crystallized from the reaction mixture. One crystallization from water gave a product (1.5 g.) melting at 259°.

Deacylation and Chromatographic Separation of Fraction I.—Fraction I (3 g.) was deacylated in a similar fashion to that used for pentaerythrityl tetrapropionate. Removal of the methanol gave a sirup which was treated in dry pyridine (50 ml.) and *p*-phenylazobenzoyl chloride[10] (3 g.). The mixture was shaken for a short time and then heated at 85° for three days. The resulting solution was shaken with water (2 ml.) for fifteen minutes and then poured onto ice (300 g.) with vigorous stirring. The resulting mixture was neutralized with sodium bicarbonate and extracted repeatedly with chloroform. The combined chloroform extracts were washed once with water and dried. Chromatographic separation was performed on a column of silicic acid 60 cm. long and 3.3 cm. in diameter. Two distinct bands were obtained. Using chloroform as the eluent, the lower band of the tri-*p*-phenylazobenzoate of methylpentaerythrityl ether was run completely through the column in order to separate the di-*p*-phenylazobenzoate of dimethylpentaerythrityl ether from the *p*-phenylazobenzoic acid. The chloroform solution of the tri-*p*-phenylazobenzoate of methylpentaerythrityl ether was concentrated to 55 ml., mixed well with ethanol (100 ml.) and allowed to stand at 0° until no more precipitate formed. The light orange crystals were filtered, washed with ethanol and recrystallized from ligroin, m. p. 190–191°.

Anal. Calcd. for $C_{45}H_{38}N_6O_7$: C, 69.77; H, 4.95; azoyl, 81.0; mol. wt., 774. Found: C, 70.08; H, 4.87; azoyl, 80.4; mol. wt. (Rast), 773, 793.

The di-*p*-phenylazobenzoate of dimethylpentaerythrityl ether was separated mechanically and removed from the silicic acid with a mixture of chloroform and ethanol. Removal of the solvent gave an orange solid which was recrystallized from ligroin, m. p. 93–94°.

Anal. Calcd. for $C_{33}H_{32}O_6N_4$: C, 68.27; H, 5.51; Found: C, 67.50; H, 5.25.

Summary

The Tollens condensation of acetaldehyde with formaldehyde in 50% methanol gives a mixture of pentaerythritol, methylpentaerythrityl ether and dimethylpentaerythrityl ether.

A mechanism for the formation of ethers in the preparation of pentaerythritol is proposed.

IOWA CITY, IOWA RECEIVED FEBRUARY 16, 1948

---

[10] Coleman, Nichols, McCloskey and Auspon, "Organic Syntheses," **25**, 87 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Oxidations of Certain Polyacetyl-β-D-thioglycosides to the Corresponding Sulfones

BY WILLIAM A. BONNER AND RICHARD W. DRISKO

A single paper by Wrede and Zimmermann[1] seems to be the only report to date considering the oxidation of carbohydrate derivatives containing divalent sulfur. These investigators prepared di-tetraacetylglucosyl sulfone, di-tetraacetylgalactosyl sulfone, di-heptaacetylcellobiosyl sulfone and methyl 6-sulfo-bis-(6-desoxy-2,3,4-triacetyl-β-D-glucoside) by oxidation of the corresponding sulfides with potassium permanganate in acetic acid. Treatment of the first three of these compounds with ammonia in methanol led to the corresponding deacetylated substances. Since the chemistry of the sulfone derivatives in the sugar series has received little attention, and since no sulfones related to the simple thioglucosides have been prepared, it seemed desirable to prepare and study a few representative members of this class of compounds.

When phenyl tetraacetyl-β-D-thioglucoside was dissolved in acetic acid and treated with a slight excess of aqueous potassium permanganate, phenyl tetraacetyl-β-D-glucosyl sulfone resulted in excellent yield and purity. Phenyl triacetyl-β-D-xylosyl, phenyl triacetyl-D-arabinosyl, and ethyl tetraacetyl-β-D-glucosyl sulfones were similarly prepared. Hydrogen peroxide in acetic acid, after the method of Gilman and Beaber,[2] was also found effective in oxidizing thioglycosides to the corresponding sulfones. Phenyl, benzyl and ethyl tetraacetyl-β-D-glucosyl sulfones were prepared in good yield in this manner. It is noteworthy that when hydrogen peroxide was used as oxidant, the oxidation process was apparently attended by deacetylation of the acetylated thioglucoside despite the acetic acid solvent. This unexpected phenomenon is under further investigation at the present time.

The alkyl and aryl polyacetyl-β-D-glycosyl sulfones prepared in this study were white, nicely crystalline substances. The physical properties of the sulfones prepared in this study are contrasted with those of the corresponding parent polyacetyl-β-D-thioglycosides in Table I. It is seen that oxidation of the divalent sulfur atom in the acetylated thioglycoside to the sulfone state brings about the substantial melting point increase usually observed in converting a thioether to its sulfone.[3] Accurate correlations of the trends in the change of optical activity accompanying oxidation of the thioglycoside to its sulfone cannot be made on the basis of the data at hand, but it is apparent from Table I that such changes in rotatory power probably depend both upon the nature of the thio-aglucone and the configuration of the glycosyl residue.

By use of the calculated quantity of potassium permanganate as oxidant an attempt has been made to convert phenyl tetraacetyl-β-D-thioglucoside into phenyl tetraacetyl-β-D-glucosyl sulfoxide, a typical representative of the class intermediate

---

[1] Wrede and Zimmermann, *Z. physiol. Chem.*, **148**, 65 (1925).

[2] Gilman and Beaber, THIS JOURNAL, **47**, 1449 (1925).

[3] *Cf.* C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 661 ff.

TABLE I

COMPARISON OF PROPERTIES OF SEVERAL ACETYLATED THIOGLYCOSIDES WITH THE CORRESPONDING SULFONES

Compound	Acetylated thioglycoside M. p., °C.	Acetylated thioglycoside $[\alpha]_{\mathrm{D}}$, °	Acetylated sulfone M. p., °C.	Acetylated sulfone $[\alpha]_{\mathrm{D}}$, °
Phenyl β-D-thioglucoside	117^{4}	$-17.5^{4,a}$	189.5	-26.9^{a}
Phenyl β-D-thioxyloside	78^{4}	$-58.9^{4,a}$	154.0	-86.8^{a}
Phenyl D-thio-arabinoside	Sirup	$+15.7^{a}$	147.0	$+29.4^{a}$
Benzyl β-D-thioglucoside	98^{5}	$-93.1^{5,b}$	199.0	-48.6^{b}
Ethyl β-D-thioglucoside	$83–84^{6}$	$-27.25^{6,b}$	154.5	-16.4^{b}

[a] In chloroform solution. [b] In ethylene dichloride solution.

in oxidation state between the thioglycosides and their sulfones. Instead of isolating the desired sulfoxide, however, a mixture of the starting thioglucoside and the corresponding sulfone was obtained. It is possible that the sulfoxide, once formed, is more readily oxidized to the sulfone than is the remaining unoxidized thioglucoside oxidized to the sulfoxide.

It was found that by the action of ammoniacal methanol phenyl triacetyl-β-D-xylosyl and phenyl tetraacetyl-β-D-glucosyl sulfones could be readily deacetylated. Both deacetylation products were crystalline solids, the latter forming a hydrate. Both products rapidly reduced Benedict solution. Wrede and Zimmermann[1] similarly report reducing properties for their sulfone derivatives. The deacetylation product of the glucose derivative has been reacetylated to yield its previous acetate, and has been propionylated to give the corresponding tetrapropionate.

An initial attempt has been made to determine the ring structure of the above deacetylation products by their oxidation with periodic acid. The reaction observed, however, seems to be more complex than that usually noted[7] in the periodic acid oxidation of sugar derivatives, since the quantity of periodic acid consumed is not that predicted. Investigations into the cause of this behavior and further ring size studies are currently in progress.

Experimental Part

Phenyl Tetraacetyl-β-D-glucosyl Sulfone.—Phenyl tetraacetyl-β-D-thioglucoside (1.00 g.) was dissolved in glacial acetic acid (25 ml.). To the solution was added slowly with stirring a 5% aqueous solution of potassium permanganate containing 0.53 g. (10% excess) of the oxidant. The mixture was heated on the hot-plate for five minutes at the end of which it had begun to boil. It was cooled and treated with a saturated aqueous solution of sodium bisulfite until clear. On dilution of the clear solution with 125 ml. of water the sulfone precipitated as a white solid; yield 0.93 g. (87%), m. p. 189.5°.[8] On recrystallization from 2-propanol the m. p. was unchanged and the sample had $[\alpha]^{24}_{\mathrm{D}}$ −26.9° (chloroform; *c*, 1.895).

In the peroxide oxidation phenyl tetraacetyl-β-D-thioglucoside (10 g.) was dissolved in glacial acetic acid (75 ml.) and treated with 30% hydrogen peroxide (14 g., 173% excess). The mixture was refluxed for two hours, cooled, and poured into an excess of water. No precipitate formed, suggesting that the compound had undergone deacetylation during the course of oxidation. The mixture was distilled to dryness *in vacuo* and the residue treated with acetic anhydride (75 ml.) and sodium acetate (1 g.). After refluxing for one and one-half hours the acetylation mixture was poured into water to give a brown oil which solidified on rapid stirring. The crude material was filtered, dried, and weighed 7.0 g. (65%). After recrystallization from 2-propanol the m. p. was 188° and $[\alpha]^{21}_{\mathrm{D}}$ −27.2° (chloroform; *c*, 8.019).

Anal. Calcd. for $C_{20}H_{24}O_{11}S$: C, 50.85; H, 5.12; S, 6.80. Found: C, 50.58, 50.71; H, 5.14, 5.11; S, 6.84.

The failure to observe a precipitate on pouring the reaction mixture from the peroxide oxidation into water was interpreted as indicative of accompanying deacetylation. To test this supposition several test-tube experiments were undertaken.

Four test-tubes were charged with the following mixtures: Tube A, phenyl tetraacetyl-β-D-thioglucoside (0.50 g.) and acetic acid (8 ml.); Tube B, phenyl tetraacetyl-β-D-thioglucoside (0.50 g.), acetic acid (8 ml.) and 30% hydrogen peroxide (1.0 g.); Tube C, phenyl tetraacetyl-β-D-glucosyl sulfone (0.50 g.), acetic acid (8 ml.), and 30% hydrogen peroxide (1.0 g.); Tube D, acetic acid (8 ml.) and 30% hydrogen peroxide (1.0 g.). The tubes were placed in boiling water for two hours and cooled. Then phenyl tetraacetyl-β-D-glucosyl sulfone (0.50 g.) was dissolved in Tube D. The contents of each tube were poured into 125 ml. of water, and the four resulting mixtures placed at 0° overnight. The products were filtered, rinsed with water, and air-dried. Tube A gave unchanged thioglucoside (0.37 g., m. p. 115.5°). Tubes B, C and D gave phenyl tetraacetyl-β-D-glucosyl sulfone as follows: Tube B, (0.19 g., m. p. 180°); Tube C, (0.43 g., m. p. 187.5°); Tube D, (0.46 g., m. p. 188°). The low yield and m. p. of the product from Tube B is interpreted as due to deacetylation accompanying the oxidation of the thioglucoside.

Phenyl Triacetyl-β-D-xylosyl Sulfone.—Phenyl triacetyl-β-D-thioxyloside (1.00 g.) dissolved in acetic acid (15 ml.) was treated with potassium permanganate (0.63 g., 10% excess) dissolved in water (10 ml.). The mixture was heated for thirty minutes on the steam-bath, then cooled, clarified by addition of sufficient solid sodium bisulfite, and diluted with 1[illegible]5 ml. of ice water. There resulted 1.09 g. (99%) of crude sulfone, m. p. 151°. After three recrystallizations from 2-propanol the compound had m. p. 154° and $[\alpha]^{22}_{\mathrm{D}}$ −86.8° (chloroform; *c*, 1.729).

Anal. Calcd. for $C_{17}H_{20}O_9S$: C, 51.0; H, 5.04. Found: C, 51.0; H, 5.11.

Phenyl Triacetyl-D-thioarabinoside.—Acetyl bromide (27 ml., equiv. amount) was cooled to 0° in a salt–ice mixture. D-Arabinose (10 g.) (α,β-mixture) was added with mechanical stirring over a period of twenty minutes. The cold bath was removed and the mixture allowed to warm slowly. Whenever the reaction became too vigorous as evidenced by excessive evolution of hydrogen bromide the cold bath was momentarily replaced. After twenty minutes of such treatment the reaction mixture was a homogeneous, amber fluid. It was stirred at room temperature for an additional twenty-four hours, then diluted with chloroform (100 ml.). The solution was washed with ice water, cold bicarbonate solution, and ice water, then treated with calcium chloride until clear. Removal of the solvent *in vacuo* at 45–50° resulted in 15.9 g. (70%) of crude acetobromo-D-arabinose, a thick, crystalline paste.

The crude product above (15.9 g.) was dissolved in

---

(4) Purves, THIS JOURNAL, **51**, 3619 (1929).

(5) Schneider, Sepp and Stiehler, *Ber.*, **51**, 214 (1918).

(6) Schneider, Gille and Eisfeld, *ibid.*, **61**, 1244 (1928).

(7) Jackson in Chap. 8, "Organic Reactions," Vol. II, John Wiley and Sons, New York, N. Y., 1944.

(8) All melting points are corrected.

chloroform (75 ml.) and treated with ethanol (75 ml.) containing potassium hydroxide (2.63 g., one equiv.) and thiophenol (5.3 ml., 10% excess) after the manner of Purves.[3] After refluxing forty minutes the mixture was washed twice with water, once with 10% potassium hydroxide solution, again with water, then dried over sodium sulfate and decolorized by filtration through Norit and Celite. Removal of the solvent at 80° *in vacuo* left 7.8 g. (45%) of clear, amber sirup. This showed no tendency to crystallize on standing in 2-propanol, in agreement with the observation of Fletcher and Hudson.[9] The 2-propanol solution was, therefore, poured into water, the mixture extracted with ether, and the extract washed as above. The resulting sirup obtained after drying and distillation of solvent was used without further purification; $[\alpha]^{23}\mathrm{D}$ +15.7° (chloroform; *c*, 4.583).

Anal. Calcd. for $C_{11}H_{11}O_6S(OCCH_3)_3$: acetyl, 35.1. Found:[10] acetyl, 34.5.

Phenyl Triacetyl-D-arabinosyl Sulfone.—One gram of the sirupy product above was oxidized exactly as described for the corresponding xylose derivative. The oxidation mixture was poured into water and the milky suspension extracted with ether. The extract was washed with water, bicarbonate solution and water, then dried over anhydrous sodium sulfate. Removal of the solvent left a clear sirup which, on treatment with 2-propanol, gave 0.50 g. (46%) of crude solid product, m. p. 144 to 145°. After four recrystallizations from 2-propanol the substance had m. p. 147° and $[\alpha]^{23}\mathrm{D}$ +29.5° (chloroform; *c*, 1.290).

Anal. Calcd. for $C_{17}H_{20}O_9S$: C, 51.0; H, 5.04. Found: C, 51.2; H, 5.02.

Benzyl Tetraacetyl-β-D-glucosyl Sulfone.—Benzyl tetraacetyl-β-D-thioglucoside[4] (2.0 g.) was dissolved in acetic acid (20 ml.), and 30% hydrogen peroxide (5 g.) was added. The mixture was refluxed for two hours, the solvent evaporated under reduced pressure, and the residue acetylated with acetic anhydride (50 ml.) and sodium acetate (2 g.) as before. Isolation of the product in the previous fashion gave 1.6 g. (75%) of crude product, m. p. 196.5°. One recrystallization from 2-propanol gave the pure material, m. p. 199°, $[\alpha]^{28}\mathrm{D}$ −44.6° (chloroform; *c*, 1.995), $[\alpha]^{22}\mathrm{D}$ −48.6° (ethylene dichloride; *c*, 1.523).

Anal. Calcd. for $C_{13}H_{16}O_7S(OCCH_3)_4$: C, 51.8; H, 5.39; acetyl, 35.4. Found: C, 51.7; H, 5.34; acetyl, 35.7.

Ethyl Tetraacetyl-β-D-glucosyl Sulfone.—Ethyl tetraacetyl-β-D-thioglucoside[4] (5.0 g.) was refluxed for two hours in acetic acid (100 ml.) containing 30% hydrogen peroxide (18 g.). The acetic acid was distilled *in vacuo* with heating below 70°, and the residue acetylated and processed in the previous manner. There resulted 5.6 g. (103%) of crude product, m. p. 154°. After one recrystallization from 2-propanol the pure product had m. p. 154.5°, $[\alpha]^{26}\mathrm{D}$ −15.0° (chloroform; *c*, 1.334), $[\alpha]^{22}\mathrm{D}$ −16.4° (ethylene dichloride; *c*, 1.095).

Anal. Calcd. for $C_8H_{12}O_7S(OCCH_3)_4$: C, 45.3; H, 5.70; acetyl, 40.7. Found: C, 45.5; H, 5.83; acetyl, 40.9.

Ethyl tetraacetyl-β-D-thioglucoside (0.60 g.) was dissolved in acetic acid (25 ml.) and 5% potassium permanganate solution (8.5 g., 32% excess) added. After heating five minutes the mixture was cooled and processed as in previous permanganate oxidations. The crude product weighed 0.44 g. (68%) and had m. p. 154.5° and $[\alpha]^{23}\mathrm{D}$ −15.5° ($CHCl_3$; *c*, 1.611).

Attempted Oxidation of Phenyl Tetraacetyl-β-D-thioglucoside to Sulfoxide.—Phenyl tetraacetyl-β-D-thioglucoside (2.00 g.) was dissolved in acetic acid (25 ml.). To this was slowly added with stirring an aqueous solution (25 ml.) containing 0.49 g. (theoretical amount for oxidation to the sulfoxide) of potassium permanganate. The solution was warmed for five minutes on the hot-plate, cooled, clarified with saturated bisulfite solution, and diluted to 125 ml. with water. The flocculent precipitate was filtered, rinsed and air-dried, m. p. 125° with preliminary softening. This was recrystallized four times from a mixture of acetone and water giving successive melting points of 145, 155, 158–160 and 162–164°. It was then recrystallized six times from 2-propanol to give successive melting points of 172–174°, 176–177°, 176–178°, 183–185°, 187–187.5° and 188°. All melting points but the last two showed preliminary softening. A mixed melting point of the final product with phenyl tetraacetyl-β-D-glucosyl sulfone showed no depression (188°). From the initial filtrate there was obtained an additional 0.18 g. of solid on further standing, m. p. 111°. On recrystallization from 2-propanol this melted at 114° and showed no mixed m. p. depression (114°) with a sample of phenyl tetraacetyl-β-D-thioglucoside of m. p. 115°.

Phenyl β-D-Xylosyl Sulfone.—Phenyl triacetyl-β-D-xylosyl sulfone (0.66 g.) was dissolved in methanol (30 ml.) which had been saturated with ammonia, and the solution permitted to stand for four days in an open beaker. The solvent evaporated to leave a white solid, m. p. 156°, dec. The product, after recrystallization from 2-propanol, readily reduced Benedict solution. The recrystallized product was extracted four times with hot ether. The remaining solid weighed 0.24 g. (53%) and had m. p. 160° dec., unchanged on further recrystallization from 2-propanol; $[\alpha]^{19}\mathrm{D}$ was −44.8° (water; *c*, 1.137).

Anal. Calcd. for $C_{11}H_{14}O_6S$: C, 48.2; H, 5.14. Found: C, 48.2; H, 5.09.

Phenyl β-D-Glucosyl Sulfone Hydrate.—Phenyl tetraacetyl-β-D-glucosyl sulfone (2.00 g.) was covered with 100 ml. of methanol saturated with ammonia, and stirred until solution was complete. The solution stood for two days in an open beaker, after which the residual solvent was evaporated in an air stream. The tan residue was extracted four times with hot ether to leave 1.32 g. (102%) of sticky tan solid. This was dissolved in a slight excess of 2-propanol and the solution decolorized with Norit. Ligroin was added to the clear solution until slightly cloudy and on cooling in ice there resulted 0.88 g. (68%) of white crystalline solid, m. p. 90–92°. A second recrystallization raised the m. p. to 91–92°. A combustion analysis and quantitative drying in an Abderhalden pistol showed that this material contained water of hydration. Consequently, the sample was recrystallized from 2-propanol containing 10% water and ligroin, m. p. 92–93°. $[\alpha]^{26}\mathrm{D}$ was −15.0° (water; *c*, 1.132).

Anal. Calcd. for $C_{12}H_{16}O_7S{\cdot}H_2O$: C, 44.7; H, 5.63. Found: C, 44.7; H, 5.73.

On reacetylation of the above sample with acetic anhydride and sodium acetate the acetylated sulfone was obtained in 87% crude yield, m. p. 188.5°, $[\alpha]^{28}\mathrm{D}$ −26.8° (chloroform; *c*, 1.047).

An attempt was made to deacetylate phenyl tetraacetyl-β-D-glucosyl sulfone by the procedure of Bonner and Koehler[11] using potassium methylate followed by potentiometric titration with perchloric acid. The product obtained, however, did not crystallize, and proved to contain around 8% of inorganic ash. Apparently the deacetylation product retained a certain amount of potassium perchlorate which could not be separated. The sirup obtained had $[\alpha]^{22}\mathrm{D}$ −14.3° (ethyl alcohol; *c*, 2.310), and was shown to be substantially phenyl β-D-glycosyl sulfone by the fact that it could be reacetylated to give the original starting material in 75% yield.

Phenyl Tetrapropionyl-β-D-glycosyl Sulfone.—Impure, sirupy phenyl β-D-glucosyl sulfone (0.14 g.) from the second reaction above was dissolved in pyridine (4 ml.) and treated with propionic anhydride (10 ml.). The mixture stood for two days at 0° and was thrown into ice

---

[9] Fletcher and Hudson, THIS JOURNAL, **69**, 1673 (1947).

[10] Since the compound in question was a sirup and incapable of further purification by convenient means, and since the sulfone prepared from this sirup gave an acceptable analysis, no attempt was made to obtain further analytical data for this compound.

[11] Bonner and Koehler, THIS JOURNAL, **70**, 314 (1948).

water. After stirring for several hours the oil was extracted into ether and the extract washed with water, 4 *N* hydrochloric acid, water, saturated bicarbonate solution, and water. After drying over sodium sulfate the solvent was distilled to yield 0.17 g. (70%) of amber sirup which could not be crystallized from 2-propanol; $[\alpha]^{19}D$ was $-23.9°$ (chloroform; *c*, 33.3).

Anal. Calcd. for $C_{24}H_{32}O_{11}S$: C, 54.5; H, 6.10. Found: C, 55.3; H, 6.24.

Summary

1. Alkyl and aryl polyacetyl-β-D-thioglycosides have been shown to be readily oxidized to the corresponding alkyl or aryl polyacetyl-β-D-glycosyl sulfones by action of either potassium permanganate or 30% hydrogen peroxide. Partial deacetylation apparently attends the latter oxidation in acetic acid medium. A number of examples of these oxidations are given, and several members of this new class of sulfones are described.

2. Two phenyl polyacetyl-β-D-glycosyl sulfones have been deacetylated using ammoniacal methanol, and the deacetylation products have been described.

STANFORD UNIVERSITY
STANFORD, CALIFORNIA

RECEIVED JANUARY 21, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

5-Alkyl (or 5-Phenyl)-5-propoxymethylhydantoins[1]

BY HENRY R. HENZE, JOE W. MELTON[2] AND EUGENE O. FORMAN

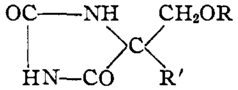
Some time ago, Henze and Rigler[3] prepared 5-ethoxymethyl-5-phenylhydantoin which later was shown to possess considerable anticonvulsant activity.[4] This behavior is in contrast to that of 5-ethyl-5-isoamyoxymethylhydantoin[3] which shows no anticonvulsant activity even in far larger doses,[4] and is, in fact, an unsatisfactory soporific, To obtain additional compounds, suitable for subsequent pharmacological testing for activity, we converted seventeen keto ethers, previously reported,[5] into the corresponding 5-alkyl (or 5-phenyl)-5-propoxymethylhydantoins. The latter have proved to be potent anticonvulsants,[4] the most active being 5-isopropoxymethyl-5-phenylhydantoin which compares favorably with 5,5-diphenylhydantoin in this respect and has merited clinical study.

Experimental

The hydantoins were obtained by warming a mixture of 1 part of keto ether, 1.1 parts of potassium cyanide and 3 parts of ammonium carbonate (U. S. P. cubes) in sufficient 50% alcohol at 58–60° for periods up to twenty-four hours. After the period of interaction, the solutions were evaporated to about half volume, acidified with hydrochloric acid and boiled to remove hydrogen cyanide. Usually, at this point, the hydantoins

TABLE I

5-ALKYL (OR 5-PHENYL)-5-PROPOXYMETHYLHYDANTOINS



—R	—R'	M. p., °C. (cor.)	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
C_3H_7-*n*	$-CH_3$	85.0	42	51.60	51.39	7.58	7.51	15.05	15.38
C_3H_7-iso	$-CH_3$	136.5	49	51.60	51.35	7.58	7.71	15.05	15.10
C_3H_7-*n*	$-CH_2CH_3$	96.0	51	53.98	54.04	8.05	7.92	13.99	14.05
C_3H_7-iso	$-CH_2CH_3$	143.5	34	53.98	54.14	8.05	8.23	13.99	14.11
C_3H_7-*n*	$-(CH_2)_2CH_3$	113.0	54	56.05	55.91	8.47	8.30	13.08	13.32
C_3H_7-iso	$-(CH_2)_2CH_3$	166.5	66	56.05	56.08	8.47	8.76	13.08	13.38
C_3H_7-iso	$-CH(CH_3)_2$	182.0	54	56.05	56.20	8.47	8.47	13.08	13.07
C_3H_7-*n*	$-(CH_2)_3CH_3$	141.5	35	57.87	57.87	8.83	8.83	12.27	12.58
C_3H_7-iso	$-(CH_2)_3CH_3$	175.8	74	57.87	57.83	8.83	9.03	12.27	12.44
C_3H_7-iso	$-CH_2CH(CH_3)_2$	221.7	65	57.87	57.78	8.83	8.95	12.27	12.52
C_3H_7-iso	$-CH(CH_3)CH_2CH_3$	180.2	64	57.87	57.73	8.83	8.86	12.27	12.51
C_3H_7-*n*	$-(CH_2)_4CH_3$	130.0	60	59.48	59.65	9.15	9.08	11.56	11.67
C_3H_7-iso	$-(CH_2)_4CH_3$	165.4	85	59.48	59.79	9.15	9.34	11.56	11.68
C_3H_7-*n*	$-(CH_2)_2CH(CH_3)_2$	180.0	45	59.48	59.70	9.15	9.24	11.56	11.63
C_3H_7-iso	$-(CH_2)_2CH(CH_3)_2$	218.2	78	59.48	59.56	9.15	9.37	11.56	11.45
C_3H_7-*n*	$-C_6H_5$	133.0	75	62.89	62.67	6.50	6.33	11.28	11.42
C_3H_7-iso	$-C_6H_5$	162.0	78	62.89	62.89	6.50	6.34	11.28	11.52

---

(1) From the M. A. thesis of J. W. M. (August, 1940) and of E. O. F. (June, 1941).

(2) Present address: Department of Chemistry, Northwestern State College, Alva, Okla.

(3) Rigler with Henze, THIS JOURNAL, **58**, 474 (1936).

(4) Merritt, Putnam and Bywater, *J. Pharmacol.*, **84**, 67 (1945).

(5) Henze, Duff, Matthews, Melton and Forman, THIS JOURNAL, **64**, 1222 (1942).