Experimental Section

Gas Chromatography.—All samples were analyzed by gas chromatography. The great majority of the results which were less successful than those described here is recorded elsewhere.[13] An aliquot of the crude phenolic products was converted to the methyl ethers as described previously.[14] A 5-μl sample of the methyl ethers dissolved in methylene chloride was then injected onto a column: 15% XF-1150 on Chromosorb W (100–140 mesh), 6 ft × 0.25 in., 160°, flow rate of He 70 ml/min, thermal conductivity detector. Retention times were anisole, 2:58 (minutes:seconds); *m*-bromo, 8:15; *p*-bromo, 10:20; *o*-bromo, 12:15; 2,6-dibromo, 20:40; 2,4,6-tribromoanisole, 45:40.

2,6-Dibromophenol.—In a 5-l. three-necked flask fitted with a good mechanical stirrer, low-temperature thermometer, and addition funnel protected with a drying tube was mixed 2.5 l. of dry toluene and 147 g (2 moles) of *t*-butylamine. The flask was surrounded by a suitable container to serve as an isopropyl alcohol and Dry Ice cooling bath. The contents were cooled to −20 to −30°, and 160 g (1 mole) of bromine was added dropwise over a period of 10 min. The solution was then cooled to −70 to −75° by the addition of more Dry Ice to the cooling bath at which time 47 g (0.5 mole) of anhydrous phenol dissolved in methylene chloride was added over a period of 5 min. The reaction mixture was allowed to warm to room temperature over a period of at least 5 to 6 hr at which time the contents were washed with 500 ml of water in a separatory funnel. The organic phase was then extracted with 300- and 200-ml portions of 10% aqueous sodium hydroxide. The combined alkaline extracts were cooled and carefully acidified. The oil which separated was extracted with 200- and 100-ml portions of methylene chloride, and the combined extracts were dried with anhydrous magnesium sulfate and filtered. The filtrate evaporated to dryness at room temperature gave 110 g (87%) of white crystals of 2,6-dibromophenol, mp 50–53°. The phenol can be further purified by recrystallization from 200 ml of hexane (94 g, 75%), mp 55–56°.

2-Bromophenol.—The above procedure was used but the amount of phenol was doubled and the amount of bromine and *t*-butylamine was halved. The oil which separated after reaction was dissolved in 1 l. of hexane and washed thoroughly with four 500-ml portions of water to remove unreacted phenol. The hexane fraction was then concentrated and the residue was distilled through a 20-cm Vigreux column, bp 186–195°. The yield was 52 g (60%) an aliquot of which showed better than 99% purity by gas chromatography. Both of the above preparations have been duplicated.

2-Isopropyl-5-methyl-6-bromophenol (*o*-Bromothymol).—On a 0.025-mole scale, thymol was brominated similarly to give 4.7 g (80%) of a light yellow oil: bp 83–84° (0.5 mm); nmr (τ = 0 ppm for tetramethylsilane) τ 3.43 and 3.16 (doublet of doublets, J_{AB} = 8 cps for aromatic hydrogen atoms). Also, the product was shown to be different from *p*-bromothymol by gas chromatography of the methyl ethers: 10% silicone rubber column at 150° and 15-ml/min flow rate of He; retention times, *o*-bromothymol 7:07 and *p*-bromothymol 8:47. The phenoxyacetic derivative, recrystallized from water, gave colorless needles, mp 90.5–91.5°.

Anal. Calcd for $C_{12}H_{15}BrO_3$: C, 50.19; H, 5.23; Br, 27.85. Found: C, 49.96; H, 5.22; Br, 28.03.

7-Bromo-8-hydroxyquinoline.—On a 0.02-mole scale, the bromination of 8-hydroxyquinoline as above gave 4.1 g (92%) of precipitated solid, mp 137–138° (lit.[15] mp 138°). It was shown to be a single substance by tlc.

2-Bromo-1-naphthol.—On a 0.1-mole scale, the bromination of 1-naphthol as above gave a deep purple solution which on warming to room temperature turned light yellow. The resulting phenol was steam distilled to give 13.6 g (61%) of white crystals, mp 44–45° (lit.[16] mp 45°), with a single spot on tlc.

Modifications in Bromination of Phenol.—Using essentially the same procedure as above (except for the stated modification) and analyzing the total crude product by glpc gave the following results: with synthesized N-bromo-*t*-butylamine[11] in place of same reagent prepared *in situ*, 60% *o*-bromo, traces of *p*-bromo, 24% 2,6-dibromo, and 16% phenol; with no basic amine, no *o*-bromophenol, over 99% *p*-bromophenol; triethylenediamine (Dabco) in place of *t*-butylamine, 75% *o*-bromo, 2% *p*-bromo, and 21% 2,6-dibromophenol (monobromo fraction 99% *ortho*); triethylamine in place of *t*-butylamine, 27% *o*-bromo, 29% *p*-bromo, 8% phenol, the remainder being polybromophenols; N-bromosuccinimide in place of bromine and *t*-butylamine, 55% *o*-bromo, 4% *p*-bromo, 14% 2,6-dibromo, and 27% phenol (monobromo fraction 93% *ortho*); *t*-butyl hypobromite in place of bromine and *t*-butylamine, 65% *o*-bromo, 22% *p*-bromo, and 13% phenol (monobromo fraction 76% *ortho*); silver phenoxide suspended in methylene chloride to which bromine in the same solvent is added dropwise in the absence of light (the best of some 40 odd brominations of phenoxides), 29% *o*-bromo, 17% *p*-bromo, 27% 2,6-dibromo, and 27% phenol.

Attempted *ortho* Bromination of Other Substances.—Anisole gave no nuclear bromination product but rather a lachrymatory mixture indicative of methyl bromination. Anisole with *t*-butyl hypobromite gave a product consisting of 93% *p*-bromoanisole and 7% anisole. Diphenyl carbonate and phenylurethan with bromine–*t*-butylamine system gave brominated products containing no more than 10% *o*-bromophenol. *m*-Chlorophenol yielded a mixture of 2-bromo-3-chloro- and 6-bromo-3-chlorophenol which could not be separated easily. Salicylic acid gave a mixture of brominated acids which could not be separated. Catechol gave oxidation products rather than clean substitution products.

Attempted *ortho* Chlorination of Phenol.—The following reagents in toluene or methylene chloride solution at low temperature gave these results: N-chloro-*t*-butylamine, 13% phenol, 58% *o*-chloro, 29% *p*-chloro, and no polychloro; chlorine with triethylenediamine, 38% *o*-chloro, 19% *p*-chloro, and 43% polychloro; N-chlorosuccinimide gave no reaction at room temperature. These results are inferior for *ortho* chlorination as compared to *ortho* bromination. Other conditions are being investigated.

Registry No.—2,6-Dibromophenol, 608-33-3; 2-bromophenol, 95-56-7; 2-isopropyl-5-methyl-6-bromophenol, 13019-31-3; 7-bromo-8-hydroxyquinoline, 13019-32-4; 2-bromo-1-naphthol, 771-15-3.

Acknowledgment.—The authors are indebted to the National Science Foundation for support of this work.

(13) R. D. Wysong, Ph.D. Thesis, Vanderbilt University, 1967.
(14) L. A. Fury, Jr., and D. E. Pearson, *J. Org. Chem.*, **30**, 2301 (1965).
(15) A. Claus and R. Giwartovsky, *J. Prakt. Chem.*, **54**, 379 (1896).
(16) H. H. Hodgson and D. E. Hathaway, *J. Chem. Soc.*, 538 (1944).

1,2-Diazetidinediones

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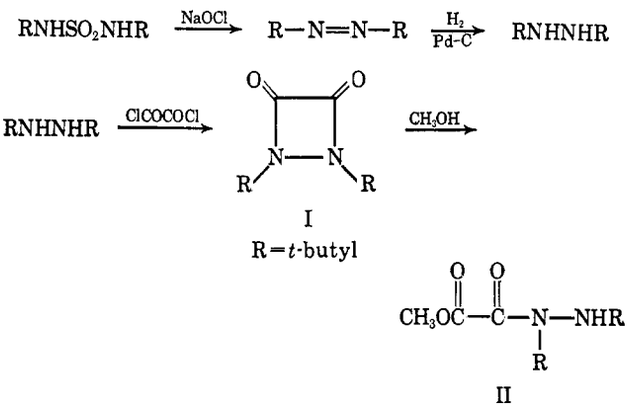
Uretidinediones, the cyclic dimers of isocyanates, are well known,[1] but no examples of 1,2-diazetidinediones have been previously established. Cyclooxalylhydrazide was claimed as a product from the pyrolysis of acetophenonesemioxamazone ($PhCCH_3$-$NNHCOCONH_2$) and similar compounds, but the product was probably polymeric oxalylhydrazide in view of its stability and insolubility.[2]

We have prepared the first examples of 1,2-diazetidinediones. The reaction of oxalyl chloride with N,N′-di-*t*-butylhydrazine afforded the yellow, crystalline di-*t*-butyl-1,2-diazetidinedione (I). This compound exhibits a carbonyl absorption in the infrared at 1813 cm^{-1} which is indicative of a strained amide carbonyl. For comparison diphenyluretidinedione absorbs at

(1) Uretidinediones are reviewed by J. A. Moore, in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 965.
(2) F. J. Wilson and E. C. Pickering, *J. Chem. Soc.*, **127**, 965 (1925); C. Bülow and M. Lobeck, *Ber.*, **40**, 708 (1907).

1775 cm^{-1},[3] unfused β-lactams absorb within the range 1760–1730 cm^{-1},[4] and diazetidinones absorb within the range 1790–1735 cm^{-1}.[5,6] Di-*t*-butyl-1,2-diazetidinedione can be stored indefinitely at room temperature under nitrogen but it decomposes rapidly upon exposure to air. It can be gas chromatographed at 150° on SE-30 columns. The addition of a trace of hydrochloric acid to a methanol solution of I caused immediate reaction to afford methyl N,N′-di-*t*-butyloxalazate (II). This reaction required 1 day for completion when the hydrochloric acid was omitted. The diazetidinedione decomposed slightly during 16 hr at 125°, but at 150° it decomposed to isobutylene, carbon monoxide, carbon dioxide, and a polymer.



I

R=*t*-butyl

II

The N,N′-di-*t*-butylhydrazine was prepared by hydrogenation of 2,2′-azobisisobutane which was, in turn, made by the reaction of N,N′-di-*t*-butylsulfamide with aqueous, alkaline sodium hypochlorite.[7]

The reaction of N,N′-diisopropylhydrazine with pyridine–oxalyl chloride complex affords diisopropyl-1,2-diazetidinedione, a yellow liquid which polymerizes at room temperature in a few hours. However, it can be stored under vacuum at −20° for several days. The infrared carbonyl absorption of this compound is at 1815 cm^{-1}.

Experimental Section

N,N′-Di-*t*-butylsulfamide.—Sulfuryl chloride (67.5 g, 0.50 mole) in 75 ml of pentane was slowly added, with stirring and ice bath cooling, to a solution of 146.2 g (2.00 moles) of *t*-butylamine in 250 ml of pentane. Water (200 ml) was slowly added and the resulting mixture was filtered. The solid was washed with water and recrystallized from 300 ml of benzene to afford 70.4 g (68%) of white solid, mp 139–142°. A sample recrystallized again from benzene had mp 140–142°; nmr ($CDCl_3$) τ 8.64 (18 H), 5.50 (2 H).

Anal. Calcd for $C_8H_{20}N_2O_2S$: C, 46.1; H, 9.7; N, 13.5; S, 15.4. Found: C, 46.0; H, 9.7; N, 13.3; S, 15.2.

2,2′-Azobisisobutane.—N,N′-Di-*t*-butylsulfamide (62.5 g, 0.30 mole), sodium hydroxide (24.0 g, 0.60 mole), sodium hypochlorite (400 ml of 1.5 *M* solution), and 100 ml of pentane were stirred together until all of the sulfamide was dissolved (about 3 hr) with occasional ice-bath cooling to keep the temperature below 36°. The pentane layer was then separated, dried over anhydrous magnesium sulfate, and distilled through a spinning-band column to give 35.7 g (84%) of yellow liquid: bp 98–109°, n^{24}D 1.3940 (lit. n^{20}D 1.3961,[8] bp 109–110°[9]).

N,N′-Di-*t*-butylhydrazine.—2,2′-Azobisisobutane (35.7 g, 0.251 mole) in 200 ml of glacial acetic acid was reduced in a Parr hydrogenator at 50 psi using 1.0 g of 5% palladium-on-carbon catalyst. After 24 hr the catalyst was removed by filtration and the acetic acid was removed by distillation. The colorless residue (acetate) solidified upon cooling. This solid was shaken with 200 ml of 40% potassium hydroxide solution and the organic layer was separated and dried over sodium hydroxide pellets to afford 33.4 g (92%) of a colorless liquid: bp 136° (729 mm), n^{20}D 1.4151. This had to be stored in the absence of air since it was readily oxidized to the azo compound.

A sample of the air-stable hydrochloride was recrystallized from carbon tetrachloride–chloroform to afford white needles, mp 211–213° (bubbles).

Anal. Calcd for $C_8H_{21}ClN_2$: C, 53.2; H, 11.7; Cl, 19.6; N, 15.5. Found: C, 53.6; H, 11.6; Cl, 19.9; N, 15.4.

Di-*t*-butyl-1,2-diazetidinedione.—Oxalyl chloride (8.46 g, 0.0667 mole) in 20 ml of pentane was added over 5 min to a stirred solution of 28.85 g (0.200 mole) of N,N′-di-*t*-butylhydrazine in 200 ml of pentane under nitrogen. This was kept near 25° with an ice bath. A white precipitate of N,N′-di-*t*-butylhydrazine hydrochloride appeared and the solution became yellow. Stirring was continued for 10 min and the mixture was filtered. The solid was washed with more pentane. The combined pentane solutions were evaporated under aspirator vacuum to give a yellow solid which was distilled into a flask in an ice bath, to give 7.66 g (58%) of a yellow, crystalline material: bp 64° (0.2 mm); mp 56–57°; $\nu_{max}^{CCl_4}$ 1813 cm^{-1}; nmr ($CDCl_3$) singlet at τ 8.16; ultraviolet spectrum (heptane) λ_{max} 374 mμ (ϵ 96), 338 (76), 322 (120), 308 (150), 295 (150), and 217 (440, shoulder). The molecular weight as determined by vapor pressure osmometry was 196 (calcd 198).

Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.6; H, 9.1; N, 14.1. Found: C, 60.3; H, 8.9; N, 14.4.

The compound was stored under vacuum at room temperature.

Methyl N,N′-Di-*t*-butyloxalazate.—To di-*t*-butyl-1,2-diazetidinedione (0.800 g, 4.04 mmoles) in 3 ml of methanol was added 1 drop of methanolic hydrochloric acid. The yellow solution immediately became colorless. The methanol was evaporated and the white, solid residue was recrystallized from hexane to afford 0.764 g (82%) of white needles: mp 74–75°; $\nu_{max}^{CCl_4}$ 1666, 1680, 1753, 3330 cm^{-1}; nmr (CCl_4) τ 5.92 (1 H, broad), 6.27 (3 H), 8.61 (9 H), 8.91 (9 H).

Anal. Calcd for $C_{11}H_{22}N_2O_3$: C, 57.4; H, 9.6; N, 12.2. Found: C, 57.7; H, 9.2; N, 12.2.

In another preparation without the methanolic hydrochloric acid, 1 day was required for completion.

Pyrolysis.—Di-*t*-butyl-1,2-diazetidinedione (0.595 g) was sealed in a 6-ml glass tube under vacuum and heated at 150° for 1 day. This afforded 0.424 g of polymeric solid and a mixture of gases. An infrared spectrum of the gas mixture indicated the presence of isobutylene, carbon monoxide, and carbon dioxide as well as a small amount of an isocyanate. When the material was heated at 125° for 16 hr only slight decomposition occurred.

N,N′-Diisopropylhydrazine was prepared by a method similar to that used by Lochte, Bailey, and Noyes[10] using 25.0 g (0.50 mole) of hydrazine hydrate, 78.8 g (1.36 moles) of acetone, 49.2 g (0.50 mole) of 37% hydrochloric acid, 0.30 g of platinum oxide, and hydrogen (50-psi initial pressure) in 150 ml of water in a Parr hydrogenator. This gave 54.2 g (93%) of N,N′-diisopropylhydrazine, n^{20}D 1.4150 (lit.[10] n^{24}D 1.4125).

Diisopropyl-1,2-diazetidinedione.—Oxalyl chloride (3.81 g, 0.030 mole) in 10 ml of hexane was added to a solution of 4.83 g (0.061 mole) of pyridine in 90 ml of hexane under nitrogen to afford a yellow precipitate. N,N′-diisopropylhydrazine (3.48 g, 0.030 mole) was added and the mixture was heated at reflux for 5 min. This was cooled and filtered and the hexane was removed under aspirator vacuum. The yellow residue was heated at 100° (0.1 mm) and the volatile material was collected in a trap. This collected yellow liquid (1.05 g) was shown to be approximately 95% pure by gas chromatographic analysis (20% yield). Pure analytical samples were collected by gas chromatography using a 20% SE-52 on Anakrom ABS column at 110°: n^{17}D

(3) I. Lengyel, Ph.D. Thesis, Massachusetts Institute of Technology, 1963, p 29.

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 214.

(5) C. W. Bird, *J. Chem. Soc.*, 674 (1963); 5284 (1964).

(6) W. Fischer and E. Fahr, *Tetrahedron Letters*, 5245 (1966); E. Fahr, W. Fischer, A. Jung, and L. Sauer, *ibid.*, 161 (1967).

(7) This is a further example of the azo compound synthesis method of R. Ohme and E. Schmitz, *Angew. Chem. Intern. Ed. Engl.*, **4**, 433 (1965).

(8) A. U. Blackham and N. L. Eatough, *J. Am. Chem. Soc.*, **84**, 2922 (1962).

(9) E. Farenhorst and E. C. Kooyman, *Rec. Trav. Chim.*, **72**, 993 (1953).

(10) H. L. Lochte, J. R. Bailey, and W. A. Noyes, *J. Am. Chem. Soc.*, **43**, 2597 (1921); **44**, 2556 (1922).

1.4462; nmr ($CDCl_3$) τ 6.25 (2 H, septuplet), 8.66 (12 H, doublet); $\nu_{max}^{CCl_4}$ 1815 cm^{-1}; ultraviolet spectrum (heptane) λ_{max} 357 mμ (ϵ 190), 319 (150, shoulder), 306 (230), 294 (250), 285 (210, shoulder), and 230 (670, shoulder).

Anal. Calcd for $C_8H_{14}N_2O_2$: C, 56.5; H, 8.3; N, 16.5. Found: C, 56.6; H, 8.4; N, 16.9.

Acknowledgment.—The author is indebted to Mr. D. P. Wilmes for technical assistance, Dr. J. J. McBrady for infrared and nmr interpretation, Mr. P. B. Olson for analytical determinations, and Mr. J. J. Neumayer for the molecular weight determination.

1-Thioacylaziridines

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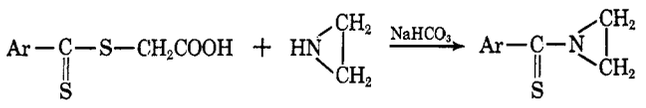
Several 1-acylaziridines are known in the literature. However, 1-thioacylaziridines are not reported except for 1-(N-alkyl- or -arylthiocarbamyl)aziridines.[1] In continuation of the study of aziridine chemistry, it appeared of interest to add new examples of 1-thioacylaziridines.

As an extension of our previous work,[2] several *para*-substituted 1-thiobenzoylaziridines were prepared by the reaction of sodium thiobenzoylthioglycolate with aziridine in water. The purified, crystalline compounds gradually polymerized on standing at room temperature.



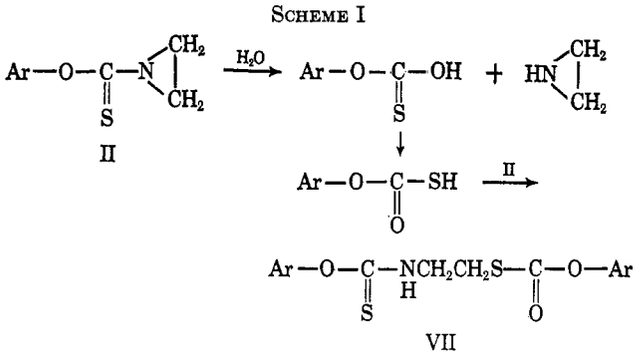
I

Ar = *p*-chlorophenyl (Ia), *p*-tolyl (Ib), and *p*-methoxyphenyl (Ic)

Compounds Ia–c were isomerized to 2-arylthiazolines (IV) by the reaction with picric or *p*-toluenesulfonic acids in refluxing benzene. Under the same conditions, I and thiophenol gave the ring-opened addition products, N-(2-phenylthioethyl)thiobenzamides, along with some thiazolines.

1-(Aryloxythiocarbonyl)aziridines (aryl = *p*-tolyl, IIa; *p*-nitrophenyl, IIb) were obtained from aryl chlorothionformates and aziridine. They were also unstable at room temperature and gave polymers of low molecular weight. Reaction with concentrated hydrochloric acid at room temperature gave 2-aryloxythiazolines (V) along with larger quantities of acid-insoluble substances (VII). The elemental analyses and the infrared and the nmr spectral data of VII all support the structure as it is written, the compounds of which structure might be formed by ring opening of IIa or IIb with thiocarbonic acid aryl esters as shown in Scheme I. *p*-Toluenesulfonic acid also gave a poor yield of 2-(*p*-nitrophenyloxy)thiazoline (Vb) from IIb. Reaction of IIa with thiophenol at

SCHEME I

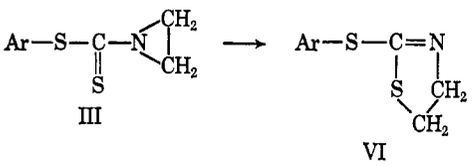


II

Ar = *p*-tolyl (VIIa) and nitrophenyl (VIIb)

room temperature gave the ring-opened addition product, while IIb and thiophenol gave 2-phenylthioethylisothiocyanate under the same condition.

1-(Aryldithiocarbonyl)aziridines (aryl = *p*-chlorophenyl, IIIa; *p*-methoxyphenyl, IIIb) were prepared from chlorodithioformic acid aryl esters and aziridine. They were rapidly polymerized at room temperature, and gradually at about 5°. 1-(*p*-Methoxyphenyldithiocarbonyl)aziridine (IIIb) was converted to 2-(*p*-methoxyphenylthio)thiazoline (VIb) on standing with concentrated hydrochloric acid at room temperature.



III VI

a, Ar = *p*-chlorophenyl
b, Ar = *p*-methoxyphenyl

With thiophenol, IIIb gave the acyclic addition product.

Including 1-(N-phenylthiocarbamyl)aziridine, 1-thioacylaziridines have a great tendency to polymerize in contrast to the corresponding 1-acylaziridines. As to the polymerization reaction of these 1-thioacylaziridines, investigation is in progress, and the results will be reported in the near future.

Experimental Section[3]

Preparation of Thiobenzoylthioglycolic Acids.—*p*-Chlorothiobenzoylthioglycolic acid was prepared from *p*-chlorobenzo trichloride in 50% yield in a same way as described in the preparation of thiobenzoylthioglycolic acid.[4] It melted at 117.5–118.5° (lit.[5] mp 115–117°).

p-Methylthiobenzoylthioglycolic acid, mp 117–118° (lit.[5] mp 118–119°), and *p*-methoxythiobenzoylthioglycolic acid, mp 121–122° (lit.[5] mp 124–125°), were prepared from *p*-chlorotoluene and *p*-chloroanisol in 43 and 46% yield in essentially the same manner as described for the synthesis of thiobenzoylthioglycolic acid from bromobenzene,[6] tetrahydrofuran being used as solvent for the Grignard reaction in these cases.

Preparation of 1-(*p*-Chlorothiobenzoyl)aziridine (Ia).—*p*-Chlorothiobenzoylthioglycolic acid (18.5 g, 0.075 mole) was neutralized with sodium bicarbonate (7 g) in 150 ml of water. Into the aqueous solution, a cold solution of 8 g (0.19 mole) of aziridine in 100 ml of water was added at 0–5°, and the mixture was stirred for 15 min. The yellow crystals were collected on a filter and dissolved in 170 ml of petroleum ether (bp 40–80°) as soon as possible at room temperature. The solution was washed

(1) *E.g.*, (a) S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895); (b) Y. Iwakura and A. Nabeya, *Bull. Tokyo Inst. Technol.*, **42**, 69 (1961); (c) M. Tišler, *Arch. Pharm.*, **291**, 457 (1958).

(2) Y. Iwakura, A. Nabeya, T. Nishiguchi, and K. Ohkawa, *J. Org. Chem.*, **31**, 3352 (1966).

(3) Melting points and boiling points are uncorrected. Nmr spectra were measured in a specified solution with tetramethylsilane as the internal standard.

(4) F. Kurzev and A. Lawson, *Org. Syn.*, **42**, 100 (1962).

(5) K. A. Jensen and C. Pedersen, *Acta. Chem. Scand.*, **15**, 1087 (1961).

(6) A. Kjaer, *ibid.*, **4**, 1347 (1950).