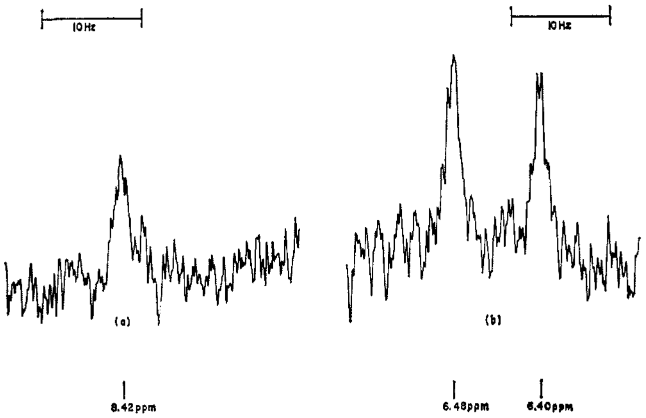

Figure 2.—Time-averaged nmr spectra, after 400 scans. Sweep rate is 1 Hz/sec: (a) compound Ia, region 80 Hz downfield of normal aromatic signal; (b) compound IIa, region 80 Hz upfield of normal aromatic signal. (Regions were chosen so as to avoid interference with the enhanced spinning side bands of the NH_2 peak.)

scans or 20-fold improvement in sensitivity—of the aforementioned satellite regions in compounds Ia and IIa. In Figure 2b, two lines with 8 Hz spacing (J_{AB}) are clearly observed, and IIa may be readily assigned to the structure bearing protons in an *ortho* relationship. In compound Ia (Figure 2a), the interaction between the *p*-hydrogens is a fraction of a Hz, and the satellite pattern consists essentially of a single, unresolved absorption.

Experimental Section[17]

2,6-Diaminobenzo[1,2-*d*:4,5-*d'*]bisthiazole.—A solution of 147 g (0.92 mol) of bromine in 200 ml of dry chloroform was slowly added, with stirring, to a suspension of 100 g (0.44 mol) of *p*-phenylenebisthiourea[18] in 1000 ml of dry chloroform in a round-bottom flask. The addition required 1 hr and the mixture was stirred at room temperature for an additional 4 hr. It was then refluxed 16 hr. After cooling, the solids were filtered off, washed with chloroform, and air dried. The product was converted into the free base by suspending it in 1 l. of 2 *N* ammonium hydroxide solution for 10 min, filtering, and washing with distilled water until the washings were neutral. Purification was accomplished by digestion in hot dimethylformamide for 30 min, cooling, filtering, and washing with acetone. The product, which was obtained in 35.8% yield, had a mp > 350°; ultraviolet maxima (80% acetic acid), 313 mμ (ε 13,900), 283 mμ (ε 15,600), 238 mμ (ε 35,600).

Anal. Calcd for $C_8H_6N_4S_2$: C, 43.23; H, 2.72; N, 25.21; S, 28.85. Found: C, 43.02; H, 2.61; N, 25.26; S, 28.79.

2,7-Diaminobenzo[1,2-*d*:4,3-*d'*]bisthiazole (a) from 1,4-diaminobenzene-2,3-dithiosulfonic acid[6] showed ultraviolet maxima (80% acetic acid) at 291 mμ (ε 18,600) and 245 mμ (ε 35,800) (*Anal.* Found: C, 43.17; H, 2.89; N, 25.10; S, 29.04) and (b) from *p*-phenylenediamine, ammonium thiocyanate, and bromine[10] was identical with (a) shown by ir and uv spectra.

The nmr spectra were obtained on a Varian HA-100 spectrometer, utilizing the Varian Autoshim accessory and the C-1024 time-averaging computer. The compounds were examined as saturated solutions in dimethyl sulfoxide-d_6, while dissolved TMS was used as the internal locking signal and chemical shift reference. The 400 time-averaged scans required approximately 13 hr.

Registry No.—Ia, 16162-28-0; IIa, 16203-56-8.

Acknowledgments.—We are indebted to Drs. W. A. Hewett and J. N. Shoolery for their helpful discussions during the course of this investigation.

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[17] Elemental analyses by Berkeley Analytical Laboratories, Berkeley, Calif.

[18] O. Billeter and S. Steiner, *Ber.*, **20**, 228 (1887).

Facile Synthesis of 1,3-Oxathiolanes from Ketones and 2-Mercaptoethanol[1]

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We wish to report a convenient and efficient synthesis of 1,3-oxathiolanes. We have found that the condensation of equimolar mixtures of carbonyl compound and 2-mercaptoethanol in dilute ether solution is readily effected by 1 equiv of boron trifluoride. The boron trifluoride scavenges the water formed and is converted into its mono- or dihydrate. The use of several other catalysts has been reported.[3,4] The oxathiolanes of three sterodial ketones have been synthesized by Fieser[5] in a condensation using excess quantities of boron trifluoride and 2-mercaptoethanol per mole of ketone in acetic acid.

In almost all cases we have examined (Table I) the yields obtained using the boron trifluoride–ether system have been better than those obtained by the generally used *p*-toluenesulfonic acid–benzene azeotrope method.[4] In particular, by the boron trifluoride method a 56% yield of pure, crystalline 2,2-diphenyl-1,3-oxathiolane can be gained easily in 3 hr. By contrast, using the azeotrope method,[4] Marshall and Stevenson[6] observed much polymer formation and experienced difficulties in obtaining even a 28.5% yield. We have been unable to effect the condensation using di-*t*-butyl ketone; however, diisopropyl ketone proceeds to oxathiolane normally. The condensation with norbornanone led to a mixture of isomers.

Reducing the amount of solvent for the condensations much below 750 ml per mole of ketone leads to greatly reduced yields of oxathiolanes and an increase in quantities of ether-insoluble, apparently polymeric materials. Similarly the presence of even a residual trace of boron trifluoride in the crude product after washing causes the oxathiolanes to decompose rapidly to the ketone and a gummy, apparently polymeric residue when distillation is attempted. The oxathiolanes themselves are generally stable toward distillation or heating under reflux for at least 2 days.[7]

When the amount of boron trifluoride used for the formation of the oxathiolane from cycloheptanone was reduced to a 2:3 molar ratio, the per cent conversion was reduced from 92 to 74% and attained only 82% when the reaction time was eight times longer. The per cent yield based on unrecovered cycloheptanone

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[1] Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support (Grant No. 209-G) of this research.

[2] National Science Foundation Undergraduate Research Participant, Summer 1965.

[3] (a) F. Kipnis and J. Ornfelt, *J. Amer. Chem. Soc.*, **71**, 3555 (1949); (b) K. K. Georgieff and A. Dupré, *Can. J. Chem.*, **37**, 1104 (1959); (c) J. Romo, G. Rosenkranz, and C. Djerassi, *J. Amer. Chem. Soc.*, **73**, 4961 (1951); (d) A. R. Pinder and H. Smith, *J. Chem. Soc.*, 113 (1954); (e) B. Sjöberg, *Ber.*, **75**, 13 (1942).

[4] C. Djerassi and M. Gorman, *J. Amer. Chem. Soc.*, **75**, 3704 (1953).

[5] L. F. Fieser, *ibid.*, **76**, 1945 (1954).

[6] J. R. Marshall and H. A. Stevenson, *J. Chem. Soc.*, 2360 (1959).

[7] K. I. H. Williams, S. E. Cremer, F. W. Kent, E. J. Sehm, and D. S. Tarbell, *J. Amer. Chem. Soc.*, **82**, 3982 (1960).

TABLE I

STARTING MATERIALS FOR, YIELDS, PHYSICAL CHARACTERISTICS, AND ANALYSES OF OXATHIOLANES

Carbonyl compound	Yield, % BF$_3$–Et$_2$O	Yield, % TsOS–PhH	Mp or bp, °C (mm)	nD (temp, °C)	Formula	Registry no.	C, % Calcd	C, % Found	H, % Calcd	H, % Found	S, % Calcd	S, % Found	Ref
				Acyclic ketones									
Diethyl ketone	82	72.5[a]	63 (17)	1.4775 (25)	$C_7H_{14}OS$	16047-97-5	57.53	57.25	9.59	9.74	21.92	22.07	
Isopropyl methyl ketone	81	64[a]	50 (1.0)	1.4762 (24)	$C_7H_{14}OS$	16047-98-6	57.53	57.37	9.59	9.77	21.92	22.05	
Diisopropyl ketone	63	57[a]	43 (0.3)	1.4850 (24)	$C_9H_{18}OS$	16047-99-7	62.04	62.12	10.41	10.53	18.30	18.47	
1-Butenyl methyl ketone	70		84–86 (19)	1.4890 (20)	$C_8H_{14}OS$	16048-00-3	60.76	60.94	8.86	8.96	20.25	20.34	
Dibenzyl ketone[b]	92	90	41–42		$C_{17}H_{18}OS$								c
Acetophenone[d]	83	78	85 (1.2)	1.5641 (25)	$C_{10}H_{12}OS$								c, e
Benzophenone	56	28.5	52–53		$C_{15}H_{14}OS$								f
				Cyclic ketones									
Cyclopentanone	74	78[a]	35 (0.6)	1.5092 (27)	$C_7H_{12}OS$	176-38-5							c, e
Cyclohexanone[g]	96	92	45 (0.2)	1.5158 (25)	$C_8H_{14}OS$								c, e
Cycloheptanone	92		77–78 (1.2)	1.5165 (25)	$C_9H_{16}OS$	184-31-6	62.79	62.56	9.30	9.48	18.60	18.85	
3-Cholestanone[i]	74	89	129–130										c, h
Norcamphor[j]	94		62 (0.6)	1.5326 (21)		172-68-9	63.53	63.59	8.23	8.40	18.82	18.62	
				Aldehydes									
Propanal	57	24[a]	63–64 (36)	1.4780 (27)	$C_5H_{10}OS$	16048-04-7	50.85	51.01	8.47	8.54	27.12	27.26	
Butyral[k]	88	82	61–62 (18)	1.4779 (24)	$C_6H_{12}OS$								l
Benzaldehyde[m]	83	80	87–88 (0.6)	1.5830 (25)	$C_9H_{10}OS$								e, n

[a] This work. [b] Lit. mp 42–43. [c] See ref 4. [d] Lit. bp 96° (2 mm), 98° (1.3 mm); n^{24}D 1.5663, n^{25}D .15640. [e] E. L. Eliel, L. A. Pilato, and V. G. Badding, *J. Amer. Chem. Soc.*, **84**, 2377 (1962). [f] See ref 6. [g] Lit. Bp 47° (0.6 mm), 106–107° (21 mm); n^{24}D 1.5155, n^{25}D 1.5152. [h] See ref 5. [i] Lit. mp 135–136°, 133–134°. [j] Mixture of geometric isomers. [k] Lit. bp 84° (34 mm). [l] B. E. Leggetter and R. K. Brown, *Can. J. Chem.*, **41**, 2671 (1963). [m] Lit. bp 98–100° (1.3 mm), 86–87° (5 mm); n^{25}D 1.5850. [n] See ref 3*a*.

remained at 92%. With cyclohexanone, however, the maximum conversion can be achieved in 2 hr even with a 2:3 molar ratio of boron trifluoride. These results can be explained in terms of the relative magnitudes of the equilibrium constants for the equilibria involved.

$$H_2O + BF_3 \rightleftharpoons H_2O{\cdot}BF_3$$

$$H_2O + H_2O{\cdot}BF_3 \rightleftharpoons 2H_2O{\cdot}BF_3$$

The oxathiolanes formed were characterized by spectral and elemental analyses. The infrared spectra indicated the absence of ketone absorption, and there were present envelopes in the nmr spectra[8] at 3.8–4.1 and 2.3–2.9 ppm downfield from TMS, characteristic of methylene groups adjacent to sulfur and oxygen atoms, respectively.

Experimental Section[9]

General Method of Preparation of Oxathiolanes.—To a stirred, refluxing solution of 56.1 g (0.5 mol) of cycloheptanone and 29.1 g (0.5 mol) of 2-mercaptoethanol in 400 ml of anhydrous ether was added dropwise over a 1-hr period 71 g (0.5 mol) of boron trifluoride etherate. After an additional hour of being heated under reflux, the solution was allowed to cool, washed twice with 100 ml of 0.1 *M* sodium bicarbonate solution and once with 100 ml of saturated sodium chloride solution, and dried over magnesium sulfate. After removal of the solvent under vacuum on a rotary evaporator, the residue was distilled under vacuum to yield a small forerun which was followed by 79.2 g (92%) of 2-oxa-5-thiaspiro[4.6]undecane: bp 77–78° (1.2 mm); n^{25}D 1.5165.

2,2-Diphenyl-1,3-oxathiolane.—The reaction was run as above using 72.8 g (0.4 mol) of benzophenone and 31.2 g (0.4 mol) of boron trifluoride etherate in 400 ml of anhydrous ether. The residue after removal of most of the solvent was filtered to remove the majoritiy of the crude solid oxathiolane. To the filtrate was added 50 ml of methanol, and the mixture was cooled at 0° to precipitate additional solid oxathiolane. The combined solid fractions (55 g, 56%) were recrystallized from isopropyl alcohol to give 52.8 g (54%) of 2,2-diphenyl-1,3-oxathiolane, mp 52–53° (lit.[10] mp 52°).

Registry No.—2-Mercaptoethanol, 60-24-2.

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[8] A detailed analysis of the nmr spectra of 1,3-oxathiolanes is available: D. J. Pasto, F. M. Klein, and T. W. Doyle, *J. Amer. Chem. Soc.*, **89**, 4368 (1967).

[9] Boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrometer. Nmr spectra were recorded with a Varian Associates Model A-60 spectrometer. Vpc analyses were carried out on an Aerograph Model 1520 vapor phase chromatograph employing helium as the carrier gas and columns of either XF1150 or DC11 on 60/80 mesh Chromosorb P. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. We wish to thank Mr. H. Talts for the spectral analyses and Miss N. Essig for technical assistance.

(10) See Table I, footnote *e*.

The Preparation of 6-Aryltetrahydro-1,3-oxazin-2-ones and Their Hydrolysis to 3-Substituted Propylamines

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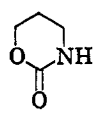
Tetrahydro-1,3-oxazin-2-one (1) has been prepared by the condensation of 3-aminopropanol with derivatives of carbonic acid.[2] However, the generality and convenience of this synthesis for certain substituted analogs of 1 is severely limited by lack of availability of the appropriate amino alcohols. We wish to report a convenient route to 6-aryltetrahydro-1,3-oxazin-2-ones (7) starting from the readily available β-aroylpropionic acids (2). The over-all yields of tetrahydrooxazines from γ-keto acids were in the range 35–50%.



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The aryl group was varied to cover a broad range of electronic characteristics. New compounds prepared by Scheme I are listed in Tables I and II.

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[1] Taken in part from the undergraduate research report of H. F. E.

[2] (a) R. Delaby, R. Damiens, and G. D'Huyteza, *Compt. Rend.*, **239**, 674 (1954); (b) E. K. Dreschel, U. S. Patent 2,701,246; *Chem. Abstr.*, **50**, 2686h (1956).