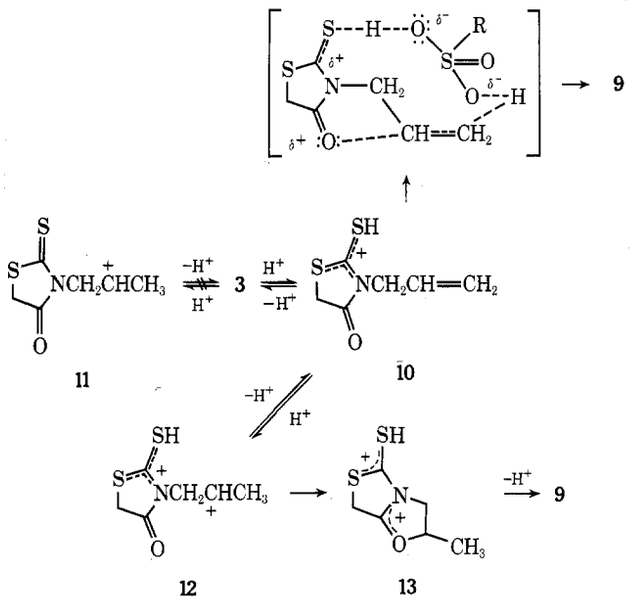
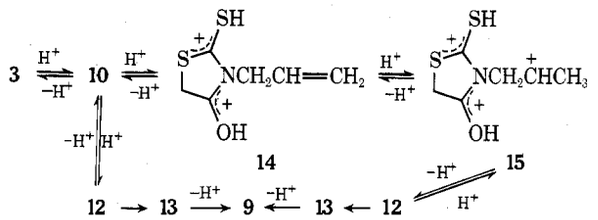
Scheme I



Scheme II



the initial protonation of the C=S is the primary reason that cyclization to oxygen rather than sulfur occurs.[13]

Experimental Section

N-Allylrhodanine was purchased from Aldrich Chemical Co., Inc. The acids were used without prior purification. Nmr spectra were determined with a Varian HA-100 MHz or a HFX-10 90 MHz instrument. The decoupling experiments were performed on the latter instrument. Tetramethylsilane was used as the reference (internal capillary) standard for all nmr measurements.

Acknowledgments. Dr. M. T. Emerson is acknowledged for his assistance in the decoupling experiments. This research was supported by a grant (to S. P. M.) from the donors of the Petroleum Research Fund, administered by the American Chemical Society, for which we are grateful. The University of Alabama Research Committee, Project Grant No. 672 (to C. U. P.) is gratefully acknowledged.

Registry No.—**3**, 1457-47-2; **9**, 52123-50-9.

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(7) Tomalia and Paige [*J. Org. Chem.*, **38**, 3949 (1973)] have incorrectly assigned the ring protons of their thiazolinium cation in their recent paper by apparently misreading the assignments of thiazolinium cations in ref 6. The assignments should be reversed. These assignments in no way affect the interesting results presented in that paper.
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(11) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969.
(12) Formation of the trication **15** is a possibility in very strong acids (see ref 9), but **15** is not expected to be important in H_2SO_4.
(13) The coordination of sulfur by acidic reagents may explain the relatively low yields of cyclic products obtained from *N*-alkenylthioamides; *cf.* P. A. S. Smith and J. M. Sullivan, *J. Org. Chem.*, **26**, 1132 (1961).

Reaction of Hexamethylphosphoric Triamide with Alkyllithiums. *In Situ* Formation of *N*-Methylmethylenimine

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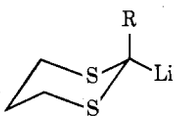
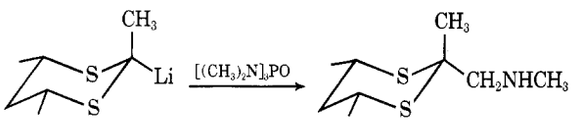
Received April 1, 1974

Hexamethylphosphoric triamide (HMPTA) is a useful solvent of high polarity and low nucleophilic character. We have employed it as a medium for nmr spectral study of 2-dithianyllithium (**1**) and 2-Phenyl-2-dithianyllithium (**2**).[1] When we tried to dissolve *r*-2-lithio-2,*cis*-4,*cis*-6-trimethyl-1,3-dithiane (**3**)[2] in the same solvent, we noted that a reaction occurred; the product, according to elemental analysis and nmr spectral evidence, was *r*-2-methylaminomethyl-2,*cis*-4,*cis*-6-trimethyl-1,3-dithiane (**4**).



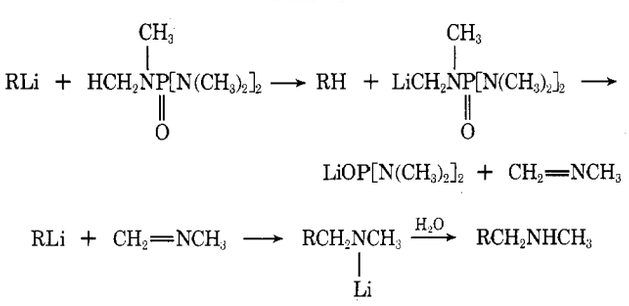
1, R = H
2, R = C_6H_5



3 **4**

About the time we carried out this experiment, a report appeared[3] describing the reaction of dialkoxyphosphoric amides with alkyllithiums to give lithium dialkoxyphosphites and Schiff bases which then react with a second mole of alkyllithium to give the lithium derivative of a secondary amine. It appeared that the reaction we had observed followed a path similar to that postulated by Savignac and Leroux[3] (Scheme I).

Scheme I



In accordance with expectations based on this scheme, we found that *n*-butyllithium, *sec*-butyllithium, and phenyllithium, when allowed to react with hexamethylphospho-

Table I

R in RLi	Solvent, temp, °C	Reaction time, days	Product	Yield, %
n-C_4H_9	Hexane–THF, −30	1	n-$C_5H_{11}NHCH_3$	50
sec-C_4H_9	Hexane–THF, −30	4	$C_2H_5CH(CH_3)CH_2NHCH_3$	68
C_6H_5	7:3 benzene–ether and THF, 0	3	$C_6H_5CH_2NHCH_3$	75

ric triamide in a 2:1 ratio, gave the homologous *N*-methylamines in 50–75% yield, as summarized in Table I.

In addition to being of potential synthetic value, these findings show that HMPTA in the presence of an alkyllithium is an *in situ* source of the very unstable species $CH_3N{=}CH_2$. Although this compound has been prepared[4,5] and studied spectroscopically,[5,6] it polymerizes[4,7] near its boiling point of −35°. Our findings also constitute a *caveat* to investigators who wish to use HMPTA as a solvent for organoalkali reagents, although we must emphasize that the less reactive lithium compounds **1** and **2** are stable in HMPTA for prolonged periods of time at 0°C and room temperature, respectively.

Experimental Section

***N*-Methyl-*N*-(2-methyl)butylamine.** A dry 200-ml round-bottom flask containing a Teflon-coated magnetic stirring bar was capped with a rubber septum and flushed with dry nitrogen using hypodermic needles; then *sec*-butyllithium (50 ml, 0.8 *M* in hexane, 0.04 mol) was introduced into the flask with a syringe. The solution was cooled by immersion in a cooling bath at −30° and diluted with 25 ml of tetrahydrofuran (THF). A solution of 3.6 g (0.02 mol) of HMPTA in 15 ml of THF was then similarly added slowly with cooling and vigorous stirring. The mixture was placed in the deep freeze at −30° for 4 days and then quenched by the addition of several ml of water with continued cooling. The product was extracted from the solution with ether using continuous liquid-liquid extraction. The ether layer was dried over magnesium sulfate, the solvents were removed with a fractionating column, and the residue was distilled, bp 107°, to yield 1.7 g of material of 80% purity (glpc) (68% yield). The material was purified by preparative gas chromatography (10 ft × ⅜ in. 20% SE-30 on 60–80 mesh Chromosorb A): ir 745 cm^{-1} (s, broad), 1110 (m), 1140 (m), 1160 (m), 1385 (m), 1470 (s), 2800 (s), 2885 (s), 2940 (s), 2965 (s), 3290 cm^{-1} (w); nmr 0.65–1 (m, 7 H, reduced to 6 H by D_2O exchange), 0.9–1.7 (m, 3 H), 2.48 ppm (s, and overlapping m, total 5 H). The picrate melted at 102–103° after three recrystallizations from benzene.

Anal. Calcd for $C_{12}H_{18}N_4O_7$: C, 43.64; H, 5.49. Found: C, 43.43; H, 5.55.

An authentic sample of the amine was prepared by treating 2-methylbutanoyl chloride with aqueous methylamine and sodium hydroxide[8] to give the *N*-methylamide, bp 70° (1 mm) [lit.[9] 70° (1 mm)] in 85% yield; reduction of the amide with ethereal lithium aluminum hydride[10] gave *N*-methyl-*N*-(2-methyl)butylamine in 80% yield, bp 107°. The nmr and ir spectra of this sample were identical with those described above.

***N*-Methyl-*N*-amylamine** was similarly prepared from 0.1 mol butyllithium (50 ml, 2*M* in hexane) in 25 ml of THF and 8.95 g (0.05 mol) of HMPTA in 25 ml of THF. The product collected on distillation weighed 2.72 g (50%): bp 116–118° (lit.[11] bp 116–118°); picrate mp 123.5–125.5° (lit.[11] mp 119–120°); nmr 0.6 (s, 1 H, disappears upon D_2O exchange), 0.75–1.08 (m, 3 H), 1.16–1.5 (m, 6 H), 2.38 (s, 3 H), 2.4–2.72 ppm (m, 2 H).

***N*-Methyl-*N*-benzylamine** was prepared from 0.06 mol of phenyllithium (33.3 ml of 1.8 *M* solution in 7:3 benzene–ether) diluted with 20 ml of THF and 5.38 g (0.03 mol) of HMPTA in 20 ml of THF to give 3.2 g of 85% pure material (75% yield): bp 80° (25 mm) [lit.[12] bp 184–185° (749 mm)]; ir (material purified by glpc) identical with that of an authenic sample;[13] nmr 1.38 (s, 1 H, disappears upon D_2O exchange), 2.44 (s, 3 H), 3.74 (s, 2 H), 7.4 ppm (s, 5 H).

***r*-2-Methylaminomethyl-2,*cis*-4,*cis*-6-trimethyl-1,3-dithiane (4).** *r*-2, *cis*-4, *cis*-6-Trimethyl-1,3-dithiane (243 mg, 1.5 mmol) was dissolved in 10 ml of a THF–HMPTA mixture (2:1) contained in a 25-ml round-bottom flask capped with a rubber septum and flushed with nitrogen as described above. Butyllithium (1.3 ml, 2.4 *M* solution in *n*-hexane, 3 mmol) was added and the mixture kept at −30° for 20 hr and then added to rapidly stirred D_2O. The product was extracted three times with 10 ml of hexane, the combined extracts were washed twice with 10-ml portions of water and dried over sodium sulfate, and the solvent was evaporated at water aspirator pressure. The product appeared homogenous upon gas chromatography on a 25 ft × ⅛ in. 25% QF-1 on Chromosorb W column at 120°: ir 730 (m), 780 (m), 1025 (m), 1065 (m), 1105 (m), 1145 (m), 1245 (s), 1370 (m), 1440 (s), 2780 (m), 2860 (s), 2910 (s), 2950 (s), 3300 cm^{-1} (w, broad); nmr 1.25 (d, J = 7 Hz) and 0.83–1.5 (B part of AB, total of foregoing peaks, 7 H), 1.84 (s, 3 H), 2–2.35 (A part of AB) and 2.23 (s) (total of these two peaks 3 H), 2.59 (s, 3 H), 3.0 (s, 2 H), 2.83–3.5 ppm (m, 2 H). The picrate melted at 180.5–182°.

Anal. Calcd for $C_{15}H_{22}N_4O_7S_2$: C, 41.47; H, 5.07. Found: C, 41.42; H, 5.10.

Acknowledgment. This work was supported under NSF Grant GP-35669, and is taken, in part, from the Ph.D. dissertation of Anthony G. Abatjoglou (University of Notre Dame).

Registry No.—4, 51932-18-4; **4** picrate, 52019-82-6; HMPTA, 680-31-8; *N*-methyl-*N*-(2-methyl)butylamine, 22431-10-3; *N*-methyl-*N*-(2-methyl)butylamine picrate, 51932-20-8; *N*-methyl-*N*-amylamine, 25419-06-1; *N*-methyl-*N*-amylamine picrate, 51932-21-9; *N*-methyl-*N*-benzylamine, 103-67-3; *r*-2, *cis*-4, *cis*-6-trimethyl-1,3-dithiane, 22452-27-3.

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Novel Synthesis of Substituted Thioacylureas. Reaction of Aryl and Alkyl Thioamides with Aryl Isocyanates

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Received April 22, 1974

The preparation of acylureas from amides and aryl and alkyl isocyanates has been described by B. Kühn,[1,2] and extended by P. F. Wiley.[3] However, when aliphatic or aromatic thioamides are refluxed with aryl isocyanate in benzene or toluene, loss of H_2S from the thioamide occurs and symmetrical diarylurea is obtained from the reaction of isocyanate and H_2S.[4]