Anal. Calcd for $C_{12}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.68; H, 7.68.

Ethyl β-Isopropyl-β-phenylglycidate (21).—Isobutyrophenone (10 g, 0.06 mol) and ethyl chloroacetate (7.5 g, 0.06 mol) were condensed to yield 10.6 g (67%) of glycidic ester **21**: bp 81–82° (0.03 mm); $n^{25}D$ 1.4933; ir (CCl_3) 1764, 1730 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.80; H, 7.69. Found: C, 71.57; H, 7.90.

Isopropyl β-Isopropyl-β-phenylglycidate (22).—Ten grams (0.06 mol) of isobutyrophenone was condensed with 8.1 g (0.06 mol) of isopropyl chloroacetate to yield 9.8 g (58.5%) of glycidic ester **22**: bp 72.5° (0.05 mm); $n^{25}D$ 1.4881; ir (CCl_4) 1761, 1727 cm^{-1} (C=O).

Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.06. Found: C, 72.38; H, 8.16.

***t*-Butyl β-Isopropyl-β-phenylglycidate (23).**—Condensation of 23 g (0.15 mol) of isobutyrophenone and 22.5 g (0.15 mol) of *t*-butyl chloroacetate yielded 24.5 g (64%) of glycidic ester **23**: bp 87–89° (0.1 mm); $n^{25}D$ 1.4915; ir (CCl_4) 1761, 1719 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.20; H, 8.46.

***t*-Butyl β-(*p*-Nitrophenyl)glycidate.**—*t*-Butyl chloroacetate (19.5 g, 0.13 mol) was condensed with *p*-nitrobenzaldehyde (19.5 g, 0.13 mol) to yield 32.4 g (92%) of crystalline glycidic ester. Recrystallization from ethanol gave 24.2 g (68.5%) of pale yellow crystals: mp 89–91°; ir (CCl_4) 1757, 1730 cm^{-1} (C=O).

Anal. Calcd for $C_{13}H_{15}NO_5$: C, 58.87; H, 5.66; N, 5.28. Found: C, 58.88; H, 5.68; N, 5.00.

***t*-Butyl α-Chloro-β-hydroxy-β-phenylpropionate.**—This compound was prepared by the method of Munch-Peterson.[5] The crude product was a brown oil which was partially purified by removing the low boiling components by distillation and chromatographing the residue over silica gel. The fraction containing the chlorohydrins was eluted with 20% ether in hexane. The chlorohydrins could not be induced to crystallize and the mixture was used directly in the cyclization studies. The absence of acetophenone, *t*-butyl chloroacetate, and glycidic esters was readily demonstrated by glpc.

Cyclization of Chlorohydrin Ester in the Presence of *p*-Nitrobenzaldehyde.—To a solution of 2.4 g (8.8 mmol) of chlorohydrin ester and 3.32 g (22 mmol) of *p*-nitrobenzaldehyde in 20 ml of *t*-butyl alcohol was added dropwise a solution of 510 mg (9.1 mmol) of potassium *t*-butoxide in 20 ml of *t*-butyl alcohol under a nitrogen atmosphere. The mixture was stirred for 3.5 hr. At the end of this time water was added and the mixture was extracted with ether. The ether layer was washed with water and dried ($MgSO_4$). Evaporation of the solvent left 3.1 g of a viscous oil. Analysis by glpc showed that the glycidic esters were composed of 13% *t*-butyl β-(*p*-nitrophenyl)glycidates and 87% *t*-butyl β-methyl-β-phenylglycidates (**19**).

Epimerization of *t*-Butyl *cis*-β-Methyl-β-phenylglycidate.—A solution of 2 g of *cis*-glycidate in 50 ml of *t*-butyl alcohol and a catalytic amount of potassium *t*-butoxide was allowed to stand at room temperature for 1 week. After this time the *t*-butyl alcohol was removed *in vacuo* and the residue was treated with a dilute solution of NH_4Cl and extracted with ether. The ether extract was dried ($MgSO_4$) and the solvent was removed by distillation. The residue was analyzed by nmr.

A second sample was treated similarly except that it was heated at 70° for 24 hr.

Epimerization of the *trans* isomer was carried out under the same conditions. The results are listed in Table II.

Analyses of *cis/trans* Glycidic Ester Ratios.—A 2-g sample of the crude ester from a Darzens condensation was chromatographed on alumina (30 g, activity II, neutral) and eluted with 300 ml of petroleum ether (bp 30–60°). The solvent was removed *in vacuo* and the residual mixture was used for analyses. Recovery of material from the column was better than 95% in all cases.

A. Nmr.—The *t*-butyl esters from acetophenone and benzaldehyde could be analyzed by nmr. Both the peaks due to the *t*-butyl group and the α proton were sufficiently separated from other peaks that satisfactory integrations were obtained.

B. Glpc.—Crude samples taken directly from the reaction mixture or samples eluted from the chromatography columns gave the same results within experimental error. The latter were used as it was easier to integrate the results. Injection of samples in ether solution on a 4-ft column of 3.8% SE-30 on Chromosorb W (acid-washed DMCS) at temperatures between 110 and 125° gave clear separations of all *cis–trans* pairs. The relative areas under the peaks were calculated using a Disc integrator. Reproducibility is within ±2%. In all cases, the *trans* isomer preceded the *cis* isomer in elution from the column.

Registry No.—**14**, 21309-17-1; **15** (*cis*), 21309-18-2; **15** (*trans*), 7042-30-0; **16**, 5441-04-3; **19** (*cis*), 21309-20-6; **19** (*trans*), 21309-21-7; **20**, 21297-89-2; **21**, 21297-90-5; **22**, 21297-91-6; **23**, 21297-92-7; *t*-butyl β-(*p*-nitrophenyl)glycidate, 21297-93-8.

Preparation of Olefins by Pyrolysis of O-Alkyl Dimethylthiocarbamates[1,2]

MELVIN S. NEWMAN AND FREDERICK W. HETZEL

The Evans Chemistry Laboratory of The Ohio State University, Columbus, Ohio 43210

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Pyrolysis of O-alkyl dimethylthiocarbamates which contain a β hydrogen affords olefins in high yield. The temperature required for pyrolysis is somewhat lower than that needed for the pyrolysis of the corresponding xanthates and is much lower than that needed for acetates. The required O-alkyl dimethylthiocarbamates of primary and secondary alcohols were prepared from the corresponding sodium alkoxides and dimethylthiocarbamyl chloride in 80–90% yields. O-Neopentyl dimethylthiocarbamate is recovered unchanged when heated to 300°.

In the course of studies on the rearrangement of O-aryl dimethylthiocarbamates to S-aryl dimethylthiocarbamates on heating,[3] the question arose as to whether a similar rearrangement would occur in the aliphatic series. Since elimination, as in the case of xanthates, would be expected if O-alkyl dimethylthiocarbamates which contained a β hydrogen were used, O-neopentyl dimethylthiocarbamate (I) was prepared. Even when heated to 30° for 20 min, I was recovered mostly unchanged. Thus, the oxygen to sulfur rearrangement occurs readily only in the aryl series.[4] This result stands in contrast to that obtained on pyrolysis of O-2,2,6,6-tetramethylcyclohexyl-S-methyl

(1) This research was supported by Research Grant GP-5552X from the National Science Foundation.

(2) Taken from the M.S. thesis presented to The Ohio State University, 1967, by F. W. H.

(3) M. S. Newman and H. S. Karnes, *J. Org. Chem.*, **31**, 3980 (1966).

(4) Professor D. Horton, The Ohio State University, in a private communication, has reported to us that certain dimethylthiocarbamates in the protected sugar series do give small yields of the corresponding S-alkyl dimethylthiocarbamates on heating in the region of 300°. Also, photochemical treatment leads to the S-alkyl derivatives in small yield. These results will be published at a later date. For similar reactions in the sugar field, see D. Horton and D. H. Hutson, *Advan. Carbohyd. Chem.*, **18**, 160 (1963).

TABLE I

PREPARATION AND PYROLYSIS OF O-ALKYL DIMETHYLTHIOCARBAMATES

$(CH_3)_2NCOR$ (S)[a]

ROH	Registry no.	Bp at 0.3 mm	Yield,[b] %	Yield,[c] %	Analysis	
					Calcd, %	Found, %
R = $CHCH_3$ | C_6H_5	21299-31-0	115–118	75	81	C 63.2	62.9
					H 7.2	7.4
					N 6.4	6.7
R = $CH_3CH(CH_2)_5CH_3$ |	21299-32-1	85–90	77	69[d]	C 60.8	60.6
					H 10.6	10.6
					N 6.5	6.7
R = $(CH_2)_4CH$–	21299-33-2	80–86	78	64	C 55.7	55.7
					H 8.8	8.9
					N 8.2	8.4
R = $(CH_2)_5CH$–	21299-34-3	104–107	78	80	C 58.4	58.5
					H 9.2	9.2
					N 7.6	7.5
R = $-(CH_2)_7CH_3$	21299-35-4	110–115[e]	97	89	C 60.8	60.8
					H 10.6	10.8
					N 6.5	6.7
R = $-C(CH_3)_2$ | C_6H_5	21299-36-5	131–137	85	82	C 64.6	64.5
					H 7.6	7.6
					N 6.3	6.2
R = $(CH_3)_3CCH_2$–	21299-37-6	56.5–57.5[f]	*g*	*h*	C 54.9	55.3
					H 9.8	9.5

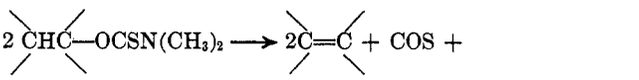
[a] The N-methyls appear in the nmr as two singlets at τ 6.7 and 6.9. [b] Yield of O-alkyl dimethylthiocarbamate. [c] Yield of olefin resulting from pyrolysis of O-alkyl dimethylthiocarbamate. [d] 36% 1-octene, 44% *trans*-2-octene, 20% *cis*-2-octene. [e] A 1-l. flask should be used, since foaming occurs when alkoxide is prepared. [f] Melting point. [g] High but not exactly determined. [h] No rearrangement.

xanthate, which rearranges to the S-cyclohexyl isomer[5] on heating to 300°.

Our attention next turned to pyrolysis of O-alkyl dimethylthiocarbamates as a method of preparation for olefins. The required O-alkyl dimethylthiocarbamates were readily prepared by reaction of the corresponding sodium alkoxide with dimethylthiocarbamyl chloride in dimethylformamide (DMF). On heating in the 180–200° range, decomposition to form olefins was complete in about 2 hr. The yields of O-alkyl dimethylthiocarbamates and of olefins resulting by pyrolysis of the latter are listed in Table I. This work indicates that the above method of olefin preparation offers certain advantages over the xanthate method.[6] In the present case, the sodium alkoxide of the alcohol to be dehydrated is treated with dimethylthiocarbamyl chloride to yield the compound which is submitted to pyrolysis, whereas, in the xanthate method, the sodium alkoxide is treated with carbon disulfide and the resulting product must further be alkylated by treatment with a suitable methylating agent before pyrolysis is effected. The xanthates thus formed are often difficult to purify.[7] The O-alkyl dimethylthiocarbamates herein reported were all readily purified by vacuum distillation.

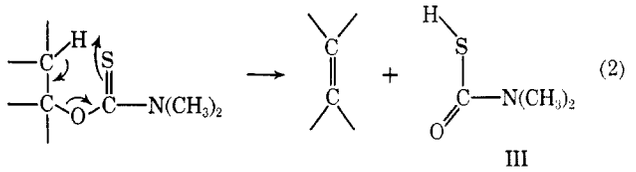
As far as yield of olefin obtained by pyrolysis of dimethylthiocarbamates is concerned, the results listed in Table I show that this method is either roughly the same as, or greatly superior to, the xanthate pyrolysis method.[8]

Experimentally, the pyrolyses were run so that volatile products, including the olefin, were swept into a cooled receiver with dry nitrogen. In all cases, the same colorless crystalline compound was obtained in addition to the olefin (or olefin mixture) and a malodorous gas presumed to be COS. Elemental analyses and the nmr spectrum showed the compound to be dimethylammonium dimethylthiocarbamate (II). This substance has previously been prepared, but no melting point, analyses, or spectra were reported.[9] The amount of II corresponded well with that consistent with the following equation.



$$2\,CHC{-}OCSN(CH_3)_2 \longrightarrow 2C{=}C + COS + (CH_3)_2NCOS^-(CH_3)_2NH^{2+} \quad (1)$$

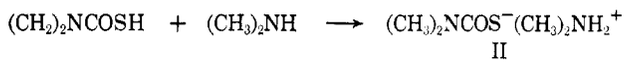
The formation of II may be explained by assuming that the pyrolysis proceeds by the cyclic mechanism shown below followed by further reaction of dimethylthiocarbamic acid (III), as shown in eq 3 and 4.



(2)

III

$$(CH_3)_2NCOSH \longrightarrow (CH_3)_2NH + COS \quad (3)$$



(4)

II

(5) V. Laakso, *Suomen Kemistilehti*, **13B**, 8 (1940); *Chem. Abstr.*, **34**, 5059 (1940). No time of pyrolysis was mentioned and simultaneous decomposition occurred to some extent.

(6) H. R. Nace, *Org. Reactions*, **12**, 57 (1962).

(7) See ref 6, p 86.

(8) Compare the results listed in ref 6, Table II, p 91 ff.

(9) J. Perrod, *Compt. Rend.*, **234**, 1062 (1952).

(10) R. F. W. Bader and A. N. Bourns, *Can. J. Chem.*, **39**, 348 (1961).

In attempts to prepare cyclohexyl dimethylthiocarbamate by treatment of cyclohexanol with dimethylthiocarbamyl chloride in the presence of pyridine, yields never exceeded 55%. The lower yields were traced to the fact that dimethylthiocarbamyl chloride also reacts with pyridine to form dimethylthiocarbamyl pyridinium chloride, IV, which does not react with cyclohexanol under the existing conditions. Since no better yields were obtained with collidine, Dabco, and triethylamine, we assume that similar salts are formed, but we made no attempt to isolate any.

Experimental Section[11]

N,N-Dimethylthiocarbamoyl Chloride.—To a refluxing suspension of 620 g (3.0 mol) of bis(dimethylaminothiocarbamoyl)-disulfide[12] (Thiram) in 1.5 l. of dry carbon tetrachloride contained in a three-necked 3-l. flask equipped with a reflux condenser, mechanical stirrer, and additional funnel was rapidly added a cold solution of 240 g (3.3 mol) of chlorine in 1 l. of dry carbon tetrachloride. After the addition was completed, 1 l. of solvent was distilled from the reaction mixture. The residue was cooled to 25° and filtered to remove the precipitated sulfur. The filtrate was further concentrated and the resulting residue was distilled through a short column to yield 595 g (80%) of a light yellow solid, bp 80–82° (0.3 mm) [lit.[13] bp 90–95° (0.5 mm)], mp 37–39°.

Preparation of O-Alkyl Dimethylthiocarbamates.—To a well-stirred, cooled solution of 0.25 mol of the alcohol (distilled samples of commercial products were used) in 200 ml of pure dry DMF in a 500-ml erlenmeyer flask was added 6.0 g (0.25 mol) of dry sodium hydride in portions during 30 min. The flask was then heated as needed to insure completion of reaction. To this cooled solution was added 35 g (0.30 mol) of dimethylthiocarbamyl chloride in portions during 20 min. The reaction mixture was then heated to 75° for 3 hr, cooled, and worked up as usual. The resulting dark liquid was vacuum distilled from a Claisen flask. A small center cut of each was used for analyses. The boiling points reported in Table I represent the entire range of product suitable for use in the next step.

Pyrolysis of O-Alkyl Dimethylthiocarbamates.—A quantity of the carbamate was weighed into a three-necked flask containing a magnetic stirring bar. One neck was fitted with an inlet tube for nitrogen, the middle neck was stoppered, and the third neck was fitted with a short path distillation head connected to a receiver cooled in an ice bath. The contents of the flask were heated to 180–200° with a polyethylene glycol bath. At these temperatures, 10 g of a thiocarbamate was converted into the corresponding olefin in 2 hr.

The olefin and a white solid (II) were vaporized upon formation at the pyrolysis temperature and collected in the cooled receiver. The olefin was separated from II by washing with ether. The solvent was removed from the washings, and the resulting residue was distilled to yield the olefins listed in Table I. The olefins were identified by boiling point, infrared spectrum, and comparison of their vpc retention times with those of standard olefin samples.[14] In all cases, mixtures of the olefin obtained by pyrolysis and an authentic sample produced only one peak.

Dimethylammonium N,N-Dimethylthiocarbamate (II).—The white solid, mp 51–53°, was insoluble in ether or hydrocarbon solvents, but soluble in water, acetone, and chloroform. The nmr spectrum contained two sharp singlets at τ 7.30 [$(CH_3)_2N^+$] and 6.90 (H_2N^+) and a broadened singlet at τ 6.82 [$(CH_3)_2N$-COS^-]. The signal at τ 6.90 disappeared in D_2O. The area ratios were 3:1:3, respectively.

Anal. Calcd for $C_5H_{14}N_2OS$: C, 40.0; H, 9.3; N, 18.6; S, 21.3. Found: C, 40.1; H, 9.0; N, 18.8; S, 21.2.

Preparation of O-Alkyldimethylthiocarbamates Using Tertiary Bases.—A typical experiment involved mixing 0.125 mol of alcohol, 20 g (0.16 mol) of dimethylthiocarbamoyl chloride, 0.20 mol of a tertiary base [pyridine, collidine, or Dabco[15] (1,4-diazobicyclo[2.2.2]octane)] and 100 ml of toluene or xylene in a 250-ml erlenmeyer flask, flushed with nitrogen, and fitted with a reflux condenser. The mixture was refluxed for 8 hr, poured onto 100 ml of 10% hydrochloric acid, and worked up as usual to give thiocarbamates in never greater than 55% (90% based on recovered alcohol) yields which never increased, despite the use of a 25 to 200% excess of dimethylthiocarbamoyl chloride and/or tertiary base.

1-(Dimethylthiocarbamoyl)pyridinium Chloride (IV).—To 50 ml of toluene in a 250-ml erlenmeyer flask, 12.4 g (0.10 mol) of dimethylthiocarbamoyl chloride and 7.99 g (0.10 mol) of pyridine were added and the mixture was refluxed for 24 hr. After refluxing, the mixture was cooled and filtered to remove the precipitated crystals of hygroscopic solid, mp 138–141°, soluble in polar solvents. The nmr of IV in D_2O contained two singlets at τ 6.9 and 6.4 and a multiplet of three doublets, J = 6.0 cps, between τ 2.0 and 0.8. The ratios of peak areas were 3:3:5, respectively. The downfield singlet resulted from deshielding of the methyl group situated over the pyridinium ring. The multiplet was shifted about 1 ppm with respect to pyridine because the aromatic ring contains a positive charge. The splitting pattern, coupling constant, and downfield shifts are identical with those of the aromatic protons of ethylpyridinium chloride.[16]

Registry No.—II, 2614-98-4; IV, 21299-30-9.

(11) All melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Samples were placed between two Pyrex glass cover plates and the temperature was increased at a rate of about 1°/min. All analyses were performed by Galbraith Laboratories, Inc., Knoxville,, Tenn. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer. Samples were dissolved in carbon tetrachloride unless otherwise noted, and tetramethylsilane served as the internal standard. Infrared (ir) spectra were recorded on a Perkin-Elmer 237 spectrometer. The spectra of solids were taken on potassium bromide disks, and liquids as films between two salt plates. Vapor phase chromatographic analyses were carried out on an F & M Model 609 flame ionization gas chromatograph, manufactured by the F & M Scientific Corp., Avondale, Pa. The unit was equipped with a Disc chart integrator and percentages of products were determined by integration of the areas under the peaks. An 8 ft × 0.25 in. stainless steel column, packed with 20% Carbowax on Chromasorb P, at temperatures of 25–125°, was used for the analyses. Reagent dimethylformamide, dried over molecular sieves, was used in the reactions described below. Sodium hydride powder, obtained by washing a 50% suspension in mineral oil with petroleum ether (bp 30–60°) and air drying in a Büchner funnel, was stored in a desiccator. All solvents, reagents, and alcohols were distilled before using and the solvents were stored over molecular sieves until used. Tertiary bases used in some experiments were treated likewise.

(12) The authors acknowledge with thanks the generous gifts of Thiram from the Pennsalt Manufacturing Co., Philadelphia, Pa.

(13) "Organic Syntheses," Coll Vol. VI, John Wiley & Sons, Inc., New York, N. Y., 1963, p 310.

(14) The authors wish to thank Dr. Kenneth Greenlee for the standard olefins furnished by the Chemical Samples Co., Columbus, Ohio 43221.

(15) The authors thank the Houdry Process Co., Marcus Hook, Pa., for a generous sample of Dabco.

(16) R. Lytle, *Chem. Eng. News*, 72 (Jan 10, 1966).