

Canadian Journal of Chemistry

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOLUME 40

JULY 1962

NUMBER 7

REACTIONS OF 2,3,5,6-TETRAKIS(β -HYDROXYETHYLMERCAPTO)-1,4-HYDROQUINONE AND RELATED COMPOUNDS

MARSHALL KULKA

Research Laboratories, Dominion Rubber Company Limited, Guelph, Ontario

Received February 19, 1962

ABSTRACT

The treatment of chloranil (I) with alkali and 2-mercaptoethanol resulted not only in replacement of the chlorine atoms but also in reduction to form 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (II). The conditions for the preparation of 2,3,5,6-tetrakis(β -chloroethylmercapto)-1,4-hydroquinone (III) from II differed from those required for the preparation of a lower-melting compound (IV) from II by such a narrow margin that exact control of temperature and concentration were necessary in order to avoid erratic behavior in the preparation. The structure of the lower-melting compound has been established as 2,3-dihydro-5,7,8-tris(β -chloroethylmercapto)-6-hydroxy-1,4-benzoxathiin (IV) by analyses and cyclization reactions. The treatment of 2,3-dichloro-1,4-naphthoquinone (VIII) with 2-mercaptoethanol yielded 2,3-bis(β -hydroxyethylmercapto)-1,4-naphthoquinone (IX) and not the quinol as was the case with chloranil. The quinone (IX) could not be converted to 2,3-bis(β -chloroethylmercapto)-1,4-naphthoquinone by treatment with hydrogen chloride because under these conditions only 1,4-oxathio-5,10-anthraquinone (X) was formed. A mechanism for the formation of X which involves intramolecular addition, elimination, and cyclization is described.

A few years ago 2,3,5,6-tetrakis(β -chloroethylmercapto)-1,4-hydroquinone (III) was synthesized in this laboratory in connection with another project. This "four-pronged" sulphur mustard was then submitted to the National Institutes of Health, Bethesda, Maryland, U.S.A., for evaluation in cancer chemotherapy. Preliminary screening results showed it to be active and curative to some extent. This provided a stimulus for further study and a second attempt to prepare III was made. Surprisingly enough the original preparation could not be duplicated and instead of III a lower-melting compound was isolated in high yield. The identification of this lower-melting compound and the explanation for the erratic behavior experienced in the preparation of III constitute the subject of this paper.

The synthesis of 2,3,5,6-tetrakis(β -chloroethylmercapto)-1,4-hydroquinone (III) consisted of two steps—the preparation of 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (II) from chloranil (I) followed by the conversion of II to III. It was the second step of the synthesis (II \rightarrow III) which proved troublesome.

In the first step, the treatment of chloranil (I) with 2-mercaptoethanol in the presence of potassium hydroxide resulted in two simultaneous reactions—the displacement of the chlorine atoms by β -hydroxyethylmercapto groups and the reduction of the quinone to form 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (II). 2-Mercaptoethanol proved to be such a powerful nucleophile (as well as a reducing agent) that it attacked

other substituted benzoquinones besides I. Thus when 2,5-dichloro-3,6-bis(dimethyl-amino)-1,4-benzoquinone or 2,5-dichloro-3,6-di-N-morpholino-1,4-benzoquinone (1) was heated with 2-mercaptoethanol and pyridine, II was formed in high yield. The reduction of chloranil (I) to the quinol by mercaptides with the accompanying nucleophilic attack has been observed before when I was treated with ω -mercapto fatty acids (2, 3).

The second step in the synthesis of III, which required the conversion of the hydroxy compound II to 2,3,5,6-tetrakis(β -chloroethylmercapto)-1,4-hydroquinone (III), presented difficulties. Thionyl chloride could not be used for this purpose because II was completely insoluble in cold thionyl chloride and the hot reagent caused decomposition. However, 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (II) dissolved readily in cold concentrated hydrochloric acid and when the solution was allowed to stand at room temperature a white precipitate deposited. Analyses and melting point of this product indicated that it was incompletely chlorinated. However, the crude precipitate was now quite soluble in chloroform and the completion of the chlorination could be accomplished with thionyl chloride in chloroform solution. The conversion of II to III was therefore satisfactorily accomplished by the consecutive treatment with concentrated hydrochloric acid and thionyl chloride at room temperature.

Some time after this method of conversion (II \rightarrow III) was developed, an attempt was made to repeat it. It was found that the treatment of II with concentrated hydrochloric acid at room temperature followed by the reaction with thionyl chloride gave a low-melting compound in high yield and no III. After considerable experimentation it became evident that the conditions required for the preparation of III and those for the preparation of the lower-melting compound differed by a small margin only and that "room temperature" had to be defined more precisely. Precise conditions for the preparation of III and those for the preparation of the lower-melting compound are described in the experimental section.

The lower-melting compound, which formed at lower temperatures (20–25°) in strong hydrochloric acid, was shown to be a product of cyclization. Analyses showed the presence of one phenolic group and three β -chloroethylmercapto groups and that its empirical formula was one hydrogen chloride molecule less than that of III. On this basis the structural formula IV was proposed. A study of the properties of this compound gave support to the postulated structure IV.

Pyrolysis of IV yielded ethylene dichloride. The liberation of ethylene dichloride on heating is characteristic of compounds bearing reactive β -chloroethylmercapto substituents (4). Infrared spectra showed the presence of a phenolic hydroxyl and this was confirmed by acetylation. The treatment of IV with 1 mole of alcoholic potassium hydroxide caused dehydrochlorination and cyclization to form 2,3,8,9-tetrahydro-5,6-bis(β -chloroethylmercapto)benzo(1,2-*b*:4,3-*b'*)bis(1,4-oxathiin) (V). The structure V was chosen in preference to the other possible isomer VI because V yielded on pyrolysis a tetracyclic compound VII which sublimed *in vacuo*. The isomer VI would be expected to yield on pyrolysis a polymer which would not sublime. Further support for the assignment of the structure IV lies in the fact that when 2,3,5,6-tetrakis(β -chloroethylmercapto)-1,4-hydroquinone (III) was treated with 2 moles of potassium hydroxide a double ring closure occurred to form the same tricyclic compound V as was obtained from IV by a similar treatment.

The properties of chloroquinones and their derivatives in the naphthalene series differed from those of the benzene series. Unlike chloranil, 2,3-dichloro-1,4-naphthoquinone (VIII) reacted with 2-mercaptoethanol and potassium hydroxide to give mostly tar and



a small yield of an orange-colored compound. When pyridine was substituted for the potassium hydroxide and the temperature strictly controlled a high yield of the orange-colored compound was obtained. This proved to be 2,3-bis(β -hydroxyethylmercapto)-1,4-naphthoquinone (IX) and not the quinol as was the case in the benzoquinone series. All attempts to convert IX to the sulphur mustard 2,3-bis(β -chloroethylmercapto)-1,4-naphthoquinone were unsuccessful. The treatment of IX with thionyl chloride, or with alcoholic hydrogen chloride, or with acetic acid - hydrogen chloride yielded in each case a chlorine-free black compound which sublimed readily *in vacuo* and crystallized as sparkling black crystals. Infrared spectra showed the presence of carbonyl group(s), the absence of hydroxyl groups, and analyses indicated the structure to be 1,4-oxathia-5,10-anthraquinone (X). Apparently this was formed by displacement of one of the β -hydroxyethylmercapto groups and cyclization.

There is one example in the literature (5) of displacement of a β -hydroxyethylmercapto group from 2,3,5,6-tetrachloro-1,4-bis(β -hydroxyethylmercapto)benzene but in this case it occurred in alkaline solution. However, the displacement of methoxy groups in the benzoquinone series by other alkoxy groups (6), by amines (1, 7, 10), and by other groups (1, 7, 8) is not uncommon.

The mechanism of the conversion of IX to X is probably similar to that proposed by Fieser (9) for the methylation of 2-hydroxy-1,4-naphthoquinone by methanolic hydrogen chloride. Intramolecular addition of one hydroxyl group to the conjugated system of the quinone IX occurs to form the intermediate XI. From this, mercaptoethanol is eliminated to form the oxathianthraquinone X.

EXPERIMENTAL

2,3,5,6-Tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (II)

(a) From Chloranil (I)

To a stirred solution of 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil) (100 g) in benzene (3.5 l.) warmed up to 45° was added dropwise a solution of 2-mercaptoethanol (200 ml) and potassium hydroxide (96 g) over 2 hours. The temperature of the reaction mixture dropped to 41° during the first few minutes and then rose gradually to 48°. The stirring was continued for another 2 hours. The dark, sticky material which precipitated changed gradually to a light-colored solid which floated in the stirred benzene. The reaction mixture was allowed to stand overnight and then the benzene was decanted from the sticky solid. The solid was stirred with cold water for $\frac{1}{2}$ hour, filtered, washed, and dried, m.p. 141-143°; yield 138 g. Crystallization from aqueous methanol yielded (120 g; 72%) yellowish sparkling crystals melting at 144-145°. Anal. Calc. for $C_{14}H_{22}O_6S_4$: C, 40.58; H, 5.31. Found: C, 40.55; H, 5.18.

Infrared spectra of this compound indicated that it was the quinol and not the quinone. Furthermore, on treatment with zinc and acetic acid, II remained unchanged.

(b) From 2,5-Dichloro-3,6-dimorpholino-1,4-benzoquinone

To a solution of 2,5-dichloro-3,6-dimorpholino-1,4-benzoquinone (3 g) (1) in benzene (250 ml) was added 2-mercaptoethanol (10 ml) and pyridine (10 ml), and the dark reaction mixture heated under reflux for 15 hours. The benzene was removed from the light-colored mixture, the residue was treated with water, and the solid was filtered and crystallized from aqueous methanol. The sparkling crystals (2 g) melted at 144-145° alone or in admixture with those obtained in (a).

(c) From 2,5-Dichloro-3,6-di(N,N-dimethylamino)-1,4-benzoquinone

2,5-Dichloro-3,6-di(N,N-dimethylamino)-1,4-benzoquinone (1) was treated with 2-mercaptoethanol as above. The chloro as well as the dimethylamino groups were replaced and reduction occurred to form 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (IV) in 70% yield.

2,3,5,6-Tetrakis(β -acetoxylethylmercapto)-1,4-hydroquinone

(a) Using Acetic Anhydride

To a solution of 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (II) (5 g) in pyridine (15 ml) was added acetic anhydride (10 ml) and the solution was heated under reflux for 2 hours. The pyridine and excess anhydride were removed *in vacuo*. The residue was pulverized, washed with water, and the white solid (6.5 g) was crystallized three times from methanol. This yielded white prisms melting at 90-91°. Anal. Calc. for $C_{22}H_{30}O_{10}S_4$: S, 21.99. Found: S, 22.42, 22.52.

(b) *Using Acetic Acid and Hydrogen Chloride*

Into a solution of 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (II) (35 g) in acetic acid (750 ml) at 60°, hydrogen chloride gas was passed until saturation, and the solution was allowed to stand overnight. The acetic acid was removed *in vacuo* from the amber solution and the residue was crystallized from benzene. The white needles (32 g) melted at 85–87°. Two further crystallizations from methanol yielded a product melting at 90–91° alone or in admixture with that obtained in (a).

2,3-Dihydro-5,7,8-tris(β -chloroethylmercapto)-6-hydroxy-1,4-benzoxathiin (IV)

(a) *Using Hydrochloric Acid Saturated with Hydrogen Chloride*

A solution of 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (II) (25 g) in concentrated hydrochloric acid (250 ml) was saturated with hydrogen chloride at room temperature (20°) and the resulting solution was allowed to stand overnight. The hard cake which precipitated was separated from the hydrochloric acid, pulverized, washed with water, and dried. This crude product (27 g), which melted at 98–105°, was dissolved in chloroform (100 ml) and treated with thionyl chloride (15 ml) at 30° in order to complete the chlorination. The solution was allowed to stand overnight and then the solvent was removed *in vacuo* and the residue crystallized from benzene. White needles (20 g) arranged in rosettes and melting at 129–130° were obtained. Repeated recrystallizations did not raise the melting point. Anal. Calc. for $C_{14}H_{17}Cl_3O_2S_4$: C, 37.21; H, 3.76; Cl, 23.6; S, 28.3. Found: C, 37.55, 37.27; H, 3.90, 3.67; Cl, 23.64, 23.19; S, 29.01, 28.84.

(b) *Using Concentrated Hydrochloric Acid*

In several other experiments the saturation of the concentrated hydrochloric acid solution with hydrogen chloride was omitted. The results obtained were the same as in (a). However, in a few runs the 2,3-dihydro-5,7,8-tris(β -chloroethylmercapto)-6-hydroxy-1,4-benzoxathiin (IV) was not obtained but instead the higher-melting 2,3,5,6-tetrakis(β -chloroethylmercapto)-1,4-hydroquinone (III) (see below) was formed. It is believed that the runs which yielded III were performed on hot and humid days.

(c) *Using a Higher Temperature*

A solution of 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (10 g) in concentrated hydrochloric acid (100 ml) was heated at 35–37° for 6 hours. The white, sticky precipitate was extracted with chloroform and the chloroform solution dried and treated with thionyl chloride (5 ml) as in (a). The yellow crystals (4.5 g) which precipitated melted at 175–176° and proved to be 2,3,5,6-tetrakis(β -chloroethylmercapto)-1,4-hydroquinone (III) (see below). The mother liquors were taken to dryness *in vacuo* and the residue on crystallization from benzene yielded 3.5 g of 2,3-dihydro-5,7,8-tris(β -chloroethylmercapto)-6-hydroxy-1,4-benzoxathiin (IV) melting at 129–130° alone or in admixture with that obtained in (a).

2,3-Dihydro-5,7,8-tris(β -chloroethylmercapto)-6-acetoxy-1,4-benzoxathiin

A mixture of 2,3-dihydro-5,7,8-tris(β -chloroethylmercapto)-6-hydroxy-1,4-benzoxathiin (10 g), acetic anhydride (50 ml), and two drops of concentrated sulphuric acid was heated on the steam bath for 4 hours. The excess anhydride was removed *in vacuo* and the residue washed with ether and with methanol and crystallized from benzene-methanol. The white prisms (5.5 g) melted at 120–122°. Anal. Calc. for $C_{16}H_{19}O_3Cl_3S_4$: C, 38.94; H, 3.85; Cl, 21.58. Found: C, 38.56, 39.32; H, 3.84, 3.99; Cl, 21.37, 21.05.

2,3,5,6-Tetrakis(β -chloroethylmercapto)-1,4-hydroquinone (III)

(a) *Using 30% Hydrochloric Acid and Thionyl Chloride*

To a solution of concentrated hydrochloric acid ($d = 1.19$, 200 ml) and water (55 ml) was added 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (II) (25 g), and the mixture shaken until dissolved. Then chloroform (250 ml) was added and the mixture was heated under reflux for 3 hours. The chloroform layer was separated, concentrated to 75 ml *in vacuo* at 40°, cooled to 30°, and treated with thionyl chloride (15 ml) at 30–35°. Precipitation began immediately. The reaction mixture was allowed to stand at room temperature for 3 hours and then cooled to 0° and filtered. The lemon-yellow prisms (20.5 g or 70%) melted at 179–181°. Anal. Calc. for $C_{14}H_{18}O_2Cl_4S_4$: C, 34.42; H, 3.69; Cl, 29.10. Found: C, 34.05; H, 3.59; Cl, 28.35, 28.94.

In another experiment, to a solution of II (35 g) in methanol (200 ml) and water (40 ml) was added concentrated hydrochloric acid (500 ml), and the solution was heated under reflux on the steam bath for $\frac{1}{2}$ hour. The precipitate was extracted with chloroform and then treated with thionyl chloride as in the first experiment above. There was obtained 27 g of III melting at 174–176° and at 178–179° after crystallization from benzene.

(b) *Using Alcoholic Hydrogen Chloride*

Methanol (450 ml) (or ethanol) was saturated with hydrogen chloride at 10°. To this was added 2,3,5,6-tetrakis(β -hydroxyethylmercapto)-1,4-hydroquinone (II) (25 g). After about half an hour of shaking it dissolved. The solution was allowed to stand at room temperature for 2 days and then cooled to 0°. The white precipitate on filtration and drying melted at 159–161°. Repeated recrystallizations raised the melting point by a few degrees only. However, when the crude product was treated with thionyl chloride in chloroform pure III melting at 180° was obtained.

*2,3,8,9-Tetrahydro-5,6-bis(β-chloroethylmercapto)benzo(1,2-b:4,3-b')bis(1,4-oxathiin) (V)**(a) From 2,3,5,6-Tetrakis(β-chloroethylmercapto)-1,4-hydroquinone (III)*

To a boiling solution of 2,3,5,6-tetrakis(β-chloroethylmercapto)-1,4-hydroquinone (III) (1.0 g) in acetone (150 ml) and methanol (50 ml) was added a solution of potassium hydroxide (0.25 g) in methanol (25 ml). The resulting solution was boiled for a few minutes. The white precipitate which formed quickly was filtered, washed, and dried. It weighed 0.45 g and melted at 226–227° with decomposition. Recrystallization from ethylene dichloride raised the melting point to 228–229° with decomposition. Anal. Calc. for $C_{14}H_{16}O_2Cl_2S_4$: C, 40.48; H, 3.86. Found: C, 40.28, 40.11; H, 3.84, 3.91.

(b) From 2,3-Dihydro-5,7,8-tris(β-chloroethylmercapto)-6-hydroxy-1,4-benzoxathiin (IV)

To a hot solution of IV (35 g) in acetone (700 ml) was added methanol (700 ml) followed by a solution of potassium hydroxide (4.5 g) in methanol (200 ml). After standing for 1 hour the reaction mixture was filtered and the white solid (22 g) melting at 218–220° with decomposition was crystallized from ethylene dichloride. The white prisms melted at 228–229° with decomposition, alone or in admixture with that obtained in (a).

2,3,8,9-Tetrahydro-5,6-ethylenedithio-benzo(1,2-b:4,3-b')bis(1,4-oxathiin) (VII) and Ethylene Dichloride from V

2,3,8,9-Tetrahydro-5,6-bis(β-chloroethylmercapto)benzo(1,2-b:4,3-b')bis(1,4-oxathiin) (V) (1.0 g) was heated in a Späth bulb at 250° for a few minutes, the distillate being collected in a dry-ice trap. The distillate was treated with a solution of excess potassium *p*-chlorothiophenate in methanol, yielding a white compound (0.32 g) which melted at 92–94° and which did not depress the melting point of 1,2-bis(*p*-chlorophenylmercapto)ethane. This showed that the distillate was mainly ethylene dichloride.

The residue in the Späth bulb was then sublimed at 250° at 0.5 mm pressure. The chlorine-free sublimate was crystallized from benzene, yielding 0.25 g of almost white needles, m.p. 239–240°. Anal. Calc. for $C_{12}H_{12}O_2S_4$: C, 45.57; H, 3.79; S, 40.50. Found: C, 45.61, 45.48; H, 4.04, 3.98; S, 40.68, 41.14.

Pyrolysis of 2,3-Dihydro-5,7,8-tris(β-chloroethylmercapto)-6-hydroxy-1,4-benzoxathiin (IV)

2,3-Dihydro-5,7,8-tris(β-chloroethylmercapto)-6-hydroxy-1,4-benzoxathiin (IV) (25 g) was heated in a distilling flask equipped with a condenser at 200° until no more liquid distilled. The distillate (5 g) had all the physical properties of ethylene dichloride. A derivative was prepared by heating the distillate (2 g) with a methanolic solution of excess potassium *p*-chlorothiophenate. The product (4 g) melted at 93–94° and did not depress the melting point of 1,2-bis(*p*-chlorophenylmercapto)ethane.

Pyrolysis of 2,3,5,6-Tetrakis(β-chloroethylmercapto)-1,4-hydroquinone (III)

2,3,5,6-Tetrakis(β-chloroethylmercapto)-1,4-hydroquinone (III) was pyrolyzed in the same manner as was IV above. Ethylene dichloride (0.5 g) was obtained from 2 g of III.

*2,3-Bis(β-hydroxyethylmercapto)-1,4-naphthoquinone (IX)**(a) Using Potassium Hydroxide and 2-Mercaptoethanol*

To a stirred solution of 2,3-dichloro-1,4-naphthoquinone (VIII) (60 g) in benzene (2 l.) was added dropwise a solution of 2-mercaptoethanol (45 ml) and potassium hydroxide (30 g) over 1½ hours. The temperature was kept at 40° by cooling. The dark reaction mixture was stirred for 2 hours and then let stand overnight. The warmed benzene solution was decanted from the salt and tar, concentrated to about 700 ml, and allowed to cool. The precipitate was filtered and crystallized from methanol, yielding orange needles (12 g) melting at 117–118°. Anal. Calc. for $C_{14}H_{14}O_4S_2$: C, 54.19; H, 4.51. Found: C, 54.53, 54.12; H, 4.51, 4.63.

(b) Using Pyridine and 2-Mercaptoethanol

A solution of 2,3-dichloro-1,4-naphthoquinone (VIII) (100 g) in benzene (1600 ml) and 2-mercaptoethanol (72 ml) was stirred and the temperature adjusted to exactly 54°. Then pyridine (80 ml) was added all at once. When the temperature reached 66° (in a few minutes) the reaction mixture was cooled occasionally on a water bath in order to keep the temperature at 65–67°. In about 15 minutes precipitation was complete and the temperature began to fall. The reaction mixture was cooled, treated with water, the precipitate filtered, washed with water, and crystallized from methanol. The yield of orange needles from two crops melting at 115–116° was 94 g. This compound turned dark and decomposed on standing in air after a few weeks.

2,3-Bis(β-hydroxyethylmercapto)-1,4-naphthoquinol

To a suspension of 2,3-bis(β-hydroxyethylmercapto)-1,4-naphthoquinone (IX) (62 g) in glacial acetic acid (620 ml) was added portionwise, with cooling on a water bath, zinc dust (25 g). The temperature was kept at 25–30°. After being stirred for 1 hour the reaction mixture was filtered and the filtrate taken to dryness *in vacuo*. The residue on crystallization from methanol yielded 39 g of white prisms melting at 124–126°. Anal. Calc. for $C_{14}H_{16}O_4S_2$: S, 20.51. Found: S, 20.52, 20.54. This quinol turned red on exposure to the air.

1,4-Oxathia-5,10-anthraquinone (X)

To a solution of 2,3-bis(β-hydroxyethylmercapto)-1,4-naphthoquinone (IX) (25 g) in methanol (300 ml) at 50° was added a solution of dry hydrogen chloride (120 g) in methanol (200 ml). The temperature rose to

60° and cooling was necessary in order to keep it below 60°. The dark purple solution was allowed to stand overnight and then the precipitated black sparkling crystals (10.5 g) were filtered, washed with methanol and benzene, and dried. This halogen-free compound melted at 230–232° and at 231–233° after sublimation at a temperature of 200° and a pressure of 1 mm. Anal. Calc. for $C_{16}H_8O_3S$: C, 62.07; H, 3.45; S, 13.8. Found: C, 61.52, 62.51; H, 3.49, 3.07; S, 14.16.

The same results were obtained when IX was treated with hydrogen chloride in acetic acid instead of in methanol.

REFERENCES

1. D. BUCKLEY, H. B. HENBEST, and P. SLADE. *J. Chem. Soc.* 4891 (1957).
2. A. BLACKHALL and R. H. THOMSON. *J. Chem. Soc.* 1138 (1953).
3. M. SCHUBERT. *J. Am. Chem. Soc.* **69**, 712 (1947).
4. M. KULKA. *Can. J. Chem.* **37**, 325 (1959).
5. M. KULKA. *J. Org. Chem.* **24**, 235 (1959).
6. C. H. SHUNK, D. E. WOLF, J. F. MCPHERSON, B. O. LINN, and K. FOLKERS. *J. Am. Chem. Soc.* **82**, 5914 (1960).
7. D. BUCKLEY, S. DUNSTAN, and H. B. HENBEST. *J. Chem. Soc.* 4901 (1957).
8. J. A. D. JEFFREYS. *J. Chem. Soc.* 2153 (1959).
9. L. F. FIESER. *J. Am. Chem. Soc.* **48**, 2922 (1926).
10. W. K. ANSLOW and H. RAISTRICK. *J. Chem. Soc.* 1446 (1939).