and dried in a vacuum oven at 80° for 24 hr. The yield of first crop was 260 g; upon evaporation of the filtrate a total of 430 g (86%) of pure ketone was obtained, mp 348–349.5°.

B. **Reaction of DL-Valine with II.**—Into a 2-l., single-necked, round-bottomed flask, equipped with a Glas-Col heating mantle, a magnetic stirrer, and a phase separator, was placed 245 g (0.50 mole) of II and 1400 ml of *m*-xylene. The mixture was heated to reflux and the solvent was recycled for 0.5 hr, then cooled slightly, and 58.5 g (0.50 mole) of DL-valine were added all at once. The reaction mixture was reheated to reflux and the solvent was recycled until all water was removed; this process usually consumed 48 hr. After the reaction was completed the solution was decolorized. The hot filtrate was chilled in an ice bath. The product was collected by suction filtration and washed with small quantities of chilled *m*-xylene. After drying in a vacuum oven at 45° for 24 hr the crude yield of 207 g (70%) was obtained. Evaporation of the mother liquor gave an additional 53 g of product giving a total crude yield of 88%, mp 178–186°.

The first and second crops were combined and dissolved in the minimum amount of refluxing toluene; a 10% excess of solvent was added and the solution was filtered while hot. The filtrate was allowed to cool to room temperature and then chilled in an ice bath. The white crystals were removed by suction filtration and dried in a vacuum oven at 45° for 24 hr to give a first, recrystallized crop of 208 g (70% yield). Evaporation of the toluene from the filtrate will give an additional 50 g of nearly pure material for a total recrystallized yield of 87%. The melting point of the pure lactone is 186–187°. The structure was confirmed by infrared spectra, nuclear magnetic resonance and elemental analysis (see Table I).

Spectra.—The reaction product from glycine (R = H) and Kepone gave an infrared spectra having the specific absorption at 2923 cm^{-1} ($\nu_{anti,sym\text{-}CH_2}$), 2850 cm^{-1} ($\nu_{sym\text{-}CH_2}$), 3320 cm^{-1} (ν_{NH}), 3300 cm^{-1}, shoulder (ν_{NH}), 1821 cm^{-1} ($\nu_{C=O}$), and 1805 cm^{-1} ($\nu_{C=O}$). There are doublets for the ν_{NH} and $\nu_{C=O}$ due to crystal splitting. There are no absorptions inconsistent with the assigned structure where R = H.[4]

The mass spectra of the same compound showed the molecular weight to be 543 (calcd: 543). The Cl^{37}/Cl^{35} ratios show the presence of ten chlorine atoms for each molecule. The most abundant ions formed were $C_5Cl_6^+$ (*m/e* 270); this is characteristic of perchloropentacyclodecane derivatives.[8] These data and the rest of the fragmentation pattern are consistent with the proposed structure although some isomers cannot be ruled out.

The nmr spectra of the compound, when R = H, were run as saturated solutions in $CDCl_3$ and in DMSO-d_6 and 19.7% w/v in pyridine. Spectra were consistent with the proposed structure, plus toluene impurity. The integrals in pyridine solution agreed with assignment; the spectra in $CDCl_3$ and in DMSO-d_6 were too weak to give useful integrals, but appeared to be consistent. There was no observable evidence for nonequivalence of the CH_2 protons. The observed coupling between NH and CH_2 protons is 8.6 ± 0.2 Hz in pyridine and is approximately the same in the other solvents. The CH_2 group was a simple doublet in all solvents (J_{HN-CH_2} = 8.6 ± 0.2 Hz in pyridine, approximately the same in $ClCl_3$ and in DMSO-d_6), and the NH proton was a triplet with the same splitting, when seen (see Table II).

TABLE II

CHEMICAL SHIFTS TAKEN AS CENTERS OF PATTERNS

Proton groups	Chemical shifts, ppm: In $CDCl_3$	In pyridine	In DMSO-d_6
NH	Not found	−5.61 ± 0.03	−4.67 + 0.03
CH_2	−3.78 ± 0.03	−4.05 ± 0.02	−3.77 ± 0.03

The nmr spectra of the compound, when R = *i*-C_3H_7 run as a 20.4% (w/v) solution in $CDCl_3$, is consistent with the assigned structure. Integration gave appropriate proton ratios. Chemical shifts, taken as the centers of the assigned structured groupings, were, ring CH, −3.78 ± 0.02 ppm; NH, −2.40 ± 0.03 ppm; isopropyl CH, −2.3 ppm; one isopropyl CH_3, −1.10 ± 0.02 ppm, other isopropyl CH_3, −1.05 ± 0.02 ppm. The isopropyl CH was relatively weak and overlapped the NH absorption, so that its position was not defined well. The NH lines were 3 Hz wide at half-height of the maximum peak. The observed coupling constants were J_{HNCH} = 9.0 ± 0.1 Hz; J_{HCCH} = 4.8 ± 0.1 Hz; J_{HCCH_3} = 6.8 ± 0.1 Hz.

(8) W. L. Dilling and M. L. Dilling, *Tetrahedron*, **23**, 1225 (1963); personal communication (M. L. D.).

Registry No.—II, 143-50-0.

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2,2′-Thiobis(benzoxazole) and 3-(2-Benzoxazolyl)-2-benzoazolinethione

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In a recent publication,[1] we reported that the reaction of sodium 2-mercaptobenzoxazole with 2-chlorobenzoxazole in dimethylformamide at temperatures of 140–150° yielded 2,2′-thiobis(benzoxazole) (**1**). It was suggested by Gloede[2] that the product isolated in the above reaction was not **1** but its rearranged isomer, 3-(2-benzoxazolyl)-2-benzoazolinethione (**2**). They reported that the reaction of 2-mercaptobenzoxazole with 2-chlorobenzoxazole at 170–180° furnished **2** in 60% yield. Upon a more careful analysis based on infared and ultraviolet spectral data, the crude product isolated under our reaction conditions contained 75 and 19% of **2** and **1**, respectively. However, by lowering the temperature to 80–90° and replacing the sodium 2-mercaptobenzoxazole with the potassium salt, we were able to obtain a crude product containing 92 and 6.5% of **1** and **2**, respectively. Attempts to analyze a recrystallized sample of **1** (99.5%) by vpc at 260° resulted in rearrangement of **1** to **2**. Moreover, **1** was converted to **2** by heating at 140–150° in dimethylformamide or without solvent at 170–180° (Scheme I). In contrast to the rearrangement of 2,2′thiobis(benzothiazole) to 3-(2-benzothizolyl)-2-benzothiazolinethione,[3] the conversion of **1** to **2** can be accomplished at much lower temperatures and without the use of a catalyst.

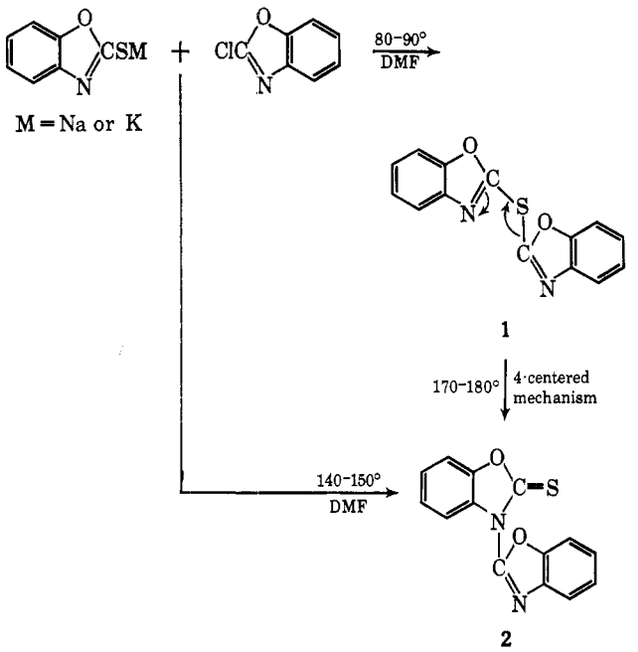
Experimental Section[4]

Analytical Methods.—Analyses of reaction products for **1** and **2** were made with a Perkin-Elmer Model 21 infrared spectrophotometer using 0.1-mm sodium chloride cells. Compound **1** had a 1506-cm^{-1} absorption band essentially free from interference from **2** while **2** had a 1028-cm^{-1} absorption band with only slight interference from **1**. Calibration curves for **1** and **2** were prepared by measuring the absorbances of standard 5% (w/v) chloroform solutions covering the range of 0–100% for each compound. The reaction products were analyzed using the same procedure as in the calibration.

The ultraviolet spectra were determined using a Cary Model 11 spectrophotometer and matched 1-cm quartz cells. The ultraviolet spectra of **1**, **2**, 2-methylthiobenzoxazole (**3**), anp

(1) J. J. D'Amico, *et al.*, *J. Org. Chem.*, **30**, 3618 (1965).
(2) H. Gross and J. Gloede, *Z. Chem.*, **5**, 178 (1965).
(3) J. J. D'Amico, *et al.*, *J. Org. Chem.*, **30**, 3628 (1965).
(4) All melting points were taken upon a Fisher-Johns block and are uncorrected.

SCHEME I



3-methyl-2-benzoxazolinethione (**4**)[5] were determined in methanol. The absorption maxima and molar extinction coefficients follow: **1**, 283 mμ (ε 18,900) and 246 (18,100); **2**, 305 (17,800), 282 (24,000), and 245 (19,500); **3**, 285 (13,100), 278 (13,200), and 248 (13,200); **4**, 305 (13,600), 300 (13,600), and 258 (4900). The higher wavelength thioamide absorption band characteristic of intramolecular charge-transfer transition[6] is present in **2** and **4** and absent in **1** and **3**, as would be expected.

2,2′-Thiobis(benzoxazole) (**1**).—To a stirred solution of 0.20 mole of anhydrous potassium 2-mercaptobenzoxazole in 200 ml of dimethylformamide, 0.20 mole of 2-chlorobenzoxazole was added in one portion. The stirred reaction mixture was heated at 80–90° for 6 hr. After cooling to 25°, the reaction mixture was added to 800 g of ice water containing 32 g (0.2 mole) of 25% aqueous sodium hydroxide. After stirring at 0–10° for 1 hr, the precipitate was collected by filtration, washed with water until the washings were neutral to litmus, and air dried at 25–30°. The crude product (yield 93.2%, mp 127–132°) contained 92.0 and 6.5% of **1** and **2**, respectively. After recrystallization from heptane, it melted at 132–133° (99.5% **1**). The infrared spectrum of recrystallized sample was determined from 2 to 12 μ in chloroform and from 12 to 15 μ in dimethylformamide and contained bands at 3002 (w) (aromatic C–H st), 1506 (vs) and 1453 (s) (C=C and C=N stretching vibrations of the 2-thiobenzoxazole), 1239 (s), 1140 (vs), 1100 (m), 807 (m), 760 (s), and 750 (s) cm^{-1} (C–H out-of-plane deformation of phenyl ring).

Anal. Calcd for $C_{14}H_8N_2O_2S$: N, 10.44; S, 11.95; mol wt, 268.3. Found: N, 10.20; S, 11.74; mol wt, 265.

3-(2-Benzoxazolyl)-2-benzoazolinethione (**2**).—The procedure was the same as described above except the stirred reaction mixture was heated at 140–150° for 6 hr. The crude product (yield 87.6%, mp 155–158°) contained 6.0 and 93.5% of **1** and **2**, respectively. After recrystallization from ethyl acetate, it melted 160° (100%). The infrared spectrum of recrystallized sample was determined from 2 to 12 μ in chloroform and from 12 to 15 μ in dimethylformamide and contained bands at 3002 (w) (aromatic C-H st), 1622 (m) (C=N st), 1570 (s), or 1480 (s) (N–C=S, thioureide), 1458 (m), 1410 (m), 1382 (m), 1325 (vs), or 1270 (s), (C=S st), 1240 (m), 1175 (w), 1089 (w), 1028 (m), 927 (w), 797 (w), 760 (s), and 752 (s) cm^{-1} (C–H out-of-plane of *ortho*-substituted phenyl ring).

Anal. Calcd for $C_{14}H_8N_2O_2S$; N, 10.44; S, 11.95; mol wt, 268.3. Found: N, 10.25; S, 11.92; mol wt, 272.

Registry No.—**1**, 4225-17-6; **2**, 2008-02-8; **3**, 13673-62-6; **4**, 13673-63-7.

(5) B. Beilenson and F. M. Hamer, *J. Chem. Soc.*, 143 (1939).
(6) B. Ellis and P. J. F. Griffithe, *Spectrochimica Acta*, **22**, 2005 (1966).

Acknowledgment.—The authors wish to acknowledge their indebtedness to Drs. J. Gloede and H. Gross for their helpful suggestion during the course of this investigation.

Polyfluorodiazo Compounds. II. 1-Phenyl-2,2,2-trifluorodiazoethane[1]

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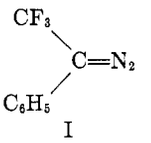
As part of a program of research into the syntheses and reactions of polyfluorodiazo compounds, it was of interest to prepare 1-phenyl-2,2,2-trifluorodiazoethane (I). We have prepared this compound by three different routes: diazotization of 1-phenyl-2,2,2-trifluoroethylamine hydrochloride, reaction of α,α,α-trifluoroacetophenone *p*-toluenesulfonylhydrazone with base,[3] and oxidation of α,α,α-trifluoroacetophenone hydrazone.



I

The previously unreported 1-phenyl-2,2,2-trifluoroethylamine used in the diazotization was prepared by the reduction of α,α,α-trifluoroacetophenone oxime[4] and was characterized as the benzoyl derivative. Diazotization was accomplished using the procedure of Gilman and Jones.[5] The yield of 1-phenyl-2,2,2-trifluorodiazoethane, estimated by reaction with *p*-toluenesulfonic acid and isolation of the resulting *p*-toluenesulfonate,[6] was 17%. This tosylate was also prepared from 1-phenyl-2,2,2-trifluoroethanol[7] and *p*-toluenesulfonyl chloride.

The *p*-toluenesulfonylhydrazone of α,α,α-trifluoroacetophenone, prepared by treating the ketone with *p*-toluenesulfonylhydrazine, gave the diazo compound in 32% yield when treated with sodium methoxide. The best route to the diazo compound (84%) was the oxidation of α,α,α-trifluoroacetophenone hydrazone with mercuric oxide.

1-Phenyl-2,2,2-trifluorodiazoethane has reasonable thermal stability. It could be heated to 100° for short periods of time with little apparent change. It also has relatively low reactivity as a diazo compound in that it does not react with benzoic acid, unlike both

(1) R. A. Shepard and P. L. Sciaraffa, *J. Org. Chem.*, **31**, 964 (1966), may be considered part I in this series.
(2) NASA Predoctoral Trainee.
(3) D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).
(4) E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961).
(5) H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **65**, 1458 (1943).
(6) Since reaction of isolated 1-phenyl-2,2,2-trifluorodiazoethane (see Experimental Section) with excess *p*-toluenesulfonic acid gave an 86% yield of 1-phenyl-2,2,2-trifluoroethyl *p*-toluenesulfonate, yields of diazo compound estimated by this technique may be considered as minima and are significant primarily as a measure of the relative efficacy of the various preparative methods.
(7) E. T. McBee, O. R. Pierce, and J. F. Higgins, *ibid.*, **74**, 1736 (1952).