br_2 + Br \\ C_4H_8O_2{\cdot}Br_2 + 2Br & \longrightarrow & C_4H_6Br_2O_2 + 2HBr \\ & & \big\downarrow H_2O \\ & & 2CH_2OH{\cdot}CHO + 2HBr \end{array}$$

This accounts for the observed ratio of hydrogen bromide produced to bromine absorbed. A positive Fehling's test showed the presence of an aldehyde. The reaction is to be studied further.

The author wishes to express his grateful appreciation to Professor Louis F. Fieser both for proposing the problem and for inspiration to its successful completion. Acknowledgment is also due Dr. Paul D. Bartlett for much helpful advice and criticism.

## Summary

1. The rate and equilibrium for the addition of bromine to phenanthrene have been measured.

2. Evidence for a chain mechanism has been presented, as well as a method for the determination of its length.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS. RECEIVED JULY 3, 1936

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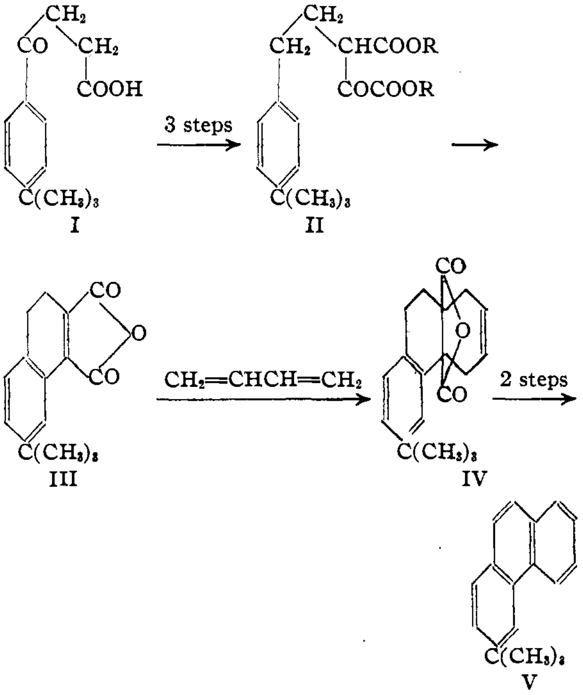
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# The Effect of Substituents on the Phenanthrene–Bromine Addition Reaction

BY LOUIS F. FIESER AND CHARLES C. PRICE

Following the observation[1] that the addition of bromine to phenanthrene proceeds to a measurable equilibrium at a conveniently measurable rate, it became of interest to investigate the effect of substituent groups in the terminal rings on the free energy and rate of the reaction. It seemed desirable to study compounds having substituents belonging to the three types distinguished by the nature of the directive influence which they exert on aromatic substitutions, and attention was directed first to 2- and 3-substituted phenanthrene derivatives since these are more readily available than the 1- and 4-isomers. As representative compounds with meta-directing groups the 2- and 3-carboxylic esters of phenanthrene were selected and found satisfactory. Halogen atoms constitute a special class of substituent since they retard substitution in the benzene ring like meta groups yet direct to the ortho–para positions, but of the compounds desired only 3-chlorophenanthrene[2] had been described at the time our work was undertaken. The 2- and 3-halophenanthrenes, however, were conveniently obtained from the acetyl compounds[3] through the oximes, acetylamines and amines, a method which has been reported by Bachmann and Boatner[4] in a preliminary communication published since the completion of our work.

It was a more difficult matter to find suitable 2- and 3-phenanthrene derivatives having ortho–para directing groups of the type that facilitate aromatic substitutions. A too powerfully directing group would lead to substitution in the terminal nucleus rather than 9,10-addition, and this apparently is the case with the methoxy- and acetylamino-phenanthrenes for they rapidly absorb more than one mole of bromine irreversibly in carbon tetrachloride solution. The same observation was made with 3-ethylphenanthrene, and it is possible that in this case the principal reaction is a side-chain substitution. The phenanthryldimethyl carbinols were investigated but they proved to be too unstable. Finally the tertiary butyl compounds were synthesized and found entirely satisfactory for the purpose. 3-*ter.*-Butylphenanthrene (V) was obtained by the synthetic method of Fieser and Hershberg[5] starting with the keto acid I resulting from the condensation of *ter.*-butylbenzene with succinic anhydride.



The structure was established by conversion to *p*-*ter.*-butylbenzoic acid and terephthalic acid. The addition of butadiene to III and the remaining steps all proceeded very satisfactorily, affording

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[1] Price, THIS JOURNAL, **58**, 1834 (1936).

[2] Sandqvist, *Ann.*, **396**, 116 (1909).

[3] Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930).

[4] Bachmann and Boatner, *ibid.*, **58**, 857 (1936).

[5] Fieser and Hershberg, *ibid.*, (a) **57**, 1851 (1935); (b) **57**, 2192 (1935).