1,4-Addition-Type Ring-Opening Polymerization of 1,3-Oxazolidine-2-thiones

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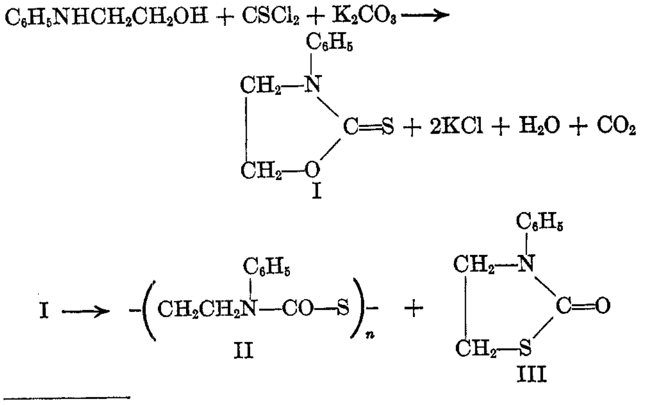
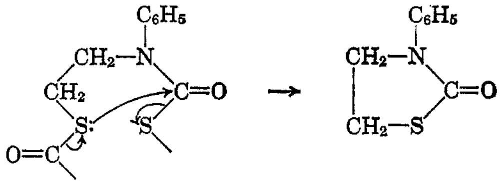
3-Phenyl-1,3-oxazolidine-2-thione was prepared from N-phenylethanolamine and thiophosgene. It was found that 3-phenyl-1,3-oxazolidine-2-thione polymerizes *via* a 1,4-addition-type ring-opening process to give poly(ethylene thiolcarbanilate) by heating at 140–160° or with boron trifluoride etherate or ferric chloride catalysts at room temperature. Further, the polymerization of N-unsubstituted 1,3-oxazolidine-2-thione was successfully carried out in the presence of similar cationic catalysts at room temperature. The mechanism of the ring-opening polymerization is discussed.

Trivalent phosphorus compounds have been used as effective deoxygenating or desulfurizing reagents. For example, ethylene O,O′-thiocarbonate is desulfurized by means of trimethyl phosphite to yield ethylene, carbon dioxide, and trimethyl phosphate in good yields.[1]

In the present study, the reaction of 3-phenyl-1,3-oxazolidine-2-thione (I) with triethyl phosphite was examined under the expectation that the desulfurization reaction would take place as established in the case of ethylene O,O′-thiocarbonate. 3-Phenyl-1,3-oxazolidine-2-thione was prepared by condensation reaction of N-phenylethanolamine with thiophosgene in the presence of potassium carbonate. When the thione (I) was heated at 140–160° for 3 hr. with an equimolar amount of triethyl phosphite, a white solid (II), m.p. 293–295° dec., was obtained, and most of the starting materials were recovered. A similar product was obtained in good yield along with the rearrangement product, 3-phenyl-1,3-thiazolidine-2-one (III), by heating the thione I alone at 179° for 10 hr. The product, which has an intrinsic viscosity of 1.08 dl. g.$^{-1}$, was characterized as poly(ethylene thiolcarbanilate) (II) by elemental analysis and its infrared spectrum, which has a strong absorption band attributable to the carbonyl group at 1655 cm.$^{-1}$, whereas the thione I has no absorption in this region. This result suggests that 3-phenyl-1,3-oxazolidine-2-thione polymerized by the repetition of 1,4-addition-type ring-opening polymerization as shown in the cases of ethylene iminocarbonates,[2] 2-imino-1,3-oxazolidines,[3] and 2-iminotetrahydrofurans.[4] It was also established that the reaction time greatly influences the yield and the intrinsic viscosity of the polymer obtained: when polymerization was carried out by heating the thione at 179° for 20 hr., the yield and the intrinsic viscosity of the polymer decreased and the yield of the rearrangement product (III) increased. These experiments suggested that depolymerization to 3-phenyl-1,3-thiazolidine-2-one (III) occurred at an elevated temperature. Indeed, when the polymer was heated at 300–310° for 10 min. under nitrogen, 3-phenyl-1,3-thiazolidine-2-one was obtained in 34% yield, and 41% of the polymer was recovered. This depolymerization[5] seems to proceed by way of an internal nucleophilic displacement as sketched below.





Further, the solution polymerization of 3-phenyl-1,3-oxazolidine-2-thione (I) in nitrobenzene was likewise successfully carried out at room temperature in the presence of cationic catalysts, such as ferric chloride and boron trifluoride etherate.

Bulk polymerization of N-substituted 1,3-oxazolidine-2-thione (IV) at 110° did not give the expected poly(ethylene thiolcarbamate) (V), but this polymer was obtained when a solution of IV in tetrahydrofuran was treated with cationic catalysts.

It is known that *exo*-imino cyclic compounds, such as ethylene iminocarbonates, 2-iminotetrahydrofurans, and 2-imino-1,3-oxazolidines, undergo 1,4-addition-type ring-opening polymerization in the presence of cationic catalysts. These polymerizations have been explained in terms of facile transformation of the monomers which are enol isomers of cyclic urethan, cyclic urea, or lactam, into the polymers having keto structures. The similar consideration suggests that flexible conversion of the thione-type compound into the thiol-type compound may play an important role for the polymerization of 1,3-oxazolidine-2-thiones. Thus, solution polymerization of the thione initiated by cationic catalysts may proceed through an initial formation of an intermediate (VI), which in turn de-

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[1] E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963).

[2] T. Mukaiyama, T. Fujisawa, H. Nohira, and T. Hyugaji, *J. Org. Chem.*, **27**, 3337 (1962).

[3] H. Nohira, Y. Nishikawa, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, **37**, 797 (1964).

[4] T. Mukaiyama and K. Sato, *ibid.*, **36**, 99 (1963).

[5] Intermolecular displacement leading to low molecular weight oligomers may also occur to some extent.

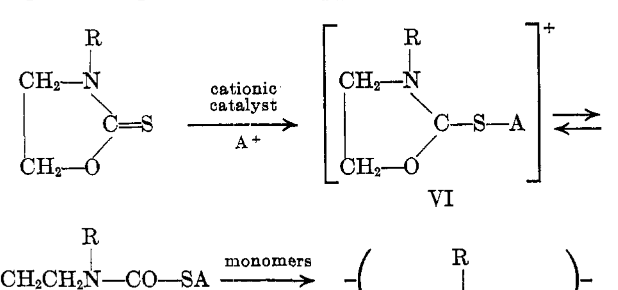
TABLE I

BULK POLYMERIZATION OF 3-PHENYL-1,3-OXAZOLIDINE-2-THIONE (I)

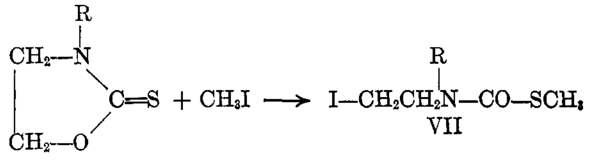
Polymn. condn.		Poly(ethylene thiolcarbanilate) (II)						3-Phenyl-1,3-thiazolidine-2-one (III),	Recovered thione I,
Temp., °C	Time, hr.	% yield	M.p. dec., °C.	$[\eta]^{30}_{m\text{-cresol}}$, dl. g.$^{-1}$	% C[a]	% H[a]	% N[a]	% yield	% yield
140–160[b]	3	13	307	...	...	...	...	...	47
179[c]	3	27	306	0.76	60.33	5.34	7.74	22	17
179[c]	10	62	300	1.08	57.19	5.16	7.55	31	0
179[c]	20	27	285–304	0.42	61.54	5.12	7.61	51	0

[a] *Anal.* Calcd. for C_9H_9NOS: C, 60.33; H, 5.06; H, 7.81. [b] Under a stream of nitrogen. [c] In a sealed tube under nitrogen; this tube was heated on a liquid–vapor bath of *o*-dichlorobenzene.

composes to give poly(ethylene thiolcarbamate) by the bond fission between the oxygen and the methylene group. This possibility is supported by the fact that



alkyl thioncarbamate reacts with alkyl halide to give the corresponding thiolcarbamate.[6] Further, it was found that the addition product of methyl N-(2-iodoethyl)thiolcarbamate (VII) was obtained by ring opening when 1,3-oxazolidine-2-thione was treated with methyl iodide.



Finally, the polymerization of 3-phenyl-1,3-oxazolidine-2-one, the oxygen isomer of 3-phenyl-1,3-oxazolidine-2-thione, was attempted under the same condition as established in the case of the thione. However, the starting material was recovered quantitatively when 3-phenyl-1,3-oxazolidine-2-one was heated at about 180° for 15 hr.

Experimental Section[7]

3-Phenyl-1,3-oxazolidine-2-thione (I).—A solution of N-phenylethanolamine (16.45 g.) in 90 ml. of dry benzene was added dropwise to a mixture of anhydrous potassium carbonate (24.9 g.) and thiophosgene (13.8 g.) in 200 ml. of dry benzene over a period of 2 hr. under nitrogen at 4–5°. Then the mixture was warmed at 55° for 40 min. under stirring and was allowed to stand overnight. The solid material was filtered off and the filtrate was evaporated under reduced pressure. The deposited 3-phenyl-1,3-oxazolidine-2-thione was recrystallized from 99% ethanol: yield 10.5 g. (49%); m.p. 95.5°. Its infrared spectrum (in KBr) showed principal bands at 1495, 1480, 1430, 1300, 1180, 940, 770, and 700 cm.$^{-1}$.

1,3-Oxazolidine-2-thione (IV).—This compound was prepared by the method of Ettlinger[8]: m.p. 98–99°.

Attempted Reaction of Triethyl Phosphite with 3-Phenyl-1,3-oxazolidine-2-thione (I).—When triethyl phosphite (1.66 g., 0.01 mole) and 3-phenyl-1,3-oxazolidine-2-thione (1.73 g., 0.01 mole) were heated at 140–160° for 3 hr. under nitrogen, 0.36 g. (21%) of poly(ethylene thiolcarbanilate) was obtained and 0.92 g. (55%) of triethyl phosphite and 1.13 g. (63%) of the thione were recovered. The polymer decomposed at 293–295°.

Anal. Calcd. for C_9H_9NOS: C, 60.33; H, 5.06; N, 7.81. Found: C, 59.77; H, 5.77; N, 8.05.

Its infrared spectrum was similar to that of ethyl N-ethylthiolcarbanilate [$C_6H_5(C_2H_5)N\text{–}CO\text{–}SC_2H_5$]; both compounds have characteristic bands at 1655 (s), 1599 (m), and 1495 cm.$^{-1}$ (m).

Bulk Polymerization of 3-Phenyl-1,3-oxazolidine-2-thione (I).—3-Phenyl-1,3-oxazolidine-2-thione (1.5 g.) was heated under the conditions shown in Table I. It was then extracted with boiling acetone and the residue was dried *in vacuo* at 110° for 3 hr. Yields, physical properties, and analytical data are shown in Table I. The extract was evaporated and the residue was recrystallized from tetrahydrofuran to give the unchanged thione, m.p. 91–94°, m.m.p. 93–95°. By evaporating the mother liquor, 3-phenyl-1,3-thiazolidine-2-one (III) was obtained and was recrystallized from ether. This compound had an infrared spectrum identical with that of the authentic sample obtained by oxidation of 3-phenyl-1,3-thiazolidine-2-thione[9]: 1655 (s), 1595 (m), 1495 (m), 1390 (m), 1310 (s), 1090 (s), and 760 cm.$^{-1}$ (m). It had m.p. 74–76° (lit. m.p. 76.5–76.7°,[9] 79°[10]).

Anal. Calcd. for C_9H_9NOS: C, 60.33; H, 5.06; N, 7.81. Found: C, 60.34; H, 5.08; N, 8.11.

Pyrolysis of Poly(ethylene thiolcarbanilate) (II).—When poly(ethylene thiolcarbanilate) (1.0 g.) was heated in a Claisen flask at 300–310° for 10 min. under nitrogen, 0.34 g. (34%) of 3-phenyl-1,3-thiazolidine-2-one (III), m.p. 74–76°, was obtained, and 0.41 g. (41%) of the polymer was recovered.

Solution Polymerization of 3-Phenyl-1,3-oxazolidine-2-thione (I).—To a solution of 3-pheny-1,3-oxazolidine-2-thione (1.0 g.) in 7 ml. of nitrobenzene was added boron trifluoride etherate (0.002 g.). After allowing the solution to stand at room temperature for 6 days, the resulting polymer was filtered, washed with refluxing acetone, and dried *in vacuo* at 110° for 3 hr.: yield 0.42 g. (42%); m.p. 309° dec.; $[\eta]^{30}_{m\text{ cresol}}$ 1.0 dl. g.$^{-1}$. The analytical sample was obtained by reprecipitation from *m*-cresol–methanol.

Anal. Calcd. for C_9H_9NOS: C, 60.33; H, 5.06; N, 7.81. Found: C, 60.46; H, 5.61; N, 7.77.

Similarly, the thione (1.0 g.) was polymerized in the presence of ferric chloride (0.002 g.): yield 0.95 g. (95%); m.p. 287° dec.; $[\eta]^{30}_{m\text{-cresol}}$ 0.7 dl. g.$^{-1}$.

Their infrared spectra were identical with those of the polymers obtained by bulk polymerization of I.

Poly(ethylene thiolcarbanilate) is soluble in *m*-cresol but insoluble in most organic solvents.

Attempted Bulk Polymerization of 1,3-Oxazolidine-2-thione (IV).—When 1,3-oxazolidine-2-thione (0.5 g.) was kept on a liquid–vapor bath of toluene (b.p. 110.6°) in a sealed glass tube

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(6) H. L. Weeler and B. Barns, *Am. Chem. J.*, **22**, 146 (1899).

(7) All intrinsic viscosities were measured in a Ubbelohde dilution viscometer in *m*-cresol at 30°, using the customary extrapolation of several values of the specific viscosity to zero concentration.

(8) M. G. Ettlingger, *J. Am. Chem. Soc.*, **72**, 4792 (1950).

(9) Yu. K. Yur'ev and S. V. Dyatlovitskaya, *Zh. Obshch. Khim.*, **27**, 3148 (1958); *Chem. Abstr.* **52**, 9077*b* (1958).

(10) W. Will, *Ber.*, **15**, 344 (1882).

under nitrogen for 10 hr., the molten thione became viscous with evolution of unidentified gas. Then the reaction mixture was washed with hot methanol, and 0.05 g. of white powder, m.p. 163–170° dec., was obtained. The infrared spectrum has broad absorption bands at about 1700–1620 and 1580–1540 cm.$^{-1}$.

Anal. Calcd. for C_3H_5NOS: C, 34.94; H, 4.89; N, 13.58. Found: C, 38.85; H, 6.46; N, 18.22.

Solution Polymerization of 1,3-Oxazolidine-2-thione (IV).—To a solution of 1,3-oxazolidine-2-thione (1.0 g.) was added boron trifluoride etherate (0.002 g.). After this solution was allowed to stand at room temperature for 6 days, the resulting polymer was washed with tetrahydrofuran, then dried *in vacuo* at 100° for 3 hr.: yield 0.14 g. (14%); m.p. 229° dec.; $[\eta]^{30}{}_{m\text{-cresol}}$ 0.06 dl. g.$^{-1}$. The analytical sample was obtained by reprecipitation from *m*-cresol–methanol.

Anal. Calcd. for C_3H_5NOS: N, 13.58. Found: N, 13.32.

Similarly, the thione was polymerized in the presence of the following catalysts (0.002 g.) (yield, melting point, and $[\eta]^{30}{}_{m\text{-cresol}}$): ferric chloride (53%, 229° dec., 0.06 dl. g.$^{-1}$), sulfuric acid (3%, 216°).

Poly(ethylene thiolcarbamate) thus obtained was soluble in *m*-cresol and dimethylformamide but insoluble in most organic solvents.

Reaction of 3-Phenyl-1,3-oxazolidine-2-thione (I) with Methyl Iodide.—A mixture of 3-phenyl-1,3-oxazolidine-2-thione (1.79 g., 0.01 mole) and methyl iodide (2.84 g., 0.02 mole) in 18 ml. of dry benzene was refluxed for 3 hr. After removal of benzene and excess methyl iodide, 3.1 g. (53%) of methyl N-(2-iodoethyl)-thiolcarbanilate was obtained. It was recrystallized from petroleum ether (b.p. 40–60°), m.p. 70.0–71.5°. Its infrared spectrum shows strong absorption at 1655 cm.$^{-1}$ (C=O).

Anal. Calcd. for $C_{10}H_{12}INOS$: C, 37.39; H, 3.77; N, 4.36. Found: C, 37.03; H, 3.69; N, 4.36.

Reaction of 1,3-Oxazolidine-2-thione (IV) with Methyl Iodide.—A mixture of 1,3-oxazolidine-2-thione (1.03 g., 0.01 mole) and methyl iodide (2.84 g., 0.02 mole) in 10 ml. of tetrahydrofuran was refluxed for 20 hr. After removal of tetrahydrofuran and excess of methyl iodide, 2.4 g. of methyl N-(2-iodoethyl)-thiolcarbamate was obtained. It was recrystallized from petroleum ether, m.p. 77.5–78.0°. Its infrared spectrum has characteristic bands for N–H (3270 cm.$^{-1}$) and for C=O (1640 cm.$^{-1}$).

Anal. Calcd. for C_4H_8INOS: C, 19.60; H, 3.29; N, 5.72. Found: C, 19.88; H, 3.43; N, 5.96.

Attempted Polymerization of 3-Phenyl-1,3-oxazolidin-2-one.—When 3-phenyl-1,3-oxazolidin-2-one (0.5 g.) was heated in a sealed tube under nitrogen for 15 hr. at about 180°, 0.48 g. (96%) of the starting material was recovered and no polymer was obtained.

When 0.001 g. of ferric chloride was added to a solution of 3-phenyl-1,3-oxazolidin-2-one (0.5 g.) in 7 ml. of nitrobenzene and the solution was kept at 20° for 6 days, 0.49 g. (98%) of the starting material was also recovered.

Heterocyclic Studies. XVII. The Preparation and Reactions of 1,2-Diazabicyclo[3.2.0]-6-heptanone Derivatives[1,2]

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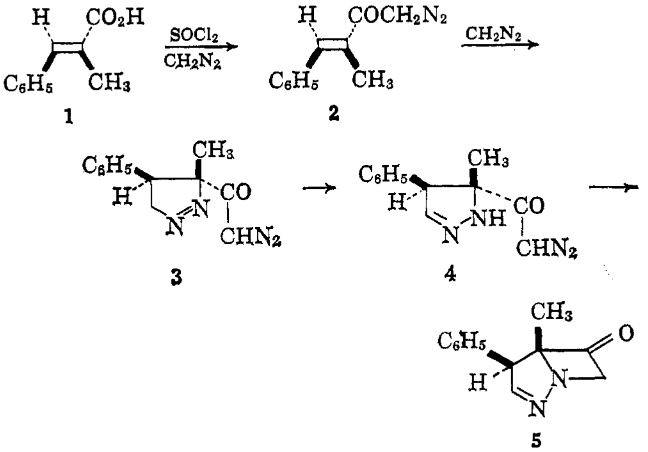
The diazoacetylpyrazoline 4 with acetic anhydride gives the acetylacetoxypyrazolidine 6 and, with acetyl chloride, pyridine, and then water, the hydroxypyrazolidine 8. In acetic acid 6 and 8 are converted to the respective 3-*endo*-substituted 1,2-diazabicyclo[3.2.0]heptanones 9 and 10. The Δ^2-bicyclic ketone 5 also gives 9 with acetic anhydride, and the 2-acetyl-Δ^3-ketone 12 with acetyl chloride. Acylation of the diazepinone 14 also leads to the 2-acyl Δ^3-bicyclic ketones in a transannular reaction; in the presence of methanol, benzoylation of 14 gives the 1-benzoyl-7-methoxydiazepinone 15. All of the bicyclic ketones and benzoylmethoxydiazepinones are deacylated to give the diazepinone 14 in acetic acid; the conversion of 5, but not the other bicyclic ketones, to 14 occurs most rapidly in base. Treatment of the 2-acyl-Δ^3 ketones 12 and 13 with acidic methanol causes ring opening to the 1-acyl-7-methoxydiazepinones 15. In strong acid all of the acyl derivatives are converted to 1-acylamido-3-hydroxypyridines 22. A mechanism involving an allylic diazepine cation and a bicyclo[4.1.0] intermediate is suggested.

The preparation of the bicyclic ketone **5** by the reactions shown in Chart I and the subsequent isomerization of **5** to a diazepinone were briefly described in an earlier paper.[3] We now present the results of more extensive work on these reactions and a number of additional compounds in the 1,2-diazabicyclo[3.2.0]heptane series.

The steric configuration of **5** and related compounds is defined as shown in Chart I by the *cis* addition[4] of diazomethane to the α-methylcinnamic acid, m.p. 76 or 81°, obtained by the Perkin condensation of benzaldehyde and propionic anhydride. The configuration of this acid has been established as *cis*-phenyl-methyl,[5] and the pyrazolines and bicyclic ketone thus have phenyl and methyl groups *cis*.

Acylation of the pyrazoline **4** and bicyclic ketone **5** led to the series of derivatives outlined in Chart II. Treatment of the pyrazoline **4** with acetic anhydride and pyridine gave a new diazoketone: $\lambda_{\max}^{\text{KBr}}$ 3.10 (NH), 4.75 ($-\overset{+}{N}\equiv N$), 5.76 (–OC=O), 6.00 (–NC=O), and 6.16 μ ($COCHN_2$); $\lambda_{\max}^{\text{EtOH}}$ 251 mμ. These data characterize the compound as the pyrazolidine **6**; this structure is authenticated by the reactions described below. With acetyl chloride and pyridine,

CHART I



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[1] Supported in part by the Geschickter Fund for Medical Research and in part by Grant DA-CML-18-108-61-6-24 from the Army Chemical Corps.

[2] Part XVI: C. L. Habraken and J. A Moore, *J. Org. Chem.*, **30**, 1892 (1965).

[3] J. A. Moore and R. W. Medeiros, *J. Am. Chem. Soc.*, **81**, 6026 (1959).

[4] R. Huisgen, *Angew. Chem. Intern. Ed. Engl.* **2**, 633 (1963), and earlier references cited there.

[5] R. Stoermer and G. Voht, *Ann.*, **408**, 47 (1915).