mg. (82%) of acidic product, m.p. $150.5-152^{\circ}$ after one recrystallization from acetone-heptane. 6-Hydroxybiphenyl-2-carboxylic acid is reported¹⁵ to melt at 154°, while the 3-hydroxy isomer¹⁷ melts at 159°.

4-Hydroxyfluorenone (VII).—A solution of 40 mg. of VI in 2.0 g. of concentrated sulfuric acid was allowed to stand for a few minutes, then diluted with water to precipitate an orange-yellow solid, m.p. 238–243°. The infrared spectrum (Nujol) showed hydroxy absorption at 3195 and a carbonyl band at 1695 cm.⁻¹. **4-Hydroxyfluorenone** is reported¹⁶ to melt at 249°, while the isomeric 1-hydroxyfluorenone¹⁸ melts at 115°.

Reaction of I with Benzonorbornadiene.—A mixture of I (1.78 g.), benzonorbornadiene (1.50 g.), and a pinch of hydroquinone was heated in a sealed tube at 150° for 89 hr. The product a reddish brown oil, readily crystallized, and was washed with a few milliliters of cold ethanol to yield 2.14 g. (65%) of the light brown adduct VIII, m.p. $110-135^{\circ}$. Four recrystallizations from acetone-heptane gave the pure material as colorless needles, m.p. $155-158^{\circ}$. The infrared spectrum showed a strong acetate band at 1740 cm.^{-1} .

Anal. Caled. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.06; H, 6.46.

Dibenzocycloheptatriene (X).—The above adduct (VIII) was recovered unchanged from passing over glass helices heated at 400-450°. Pyrolysis was effected by passing VIII (0.38 g.) in a stream of nitrogen over glass helices at 575-600°. The light brown crude product was purified by sublimation at reduced pressure, then recrystallized from heptane to give white plates (0.11 g., 47%) of 1,2,5,6-dibenzocycloheptatriene¹⁹ (X), m.p. 132-133°. In accord with this assignment of structure, the n.m.r. spectrum (in CS₂) showed three singlets, at τ 3.45 (8H), 3.7 (2H), and 7 (2H). The melting point was not depressed by mixing with an authentic sample,²⁰ m.p. 132°.

Pyrolytic Rearrangement of Benzonorbornadiene.—Benzonorbornadiene (0.25 g.) was passed over glass helices at 575–600° in a stream of nitrogen. The liquid (0.2 g.) that collected in the cooled receiver had different infrared and ultraviolet spectra than the starting material. It was assigned the structure of 1,2-benzocycloheptatriene (XI) on the basis of its ultraviolet

- (18) G. Heyl, ibid., 31, 3033 (1898).
- (19) W. Treibs and H. J. Klinkhammer, ibid., 84, 671 (1951).

(20) We are grateful to Professor M. P. Cava of The Ohio State University for sending us a sample for comparison; cf. M. P. Cava, R. Pohlke, B. W. Erickson, J. C. Rose, and G. Fraenkel, *Tetrahedron*, **18**, 1005 (1962).

spectrum, $\lambda_{\text{max}} 282 \text{ m}\mu$, $\lambda_{\text{min}} 241 \text{ m}\mu$ (lit.²¹ $\lambda_{\text{max}} 276 \text{ m}\mu$, $\lambda_{\text{min}} 240 \text{ m}\mu$).

Reaction of 1-Acetoxybutadiene with Acetylenes. A.—A mixture of 1-acetoxybutadiene²² (1.12 g.), dimethyl acetylenedicarboxylate (1.42 g.), and hydroquinone (0.01 g.) was heated in a sealed tube at 115–120° for 6 days. The oily product was taken up in 80% aqueous ethanol, 5.0 g. of sodium hydroxide was added, and the mixture was refluxed for 4 hr. The dark solution was acidified with 30% sulfuric acid and extracted with eight 20ml. portions of ether; the combined extracts were dried over sodium sulfate and filtered through charcoal. Concentration of the ether solution gave pale yellow plates of phthalic acid (0.72 g., 43%), m.p. 206–209°. The infrared spectrum was identical with that of authentic phthalic acid, m.p. 206–208°.

B.—A mixture of 1-acetoxybutadiene (1.12 g.), methyl phenylpropiolate (1.60 g.), and hydroquinone (0.01 g.) was heated in a sealed tube at 110° for 6 days. The oily product was saponified as described in part A, acidified, and extracted with chloroform. The crude biphenyl-2-carboxylic acid obtained by evaporation of theext racts did not crystallize and was therefore converted to fluorenone for ease of isolation. The oil was taken up in 10 ml. of concentrated sulfuric acid, kept for a few minutes, then carefully added to water. The solution was extracted with five 50-ml. portions of ether and the extracts were washed with saturated sodium bicarbonate solution and brine, then dried. Concentration of the extracts and chromatography of the residue on alumina gave a yellow substance, eluted with 50% benzenehexane, and identified as fluorenone (0.10 g., 5.5%), m.p. 82-83° (lit. m.p. 84°) from its infrared spectrum.

C.—To a stirred and refluxing solution of 1-acetoxybutadiene (2.24 g.) and *n*-butyl nitrite (2.22 g.) in 20 ml. of methylene dichloride was added dropwise, over a period of 70 min., a solution of anthranilic acid (3.00 g.) in 10 ml. of tetrahydrofuran. After refluxing for an additional 15 min., the solution was concentrated at reduced pressure, and the red oily residue was chromatographed on alumina. Elution with hexane gave naphthalene (0.29 g., 11%), m.p. 76–78°, in the early fractions. Its infrared spectrum was identical with that of authentic naphthalene, m.p. 80°.

Acknowledgment.—This work was supported, in part, by a research grant (GM-06568) from the Public Health Service, and also by an National Institutes of Health Predoctoral Fellowship to R. M. C., for both of which we express our gratitude.

(21) G. Wittig, H. Eggers, and P. Duffner, Ann., 619, 10 (1958).
(22) O. Wichterle and M. Hudlický, Collection Czech. Chem. Commun., 12, 564 (1947).

The Synthesis of Silyl Hydroperoxides and Bissilyl Peroxides¹

RALPH L. DANNLEY AND GEORGE JALICS

The Morley Chemical Laboratory, Western Reserve University, Cleveland 6, Ohio

Received February 1, 1965

Triphenylsilyl, methyldiphenylsilyl, tribenzylsilyl, and tri-n-hexylsilyl hydroperoxides have been synthesized from the corresponding silylamines. Practical laboratory syntheses starting with chlorosilanes, ammonia, and hydrogen peroxide, proceed through silylamine intermediates. The hydroperoxides are so stable that they may be stored indefinitely at room temperature. Bis(triphenylsilyl) and bis(tribenzylsilyl) peroxides were prepared and found to be even more stable than the corresponding hydroperoxides.

The hydroperoxides and bis peroxides of silicon constitute a field of research which has received little attention. The only hydroperoxide isolated, trimethylsilyl hydroperoxide,² was characterized merely by

(2) W. Hahn and L. Metzinger Makromol. Chem., 21, 113 (1956).

peroxide content and was reported to decompose below room temperature.

The papers which have appeared on bissilyl peroxides have usually described compounds of limited purity. Berry³ claimed to have prepared a solution of bis(triphenylsilyl) peroxide but did not isolate the compound. Buncel and Davies⁴ attempted to crystallize pure bis(triphenylsilyl) peroxide but obtained an unstable solid with only a 70% content of the theoretical

(3) K. L. Berry, U. S. Patent 2,692,887 (1952).

⁽¹⁶⁾ C. Graebe and P. Schestakow, Ann., 284, 316 (1895).

⁽¹⁷⁾ W. Staedel, Ber., 28, 111 (1895).

^{(1) (}a) Supported in part by the U. S. Army Research Office (Durham) through Grant No. DA-ARO(D)-31-124-G242 and in part by a Texaco Company Fellowship. (b) Taken in part from the dissertation of George Jalics, submitted June 1964, to the Graduate School of Western Reserve University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (c) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963.

⁽⁴⁾ E. Buncel and A. G. Davies, J. Chem. Soc., 1550 (1958).

active oxygen. Hahn and Metzinger² described bis-(trimethylsilyl) peroxide but the analytical figures were not entirely satisfactory. Simon and Arnold⁵ isolated bis(triethylsilyl) peroxide. Pike and Shaffer⁶ repeated some of these preparations but could not get products of improved purity. They ascribed these difficulties to molecular rearrangements occurring with low activation energies (6.3 kcal./mole). Jenkner⁷ attempted to synthesize a polymeric silicon peroxide from diethyldichlorosilane but the product had a low peroxide content. This was attributed to molecular rearrangements leading to ethoxy structures.

These data uniformly lead to the conclusion that silyl hydroperoxides and bissilyl peroxides are quite unstable (sometimes even explosive). This conclusion is not consistent, however, with the known stability of analogous carbon compounds and the demonstrated resistance toward oxidation of the carbon-silicon bond. The thermal instabilities observed might be due to impurities which catalyzed the degradation processes. The present work was undertaken specifically to prepare some silyl hydroperoxides and bissilyl peroxides in a pure form.

Results and Discussion

Synthesis of the Silyl Hydroperoxides.—Initial attempts to synthesize bis(triphenylsilyl) peroxide from the chlorosilane and ammoniacal hydrogen peroxide resulted in products of low active-oxygen content. An alkali-catalyzed decomposition of the initially formed peroxide was considered a possible cause of these low values. The reaction times were therefore shortened successively until, with only 1 min. of contact between the chlorosilane and ammoniacal hydrogen peroxide, relatively pure triphenylsilyl hydroperoxide was isolated.

The preparation of triphenylsilyl hydroperoxide from the corresponding pure silylamine was then undertaken merely as an investigation of the mechanism of the reaction. The yields of hydroperoxide obtained were so high, however, that a simple modification (in which the silvlamine is prepared in solution but not isolated) became the preferred routine method for the synthesis of methyldiphenylsilyl, tribenzylsilyl, and tri-n-hexylsilyl hydroperoxides. The use of amines as intermediates in peroxide syntheses is not a new procedure; Rieche and Dahlmann,8 for example, have prepared bisgermanium peroxides from the corresponding germanium amines. The silvl hydroperoxides here obtained were all so stable that they could be stored for weeks at room temperature without a significant decrease in peroxide content.

The formation of a silyl hydroperoxide from the amine could proceed via an initial displacement involving either a perhydroxide ion or a molecule of hydrogen peroxide (for the silylamines are well known to undergo similar displacements very readily with water to give silanols). Although the perhydroxide ion concentration would be small initially, it would increase rapidly as ammonia is liberated. It is therefore shown as the reactant in the equation given below. The inter-

$$HOO^{-} + Ph_{3}SiNH_{2} \longrightarrow [HOOSiPh_{3}NH_{2}^{-}] \xrightarrow{H_{2}O_{2}} HOOSiPh_{3} + NH_{3} + OOH^{-}$$

mediate has greater stability than would be expected in a corresponding activated complex of carbon because of the ability of silicon to exist in pentavalent or hexavalent structures. Inversion may or may not occur.⁹

The reaction of the chlorosilane with ammoniacal hydrogen peroxide probably involves conversion to the amine which then undergoes the displacement shown above. Although the present work does not preclude the possibility that a direct nucleophilic displacement upon a chlorosilane can produce a hydroperoxide, successful syntheses were achieved only when the reaction conditions permitted the formation of a silylamine intermediate.

Synthesis of the Bissilyl Peroxides.—Bis(triphenylsilyl) peroxide was first obtained in the present work by the reaction of triphenylsilyl hydroperoxide with triphenylchlorosilane in the presence of a tertiary amine. This procedure is reported here because it may be useful in the future for the preparation of unsymmetrical silyl peroxides. The one-step process which is reported using triphenylchlorosilane is, however, a more simple over-all procedure for symmetrical peroxides and gives better yields.

The ability to convert triphenylchlorosilane and tribenzylchlorosilane to the bis peroxides by treatment with the corresponding hydroperoxide and an equimolecular quantity of tertiary aliphatic amine supports the following mechanism. Again pentavalent silicon

$$\begin{array}{l} (\mathrm{CH}_{\mathtt{3}})_{\mathtt{5}}\mathrm{N} \ + \ \mathrm{Ph}_{\mathtt{3}}\mathrm{SiOOH} \longrightarrow \mathrm{Ph}_{\mathtt{3}}\mathrm{SiOO}^{-} + \ (\mathrm{CH}_{\mathtt{3}})_{\mathtt{3}}\mathrm{NH}^{+} \\ \mathrm{Ph}_{\mathtt{3}}\mathrm{SiOO}^{-} \ + \ \mathrm{Ph}_{\mathtt{3}}\mathrm{SiOI} \longrightarrow \ [\mathrm{Ph}_{\mathtt{3}}\mathrm{SiOOSiPh}_{\mathtt{3}}\mathrm{Cl}^{-}] \longrightarrow \\ \mathrm{Ph}_{\mathtt{3}}\mathrm{SiOOSiPh}_{\mathtt{3}} \ + \ \mathrm{Cl} \end{array}$$

may be an intermediate and inversion may or may not occur. 9

The synthesis from the silylamine is a displacement which occurs very readily.

$$\begin{array}{r} Ph_{3}SiOO^{-} + Ph_{3}SiNH_{2} \longrightarrow [Ph_{3}SiOOSiPh_{3}NH_{2}^{-}] \xrightarrow{Ph_{3}SiOOH} \\ Ph_{3}SiOOSiPh_{3} + NH_{3} + Ph_{3}SiOO^{-} \end{array}$$

The bissilyl peroxides reported here did not respond to the conventional methods for active-oxygen analysis. Rearrangements (which will be discussed in a later paper) apparently occur concurrently with the analytical reaction and partially consume the O-O linkages present so that low peroxide values are obtained. Hahn and Metzinger² and Simon and Arnold⁵ reported no difficulties in titrating bis(trialkylsilyl) peroxides. This is very surprising in that bis(tribenzylsilyl) peroxide does not respond to a variety of common analytical procedures for peroxides. The melting point and titration figures obtained by Buncel and Davies⁴ for a sample they described as crude bis(triphenylsilyl) peroxide were found in the present work to correspond to a mixture of triphenylsilyl hydroperoxide and triphenylsilanol.

Experimental

Solvents.—Ether was dried over lithium aluminum hydride and distilled under nitrogen. All other solvents were obtained in reagent grade purity or distilled before use.

⁽⁵⁾ A. Simon and H. Arnold, J. prakt. Chem., 8, 241 (1959).

⁽⁶⁾ R. A. Pike and L. H. Shaffer, Chem. Ind. (London), 1294 (1957).

⁽⁷⁾ H. Jenkner, Z. Naturforsch., 11b, 757 (1956).

⁽⁸⁾ A. Rieche and J. Dahlmann, Angew. Chem., 71, 194 (1959).

⁽⁹⁾ L. H. Sommer, ibid., 74, 176 (1964).

Triphenylsilylamine.—The method of synthesis of Kraus and Rosen¹⁰ using sodium in liquid ammonia was found to be unsatisfactory. The solvolysis of triphenylchlorosilane by anhydrous ammonia to the desired silylamine proceeded very readily if some dry ether was added to increase the solubility of the silyl chloride. Triphenylchlorosilane (25 g.) was added to anhydrous ammonia (200 ml.) and anhydrous ether (50 ml.) and the mixture was refluxed (using a Dry Ice condenser) for 2 hr. After the ammonia and ether had been removed, the residue was recrystallized from petroleum ether (300 ml., b.p. 30–60°) to give triphenylsilylamine (21 g., 90% yield) of m.p. 56–57° (lit.¹⁰ m.p. 55–56°).

Triphenylsilyl Hydroperoxide from Triphenylchlorosilane.-To a well-stirred solution of triphenylchlorosilane (5 g., 0.017 mole) in anhydrous ether (200 ml.) cooled to 0° was added 98% hydrogen peroxide (5 ml., 0.2 mole, Buffalo Electrochemical Co.). After 2-3-min. stirring to permit cooling again to 0°, anhydrous ammonia (excess) was bubbled rapidly into the reaction mixture for 60 sec. To prevent a base-catalyzed decomposition of the hydroperoxide, the reaction was then quenched immediately by adding 60 ml. of distilled water. The ether layer was separated, washed four times with 40-ml. portions of water, dried with anhydrous magnesium sulfate, and filtered, and the ether was removed in vacuo from the filtrate. The white crystalline residue was dissolved in hot carbon tetrachloride (30 ml.) and the solution was cooled to -20° to yield 3 g. of silvl hydroperoxide containing occluded carbon tetrachloride. The crude product (3 g.) was dissolved in a minimum amount of petroleum ether (40-50 ml.) and the solution was cooled to -20° . The white, crystalline triphenylsilyl hydroperoxide (2.8 g., 56.2%)which was collected by filtration melted at 110-112° and showed a strong peak in the infrared spectrum at 890 cm. $^{-1}$ for the O–O stretch.

Anal. Calcd. for $C_{18}H_{16}O_2Si$: C, 73.96; H, 5.52; Si, 9.60; active O, 5.48. Found: C, 73.92; H, 5.61; Si, 9.28, 9.58, 9.70; active O, 5.38.

Carbon tetrachloride is the best solvent for recrystallization of the hydroperoxide but at -20° the solvent becomes viscous and carbon tetrachloride is occluded in the crystals. The last recrystallization from petroleum ether is performed to remove these trapped solvent molecules.

Triphenylsilyl Hydroperoxide from Triphenylsilylamine.—To triphenylsilylamine (1.5 g., 0.0055 mole) in anhydrous ether (25 ml.) was added 98% hydrogen peroxide (1.5 ml., 0.062 mole) and the mixture was stirred for 10 min. The reaction was then quenched by adding 5 ml. of water. The ether layer was separated, washed with water four times, dried with anhydrous magnesium sulfate, and then cooled to deposit crude triphenylsilyl hydroperoxide (1 g., 55% yield, m.p. 102–105°). Recrystallization as previously described from carbon tetrachloride and petroleum ether gave the pure hydroperoxide, m.p. 110–112°.

Methyldiphenylsilyl Hydroperoxide.—Into a solution of methyldiphenylchlorosilane (5 g., 0.0215 mole) and anhydrous ether (100 ml.) cooled to 0° was passed anhydrous ammonia gas for 3 min. The white ammonium chloride crystals which had precipitated dissolved when 98% hydrogen peroxide (5 ml., 0.2 mole) was added. After 3 min. the reaction mixture was quenched with 25 ml. of distilled water. The ether layer was separated, washed four times with 20-ml. portions of water, dried with anhydrous magnesium sulfate, and filtered, and the ether was removed *in vacuo*. The heavy oil which remained was dissolved in 50 ml. of petroleum ether and cooled to -20° for 48 hr. to precipitate methyldiphenylsilyl hydroperoxide (2.7 g., 54% yield), m.p. 40-41°. The crystallization is greatly facilitated by seeding and it is difficult to obtain crystals the first time. The infrared spectrum shows a distinct peak at 890 cm.⁻¹ for the O-O stretch.

Anal. Calcd. for $C_{13}H_{14}O_2Si$: C, 67.77; H, 6.12; Si, 12.20; active O, 6.94. Found: C, 67.63; H, 6.22; Si, 12.40; active O, 6.80.

Tribenzylsilyl Hydroperoxide.—Into a solution of tribenzylchlorosilane (5 g., 0.0149 mole) in tetrahydrofuran (50 ml.) and anhydrous ether (150 ml.) cooled to 0°, ammonia gas was bubbled for 45 sec. The mixture was stirred for 90 sec. after the addition of 98% hydrogen peroxide (5 ml., 0.2 mole) and then

(10) C. A. Kraus and R. Rosen, J. Am. Chem. Soc., 47, 2739 (1925).

quenched with water. By following the procedure described for methyldiphenyl hydroperoxide, crude tribenzylsilyl hydroperoxide was obtained in 75% purity and 63% yield. Further purification was very difficult. Finally, after several recrystallizations from both nitromethane and petroleum ether, an analytical sample, m.p. 60–61°, was obtained. A slow crystallization from nitromethane at 0° gave macrocrystals weighing up to 1 g. The usual absorption peak at 890 cm.⁻¹ in the infrared spectrum was observed.

Anal. Calcd. for $C_{21}H_{22}O_2Si$: C, 75.40; H, 6.63; Si, 8.38; active O, 4.78. Found: C, 75.49; H, 6.49; Si, 8.20; active O, 4.68.

Tri-*n*-hexylsilyl Hydroperoxide.—By a procedure identical with that used for tribenzylsilyl hydroperoxide, trihexylsilyl hydroperoxide was obtained as a light-colored viscous oil (83% yield) which could not be crystallized. A sample with a peroxide content corresponding to 95% purity had a refractive index of 1.4550 at 20° and showed the characteristic peak at 890 cm.⁻¹ in the infrared spectrum.

Anal. Calcd. for $C_{18}H_{40}O_2Si:$ C, 68.29; H, 12.73; Si, 8.87; active O, 5.05. Found: C, 68.77; H, 12.51; Si, 8.65; active O, 4.80.

Bis(triphenylsilyl) Peroxide from Triphenylsilyl Hydroperoxide.—A solution of triphenylsilyl hydroperoxide (2.5 g., 0.0085 mole) and triphenylchlorosilane (2.5 g., 0.0085 mole) in dry ether (100 ml.) was cooled to 0° and anhydrous trimethylamine was added (5 ml., 0.056 mole). After stirring for 20 min., the reaction mixture was evaporated *in vacuo* to one-third its volume. The precipitate which formed was collected on a filter, washed with water, and dried *in vacuo* at room temperature to yield 1.7 g. (36.2% yield) of white, crystalline bis(triphenylsilyl) peroxide, m.p. 140–141°. The infrared spectrum showed no peak at 890 cm.⁻¹.

Anal. Calcd. for $C_{36}H_{s0}O_2Si_2$: C, 78.50; H, 5.49; Si, 10.19. Found: C, 78.39, 78.61; H, 5.53, 5.65; Si, 10.04, 10.19, 10.15.

When a mixture of concentrated nitric and concentrated sulfuric acids was poured upon the peroxide it ignited and burned explosively. The usual methods of peroxide titration (e.g., including that of Kokatnur and Jelling¹¹) did not give reproducible results and the analytical figures ranged from 1.1 to 2.2%active oxygen (2.91% theoretical).

Bis(tribenzylsilyl) **Peroxide**.—To a solution of tribenzylsilyl hydroperoxide (1 g., 0.003 mole) and tribenzylchlorosilane (1 g., 0.003 mole) in anhydrous ether (80 ml.) was added triethylamine (2 ml., 0.0145 mole) and the mixture was stirred for 10 min. The mixture was evaporated to dryness *in vacuo* and the residue was recrystallized from petroleum ether to yield white, crystalline bis(tribenzylsilyl) peroxide (0.7 g., 37% yield), m.p. 110–111°. The compound had no peak in its infrared spectrum at 890 cm.⁻¹ and did not respond to the normal peroxide analytical procedures (1.0 to 1.5% active oxygen instead of the theoretical 2.52%).

Anal. Caled. for $C_{42}H_{42}O_2Si_2$: C, 79.44; H, 6.66; Si, 8.85; mol. wt., 635. Found: C, 79.30; H, 6.50; Si, 8.60; mol. wt., 648.

Bis(triphenylsilyl) Peroxide from Triphenylsilylamine and Triphenylsilyl Hydroperoxide.—When a solution of triphenylsilyl hydroperoxide (1 g., 0.0034 mole) and triphenylsilylamine (0.95 g., 0.0034 mole) in anhydrous ether (50 ml.) was stirred at room temperature for 2 days, bis(triphenylsilyl) peroxide (0.5 g., 27% yield) of m.p. 140–141° precipitated.

Bis(triphenylsilyl) Peroxide from Triphenylsilylamine.—When a solution of triphenylsilylamine (2 g., 0.0071 mole) and 98%hydrogen peroxide (0.5 ml., 0.02 mole) in 20 ml. of anhydrous ether was stirred vigorously at room temperature for 1.5 hr., a precipitate of bis(triphenylsilyl) peroxide (0.8 g., 41\%), m.p. 140-141°, was obtained.

Bis(triphenylsilyl) Peroxide from Triphenylchlorosilane in a One-Step Process.—Anhydrous ammonia was bubbled for 60 sec. into a cooled (0°) solution of triphenylchlorosilane (5 g., 0.017 mole) in anhydrous ether (150 ml.). Next 98% hyrogen peroxide (5 ml., 0.02 mole) was added and after 90 sec. the mixture was quenched with water (30 ml.). The ether layer was separated, washed, dried, and partially evaporated to yield crystalline bis-(triphenylsilyl) peroxide (2.5 g., 53% yield), m.p. 140–141°.

(11) V. R. Kokatnur and M. Jelling, ibid., 63, 1432 (1941).