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The Configuration of Organic Telluroxides. Mixed Crystals of Telluroxides with Selenoxides

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The configuration of telluroxides is unknown. Attempts to resolve dissymmetric telluroxides into the optically active forms have not as yet succeeded.[1]

As diphenyl telluride[2] and di-*p*-tolyl telluride are isomorphous with the corresponding selenides (Fig. 3b) a study was undertaken as a contribution to this problem, not yet solved, by means of the thermal analysis of the binary systems of *diphenyl telluroxide* with *diphenyl selenoxide* and *di-p-tolyl telluroxide* with *di-p-tolyl selenoxide.* In both cases formation of continuous mixed crystal series of the compounds according to the type I of Bakhuis-Roozeboom's classification was observed (Fig. 1). From this result the conclusion can be drawn that the telluroxides have a similar configuration as the corresponding selenoxides. As far as the last are concerned and owing to the fact that they are completely isomorphous with the pertaining selenones and form illimited mixed crystal series with the corresponding sulfoxides, it was pointed out in an earlier paper[3] the probability of attributing to these compounds a tetrahedral configuration. Therefore it has to be attributed to the telluroxides an identical configuration, the tellurium atom being in the center of a tetrahedron in which vertices are located the two organic radicals, the oxygen atom and an unshared electron pair. Comparison of the phase diagrams solid-liquid of the correspondent binary systems of sulfoxides and selenoxides with those of selenoxides and telluroxides shows that in the last ones the liquidus and solidus curves are much farther apart than in the case of the first ones (Fig. 4b).[4]

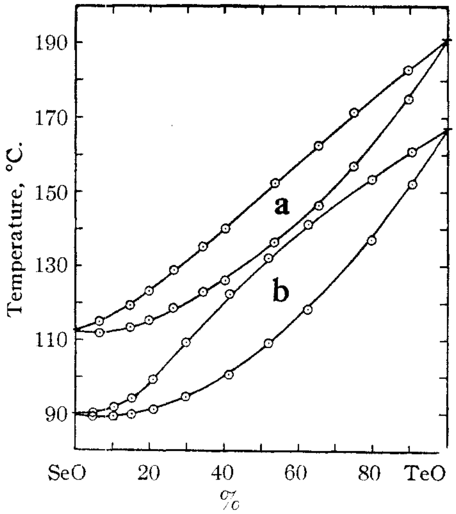

Fig. 1.—Binary system of: (a) di-phenyl telluroxide and selenoxide; (b) di-*p*-tolyl telluroxide and selenoxide.

Diphenyl telluroxide forms with *diphenyl selenone* a continuous mixed crystal series of type III (Fig. 2) showing thus the same behavior as diphenyl selenoxide in relation to diphenyl sulfone.[5] This fact may be considered as another confirmation of the tetrahedral configuration of this telluroxide.

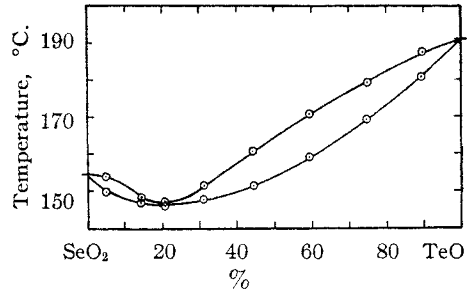

Fig. 2.—Binary system of diphenyl telluroxide and selenone.

Di-*p*-tolyl telluride does not give mixed crystals with the pertaining telluroxide showing thus the same behavior as sulfides and selenides toward the corresponding sulfoxides[6] and selenoxides.[3]

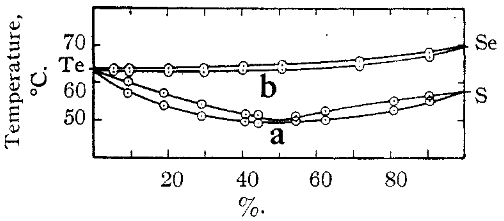

Fig. 3.—Binary systems of: (a) di-*p*-tolyl telluride and sulfide; (b) di-*p*-tolyl telluride and selenide.

The two telluroxides examined do not give however mixed crystals with the corresponding sulfoxides or sulfones, the four binary systems showing a single eutectic of the pure components. This fact, contrary to the behavior of the corre-

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[1] R. L. Shriner and R. Adams, in H. Gilman, "Organic Chemistry," Vol. I, 2 ed., J. Wiley and Sons, New York, N. Y., 1943, p. 424; Th. M. Lowry and Fr. L. Gilbert, *J. Chem. Soc.*, 2867 (1929); L. Reichel and E. Kirschbaum, *Ann.*, **523**, 215, 233 (1936).

[2] P. Pascal, *Bull. soc. chim.*, [4] **11**, 1030 (1912); continuous mixed crystal series with minimum (type III).

[3] H. Rheinboldt and E. Giesbrecht, THIS JOURNAL, **68**, 2671 (1946).

[4] In regard to the binary systems of diphenyl sulfoxide and sulfone with diphenyl selenoxide see ref. (3), Fig. 2.

[5] H. Rheinboldt and E. Giesbrecht, THIS JOURNAL, **69**, 644 (1947).

[6] H. Rheinboldt and E. Giesbrecht, *ibid.*, **68**, 973 (1946).

sponding selenoxides (Fig. 4b),[4] is *a priori* unexpected as according to P. Pascal[2] diphenyl sulfide and telluride form a continuous mixed crystal series of the type with minimum, showing the study of the binary system of di-*p*-tolyl sulfide and telluride the same behavior as these compounds (Fig. 3b). By accepting the tetrahedral configuration in all the three series of compounds one must suppose that the bond angles in sulfoxides and telluroxides differ already in such an amount that the tetrahedral forms are no longer commensurable.

Experimental

The phase diagrams, solid–liquid, of the binary systems were elaborated with the "thaw-melting point method" as described in a previous paper.[6] The mixtures of the components of all systems, with exception of those of system 9, were prepared by complete and homogeneous melting and the solidified masses were closely ground in an agate mortar. All the percentages indicated in the tables are by weight; "Th. p." means thawing point.

Binary Systems

1. **Diphenyl Telluroxide and Diphenyl Selenoxide.**[7]—*Diphenyl telluroxide* was prepared by hydrolysis of diphenyltellurium dibromide with 5% solution of sodium hydroxide at 50°. The raw product dried under vacuum over calcium chloride (yield 90%, melting about 180°) was recrystallized from water in presence of active charcoal and gave white brilliant needles that, after drying under vacuum over phosphorus pentoxide until constant weight, melted at 191.1°. Reported melting points are, over 185° (with decomposition)[8] and 192–193° (without decomposition)[9]—continuous mixed crystal series of type I.

TABLE I (FIG. 1a)

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	111.7	112.8	40.2	126.2	140.1
6.5	112.0	115.1	53.6	136.7	152.7
14.8	113.7	119.5	65.2	146.4	162.8
19.9	115.5	123.4	74.7	157.0	171.3
26.4	118.8	129.0	89.4	175.1	183.0
34.3	123.1	135.3	100.0	190.1	191.1

2. **Di-*p*-tolyl Telluroxide and Selenoxide.**—Di-*p*-tolyl telluroxide was prepared by hydrolysis of the corresponding dibromide. To a solution of 4 g. of the telluride in 25 cc. of ether, cooled at 0°, was carefully added under vigorous stirring 2.1 g. of bromine. The material was left for thirty minutes at room temperature, cooled again to 0° and the crystalline precipitate separated by filtration. The last, rinsed with a small amount of cold ether and dried under vacuum (yield 5.5 g. or 91%, m. p. 200°), was slowly added with vigorous stirring to 100 cc. of a 5% solution of sodium hydroxide. After heating for a short time at 50°, the solution was cooled to 0° and the precipitate separated by filtration, rinsed with ice water and dried over calcium chloride; yield was 3.2 g. or 84%, m. p. 160–162°. After many crystallizations from dry toluene in presence of active charcoal (benzene did not give satisfactory results) a white microcrystalline powder was obtained which, after drying under vacuum over phosphorus pentoxide, melted at 167.2°; reported melting point 166–167°.[10]

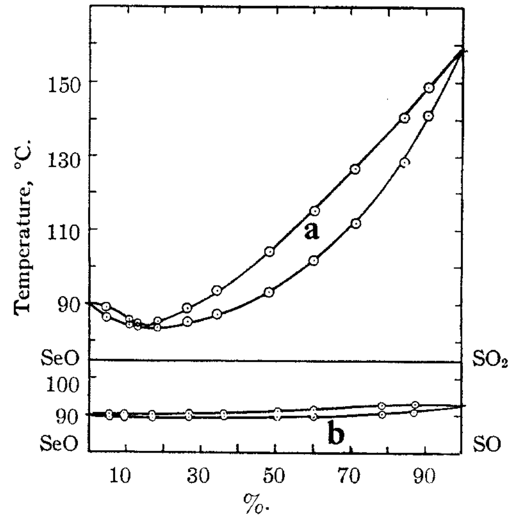

Fig. 4.—Binary systems of: (a) di-*p*-tolyl selenoxide and sulfone; (b) di-*p*-tolyl selenoxide and sulfoxide.

Di-p-tolyl selenoxide was prepared by hydrolysis of di-*p*-tolylselenium dibromide[11] obtained from the selenide with a yield of 94%. To a 5% solution of sodium hydroxide was slowly added under vigorous stirring 10.5 g. of the dibromide. After heating for fifteen minutes at 40° the solution was cooled to 0°. The precipitate, separated by filtration and dried under vacuum over calcium chloride (yield 6 g. or 85%), melted at 85–86°. After many recrystallizations from dry benzene in presence of active charcoal and drying under vacuum over phosphorus pentoxide, a white and brilliant solid material was obtained melting sharply at 90.0°. Zeiser[11] prepared this selenoxide by hydrolysis of the corresponding dichloride (without further indications) and reports m. p. *ca.* 90°.

TABLE II (FIG. 1b)

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	89.2	90.0	41.5	100.6	122.5
4.7	89.2	90.2	51.9	109.3	132.6
10.2	89.4	91.8	62.5	118.4	141.4
15.2	89.8	94.1	79.7	137.1	153.5
21.0	91.2	99.2	90.8	152.2	161.0
29.7	94.5	109.4	100.0	166.3	167.2

Continuous mixed crystal series of type I.

3. **Diphenyl Telluroxide and Selenone.**[7]—Continuous mixed crystal series of type III with minimum at 146° and 20% of telluroxide.

TABLE III (FIG. 2)

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	153.8	154.9	44.3	151.5	160.8
5.4	150.2	154.2	59.4	159.0	170.6
14.3	146.8	148.5	75.0	169.1	179.2
20.9	146.0	147.5	89.5	180.4	187.1
31.0	147.9	151.4	100.0	190.1	191.1

4. **Di-*p*-tolyl Telluride and Selenide.**—The telluride was prepared according to a simplified modification of the method used by Zeiser.[12] An intimate mixture of 26 g. of di-*p*-tolylmercury (m. p. 236–238°) with 18.5 g. of

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[7] On the preparation and purification of this compound see ref. 3.

[8] F. Krafft and R. E. Lyons, *Ber.*, **27**, 1770 (1894), crystallized from xylene; K. Lederer, ref. 9, reports that this substance melts at 187° with decomposition.

[9] K. Lederer, *Ann.*, **391**, 338 (1912); crystallized from water.

[10] K. Lederer, *ibid.*, **391**, 342 (1912).

[11] F. Zeiser, *Ber.*, **28**, 1673 (1895).

[12] F. Zeiser, *ibid.*, **28**, 1671 (1895).

tellurium was heated for twenty hours at 230° in an atmosphere of carbon dioxide. After extraction with 250 cc. of ether, the solution was dried with anhydrous sodium sulfate and the solvent separated by distillation. The residue obtained was a red oil that became solid at room temperature. The raw product melting at 56–60° (yield 9 g. or 42%) was repeatedly crystallized from ethanol in presence of active charcoal yielding small crystals slightly yellowish with melting point 63.6°. Reported m. p. is 63–64°.[12]

Di-*p*-tolyl selenide was obtained following the standard method elaborated for preparation of diphenyl selenide.[13] The combined chloroform extracts dried with anhydrous sodium sulfate left after evaporation of the chloroform a brownish oil that became solid and melted at 58–60°; yield was 35 g. from 33 g. of *p*-toluidine, 86% of the theoretical amount. This raw product submitted to a distillation gave a yellowish oil that distilled at about 700 mm. from 310 to 320° and became solid at room temperature. Many crystallizations from ethanol in presence of active charcoal gave slightly yellowish needles that after grinding had the aspect of a white powder and melted at 69.5°. Reported melting points are 63.5–66.5,[14] 68.0,[15] 69,[16] 69–69.5,[17] 69.5–70.5[18] and 70°,[19]—continuous mixed crystal series of type I.

TABLE IV (FIG. 3b)

Selenide, %	Th. p., °C.	M. p., °C.	Selenide, %	Th. p., °C.	M. p., °C.
0.0	62.8	63.6	40.2	63.1	64.4
5.3	62.8	63.6	50.8	63.4	64.8
9.8	62.8	63.8	71.5	64.2	65.6
20.0	62.8	63.9	90.4	66.9	68.0
29.9	62.9	64.0	100.0	68.7	69.5

5. **Di-*p*-tolyl Telluride and Sulfide.**—Di-*p*-tolyl sulfide was obtained according to a general method outlined by J. H. Ziegler[20] but not described for the preparation of this sulfide. A solution of *p*-toluenediazonium chloride prepared from 10 g. of *p*-toluidine was added drop by drop under vigorous stirring to a solution of 12.5 g. of *p*-thiocresol and 4.5 g. of sodium hydroxide in 60 cc. of water heated to 60°. After the addition of that solution the temperature was kept at 60–70° for half an hour more under stirring. The solution was then diluted with ice water bringing forth a separation of a red oil that soon became solid. The solid material was rinsed with water, dried under vacuum over calcium chloride and distilled. The fraction passing between 290 and 310° at *ca.* 700 mm. was collected. This fraction solidified quickly at room temperature and the solid white material melted at *ca.* 54°; the yield was low (7.5 g. or 36%). This raw product repeatedly crystallized from ethanol in presence of active charcoal gave small colorless needles of m. p. 57.5°. Reported melting points are 56,[21] 56–57[22] and 57.3[23]—continuous mixed crystal series of type III with minimum at 49.5° and *ca.* 50% of the telluride.

TABLE V (FIG. 3a)

Telluride, %	Th. p., °C.	M. p., °C.	Telluride, %	Th. p., °C.	M. p., °C.
0.0	57.0	57.5	59.1	49.4	51.5
9.6	54.8	56.6	71.0	51.1	54.1
19.4	52.4	55.0	81.2	53.8	57.1
37.8	50.0	52.1	90.7	57.2	60.2
45.5	49.5	51.1	100.0	62.8	63.6
55.7	49.2	51.2			

6. **Di-*p*-tolyl Selenoxide and Sulfoxide.**[24]—Continuous series of mixed crystals of type I.

TABLE VI (FIG. 4b)

Sulfoxide, %	Th. p., °C.	M. p., °C.	Sulfoxide, %	Th. p., °C.	M. p., °C.
0.0	89.2	90.0	50.4	89.3	90.8
5.4	89.2	90.0	60.6	89.3	91.7
9.6	89.2	90.0	78.8	90.0	92.5
17.1	89.2	90.1	87.5	90.8	92.8
26.8	89.2	90.1	100.0	92.1	93.1
36.2	89.3	90.2			

7. **Di-*p*-tolyl Selenoxide and Sulfone.**[24]—Continuous mixed crystal series of type III with minimum at 83.5° and 16% sulfone.

TABLE VII (FIG. 4a)

Sulfone, %	Th. p., °C.	M. p., °C.	Sulfone, %	Th. p., °C.	M. p., °C.
0.0	89.2	90.0	48.4	93.1	104.1
4.8	86.1	89.1	60.5	101.8	115.1
10.7	84.0	85.9	71.2	111.6	126.4
13.0	83.5	85.0	84.5	128.2	140.5
18.5	83.6	85.2	91.0	140.2	148.7
26.5	84.9	88.8	100.0	157.3	158.1
34.2	87.0	93.7			

8. **Diphenyl Telluroxide and Sulfoxide.**[24]—Simple eutectic system with eutectic point at 68.1° and 1.5% telluroxide.

TABLE VIII

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	70.1	71.0	49.9	68.0	154.5
5.4	68.2	92.7	62.3	68.2	164.6
10.4	68.0	105.8	74.9	68.2	174.2
24.8	68.1	129.0	89.0	68.2	184.2
35.2	68.0	140.4	100.0	190.1	191.1

9. **Diphenyl Telluroxide and Sulfone** (*β*).[24]—Simple eutectic system with eutectic point at 118.2° and 8.5% of the telluroxide.

TABLE IX

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	127.0	127.8	40.8	118.1	149.3
5.6	118.1	123.1	55.7	118.3	162.2
11.3	118.0	121.0	70.6	118.2	174.0
16.2	118.1	125.8	90.2	118.5	186.9
19.5	118.2	129.0	100.0	190.1	191.1
25.3	118.2	134.5			

All mixtures of this sytem were prepared by close grinding of the components and the thawing and melting points determined in different samples.

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(13) "Organic Syntheses," Coll. Vol. II, 238 (1943).

(14) S. Keimatu, I. Satoda and T. Kobayashi, *J. Pharm. Soc. Japan*, **57**, 190 (1937); *C. A.*, **33**, 624 (1939).

(15) J. H. Crowell and W. E. Bradt, THIS JOURNAL, **55**, 1501 (1933).

(16) H. M. Leicester and F. W. Bergstrom, *ibid.*, **53**, 4433 (1931).

(17) F. Zeiser, *Ber.*, **28**, 1673 (1895).

(18) F. Challenger, A. Th. Peters and J. Halévy, *J. Chem. Soc.*, 1893 (1926).

(19) O. Behaghel and H. Seibert, *Ber.*, **66**, 712, note 24 (1933).

(20) I. H. Ziegler, *ibid.*, **23**, 2471 (1890).

(21) H. C. Parker, *Ber.*, **23**, 1845 (1890).

(22) R. Otto, *ibid.*, **12**, 1176 (1879); K. W. Rosenmund and H. Harms, *ibid.*, **53**, 2235 (1920).

(23) F. Zeiser, *ibid.*, **28**, 1674 (1895); Ed. Bourgeois, *ibid.*, **28**, 2325 (1895).

(24) On the preparation and purification of this compound see ref. 5.

10. **Di-*p*-tolyl Telluroxide and Sulfoxide.**[24]—Simple eutectic system with eutectic point at 84.5° and 6% of telluroxide.

TABLE X

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	92.1	93.1	48.7	84.5	127.6
3.4	84.5	88.0	70.2	84.6	146.0
11.0	84.4	90.9	89.8	84.6	160.5
20.9	84.6	100.9	95.0	84.8	164.1
34.7	84.5	114.7	100.0	166.3	167.2

11. **Di-*p*-tolyl Telluroxide and Sulfone.**[24]—Simple eutectic system with eutectic point at 134.3° and 40% of the telluroxide.

TABLE XI

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	157.3	158.1	60.4	134.2	148.8
5.0	134.2	157.0	76.0	134.4	157.1
14.2	134.1	153.2	88.5	134.5	162.5
26.3	134.3	145.8	95.4	134.5	165.4
34.3	134.3	139.1	100.0	166.3	167.2
47.8	134.3	140.8			

12. **Di-*p*-tolyl Telluroxide and Telluride.**—Simple eutectic system with eutectic point at 59.2° and 3% of telluroxide.

TABLE XII

Telluroxide, %	Th. p., °C.	M. p., °C.	Telluroxide, %	Th. p., °C.	M. p., °C.
0.0	62.8	63.6	40.6	59.4	117.1
4.3	59.1	63.5	59.9	59.3	135.6
11.9	59.0	78.7	80.2	59.4	152.0
17.1	59.0	87.3	95.4	59.6	164.7
26.1	59.2	100.0	100.0	166.3	167.2

Summary

1. It is shown by the thermal analysis method that diphenyl and di-*p*-tolyl telluroxide form with the pertaining selenoxides continuous mixed crystal series of the ascendant type (type I). Diphenyl telluroxide gives with the corresponding selenone a continuous series of mixed crystals of the type with minimum (type III). Di-*p*-tolyl telluride do not give mixed crystals with the pertaining telluroxide.

These facts lead to the conclusion that telluroxides must have the same steric configuration as the corresponding selenoxides or selenones. In accordance with our previous studies on the configuration of selenoxides[3] and sulfoxides[5] the tetrahedral configuration of telluroxides is postulated.

2. Diphenyl and di-*p*-tolyl telluroxide form with the corresponding sulfoxides and sulfones only simple eutectic systems without even a limited formation of mixed crystals. Di-*p*-tolyl selenoxide gives however with the corresponding sulfoxide a continuous mixed crystal series of type I and with the sulfone a series of type III; di-*p*-tolyl telluride forms with the corresponding selenide a continuous mixed crystal series of type I, and with the sulfide a series of type III.

These facts are explained by the admission that the bond angles in the telluroxides and the corresponding sulfoxides differ already in such an amount that the tetrahedral forms of these molecules are no more commensurable.

SÃO PAULO, BRAZIL RECEIVED JANUARY 29, 1947

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

cis- and *trans-*Piperylenes[1,2]

BY ROBERT L. FRANK, ROBERT D. EMMICK AND RAYNER S. JOHNSON

Piperylene is perhaps the most readily available diene existing in *cis* and *trans* forms. As shown by Craig[3] and by Robey, Morrell and Wiese,[4] the two isomers differ markedly in their reactions. Further study of their preparation and reactions, carried out because of increased interest in piperylene as a by-product in the cracking process for isoprene, is described in this paper.

Because one of the reactions we desired to study was the polymerization of *cis-* and *trans-*piperylenes, and since traces of impurities have a marked effect on such reactions,[5] it was considered necessary to obtain the material in high purity. Indeed, one of the most likely impurities in piperylene from cracked petroleum, cyclopentadiene, is also one of the most powerful polymerization inhibitors among hydrocarbons.[5]

Means of purification involving solid intermediates which might be purified by recrystallization are not available for piperylene. For example, the cyclic sulfone, although useful, is not crystalline as in the case of isoprene sulfone.[5a] Cuprous chloride complexes are likewise not obtainable as crystalline solids.[3] Another derivative, the tetrabromide, can be obtained as the crystalline isomer only in yields of approximately 20%.[3] A fourth means of purification, regeneration by pyrolysis of the maleic anhydride adduct

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(1) Presented before the Organic Division at the Chicago meeting of the American Chemical Society, September 9–13, 1946.

(2) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(3) Craig, THIS JOURNAL, **65**, 1006 (1943); U. S. Patent 2,403,054 (July 2, 1946).

(4) Robey, Morrell and Wiese, *ibid.*, **63**, 627 (1941); Robey, *Science*, **96**, 470 (1942); Robey and Wiese, U. S. Patent 2,357,910 (Sept. 12, 1944).

(5) (a) Frank, Adams, Blegen, Deanin and Smith, *Ind. Eng. Chem.*, **39**, 887 (1947); (b) Frank, Blegen, Inskeep and Smith, *ibid.*, **39**, 893 (1947).