Compound **19** was dissolved in 20 ml of glacial acetic acid and hydrogenated over 0.1 g of platinum oxide at 50 psig and 75° for 8 hr. The acetic acid was evaporated and the residual amide was hydrolyzed by refluxing it in 10 ml of concentrated hydrochloric acid for 16 hr. The mixture was diluted with water and extracted with ether. The ether was evaporated to obtain *α*-phenyl-*p*-toluic acid: mp 156–157°; mmp with authentic sample (prepared by hydrogenation of 4-benzoylbenzoic acid in acetic acid over palladium–charcoal at 65° and 50 psig), 158–160°.

E. **Trifluoroacetic Anhydride.**—Trifluoroacetic anhydride was added dropwise to the filtrate until **16** just disappeared (nmr monitor). The viscous precipitate which formed was separated from the supernatant by decantation. The supernatant was shown to contain *N*,*N*-dimethyltrifluoroacetamide[18] by vpc and mass spectroscopy (*m/e* 171). The viscous precipitate was taken up in acetonitrile, the solution was extracted with pentane, and the actonitrile was evaporated. The residue was dissolved in 2 *N* sodium hydroxide and the mixture was extracted with ether. The ether was evaporated, the residue was separated by vpc, and the components were examined by mass spectroscopy; the presence of *N*,*N*-dimethylbenzamide and compound **19** (major component) was confirmed.

Registry No.—**3,** 815-62-3; **5,** 30482-28-1; **12,** 30482-29-2; **12** HCl, 30482-30-5; **12** hexafluorophosphate, 30471-97-7; **15,** 19111-89-8; **16,** 30482-32-7; **17,** 13880-55-2; **19,** 30482-34-9; tetramethylammonium hexafluorophosphate, 558-32-7; *N*,*N*,*N'*,*N'*-tetramethylbenzamidinium hexafluorophosphate, 30482-36-1.

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[18] E. R. Bissell and M. Finger, *J. Org. Chem.*, **24**, 1256 (1959).

Notes

α,*α*,*α*-Tris(dimethylamino)toluene, a New *gem*-Triamine

Charles F. Hobbs* and Harold Weingarten

Central Research Department, Monsanto Company,
St. Louis, Missouri 63166

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Recently there has been considerable interest in the synthesis[1-5] and reactions[4-8] of *gem*-triamines. The majority of *gem*-triamines thus far synthesized have been N derivatives of methanetriamine with hydrogen as the substituent on the central carbon. Although a higher homolog, 1,1,1-tripiperidinoethane, has been twice reported,[9,10] both assignments subsequently were shown to be in error.[11] More recently, *gem*-triamines with trifluoromethyl[12] and chlorodifluoromethyl[13] groups on the central carbon have been reported.[14] An attempt to synthesize an aryl-substituted *gem*-triamine, *α*,*α*,*α*-tris(dimethylamino)toluene, by the amination of *N*,*N*-dimethylbenzamide with tetrakis(dimethylamino)titanium was unsuccessful.[1]

We now have found that *α*,*α*,*α*-tris(dimethylamino)toluene can be simply and conveniently prepared by the reaction of phenyllithium with hexamethylguanidinium chloride,[15] the latter being prepared in novel fashion by an exchange reaction between tetramethylchloroformamidinium chloride and tetrakis(dimethylamino)methane. The structure of *α*,*α*,*α*-tris(dimethylamino)toluene was proven by its nmr spectrum and elemental analysis, and by hydrolysis in dilute acid to the *N*,*N*,-*N'*,*N'*-tetramethylbenzamidinium ion, which underwent further hydrolysis to *N*,*N*-dimethylbenzamide upon basification.

Experimental Section[16]

N,*N*,*N'*,*N'*,*N''*,*N''*-**Hexamethylguanidinium Chloride.**—A solution of 3.42 g (0.020 mol) of *N*,*N*,*N'*,*N'*-tetramethylchloroformamidinium chloride[17] in a minimum amount of acetonitrile was added slowly to an acetonitrile solution of 3.95 g (0.021 mol) of tetrakis(dimethylamino)methane.[18] The reaction was sufficiently exothermic to cause reflux of the acetonitrile. The solution was allowed to cool and ether was added to precipitate the hexamethylguanidinium chloride, yield 6.72 g (94%), nmr (CD_3CN) τ 7.06 (s). Addition of sodium hexafluorophosohate solution to an aqueous solution of the guanidinium chloride precipitated the hexafluorophosphate, mp 342–347° dec, nmr (CD_3CN) τ 7.16 (s).

Anal. Calcd for $C_7H_{18}F_6N_3P$: C, 29.07; H, 6.27; F, 39.42; N, 14.53; P, 10.71. Found: C, 29.07; H, 6.44; F, 39.58; N, 14.14; P, 10.69.

α,*α*,*α*-**Tris(dimethylamino)toluene.**—To a slurry of 5.0 g (0.028 mol) of *N*,*N*,*N'*,*N'*,*N''*,*N''*-hexamethylguanidinium chloride in 35 ml of ether was added dropwise 22.8 ml (0.028 mol) of phenyllithium (1.226 *M* in ether). The mixture was refluxed for 2 hrs and then cooled and filtered. Ether was removed from the filtrate by distillation. The dark crystalline residue was taken up in pentane and filtered. The filtrate was freed of pentane by evaporation to obtain 3.93 g (52%) of *α*,*α*,*α*-tris(dimethyl-

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[1] H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 2874 (1966).

[2] H. Bredereck, F. Effenberger, T. Brendle, and H. Muffler, *Chem. Ber.*, **101**, 1885 (1968).

[3] H. Bredereck, G. Simchen, and H. W. Schenck, *ibid.*, **101**, 3058 (1968).

[4] H. Bredereck, F. Effenberger, and T. Brendle, *Angew. Chem., Int. Ed. Engl.*, **5**, 132 (1966).

[5] J. W. Scheeren and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **88**, 289 (1969).

[6] H. Bredereck, F. Effenberger, and H. J. Bredereck, *Angew. Chem., Int. Ed. Engl.*, **5**, 971 (1966).

[7] H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 3427 (1966).

[8] H. Weingarten and N. K. Edelmann, *ibid.*, **32**, 3293 (1967).

[9] J. Buss and A. Kekule, *Chem. Ber.*, **20**, 3247 (1887).

[10] H. M. Barnes, D. Kundiger, and S. M. McElvain, *J. Amer. Chem. Soc.*, **62**, 1281 (1940).

[11] H. Böhme and F. Soldan, *Chem. Ber.*, **94**, 3109 (1961).

[12] G. M. J. Slusarczuk and M. M. Joullie, *Chem. Commun.*, 469 (1970).

[13] F. Lautenschlaeger, *J. Heterocycl. Chem.*, **7**, 1413 (1970).

[14] *N*-Acyl derivatives of the *gem*-triamine system are also known: H. E. Winberg and D. D. Coffman, *J. Amer. Chem. Soc.*, **87**, 2776 (1965); E. Dyer, T. E. Majewski, and J. D. Travis, *J. Org. Chem.*, **33**, 3931 (1968).

[15] This result is in contrast to the assertion that reaction of guanidinium salts with organometallic reagents does not lead to triaminomethane derivatives.[11]

[16] Melting points are corrected. Amidinium salts were handled in an atmosphere of dry nitrogen unless otherwise noted.

[17] H. Eilingsfeld, G. Neubauer, M. Seefelder, and H. Weidinger, *Chem. Ber.*, **97**, 1232 (1964).

[18] H. Weingarten and W. A. White, *J. Amer. Chem. Soc.*, **88**, 2885 (1966).

amino)toluene, analytical sample, mp 83–84° ($\mathrm{CH_3CN}$); nmr ($\mathrm{C_6D_6}$) τ ~2.66 (m, 5, aromatic) and 7.58 (s, 18, $\mathrm{NMe_2}$).

Anal. Calcd for $\mathrm{C_{13}H_{23}N_3}$: C, 70.54; H, 10.47; N, 18.98. Found: C, 70.35; H, 10.72; N, 18.72.

Treatment of the triamine with 6 *N* hydrochloric acid afforded dimethylammonium ion and *N,N,N′,N′*-tetramethylbenzamidinium ion:[19,20] nmr ($\mathrm{H_2O}$) τ 2.4 (s, 5, aromatic), 6.8 (s, 12, $\mathrm{N^+Me_2}$), and 7.3 (t, 6, $\mathrm{H_2N^+Me_2}$). The solution was made basic and was extracted with ether. Evaporation of the ether gave *N,N*-dimethylbenazmide, identical (nmr and vpc) with an authentic sample.

Registry No.—*N,N,N′,N′,N″,N″*-Hexamethylguanidinium chloride, 30388-20-6, 30388-21-7 (hexafluorophosphate); α,α,α-tris(dimethylamino)toluene, 30388-25-1.

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[19] C. F. Hobbs and H. Weingarten, *J. Org. Chem.*, **36**, 2881 (1971).

[20] C. G. Raison, *J. Chem. Soc.*, 3325 (1949).

A Novel Preparation of 3-Oxazoline-2(1*H*)-2-thiones Involving a Benzilic Acid Type Rearrangement

David N. Harpp* and P. Mathiaparanam[1]

Department of Chemistry, McGill University, Montreal, Canada

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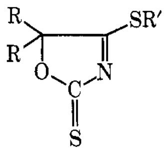
We wish to report that α-benzoyl-α-chlorobenzyl sulfides[2] (2) can be converted in high yield to substituted 3-oxazoline-2(1*H*)-2-thiones (1) by treatment with potassium thiocyanate. When sulfide 2 [pre-



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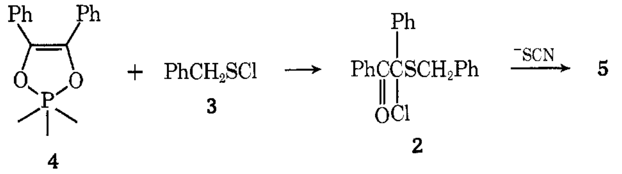
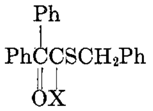
pared by the action of benzyl sulfenyl chloride (3) on the 1,3,2-dioxaphospholene derivative 4][2] was combined with potassium thiocyanate, compound 5 was isolated in 90% yield. Exact mass measurement of 5 (*m/e* 375.0739) gave a molecular formula of $\mathrm{C_{22}H_{17}NOS_2}$.



The structure of 5 was deduced as follows. The lack of –CO, –NCS, and –SCN stretching frequencies in the ir spectrum of 5 showed that it was not a simple substitution product (6 or 7).[3] A more deep-seated

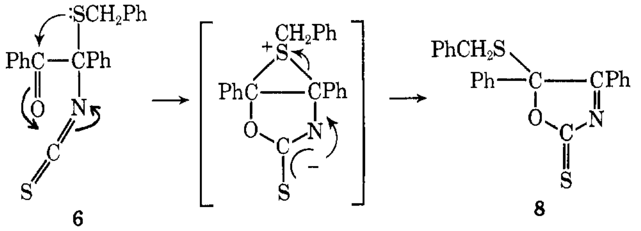


$\mathrm{Ph\underset{\overset{\|}{O}}{C}\underset{\overset{|}{X}}{\overset{\overset{Ph}{|}}{C}}SCH_2Ph}$

6, X = –NCS
7, X = –SCN

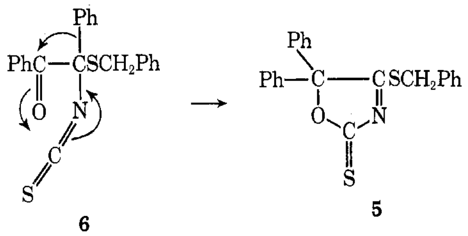
transformation can be envisaged. From a mechanistic viewpoint two structures for 5 following from 6 are reasonable. Path a, involving an episulfonium intermediate, predicts 8 as the product. Participation by

path a



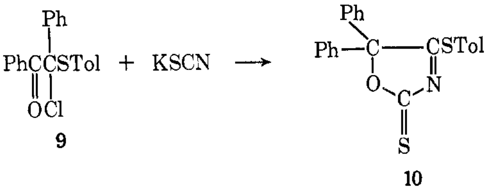
sulfur would not be unexpected and has ample precedent in the literature.[4] Alternatively, phenyl migration, as depicted in path b suggests that thione 5 might be formed.

path b



The nmr spectrum of 5 reveals a sharp singlet as the only upfield signal (τ 5.77). This observation is consistent only with structure 5. If 8 were the correct structure, an AB pattern would have been observed for the diastereomeric protons on the benzylic carbon atom.[5] Phenyl migration of this kind has literature precedent in the benzilic acid rearrangement.[6]

Similarly, sulfide 9 was treated with KSCN. An oil, 10, was isolated in 82% yield: tlc homogeneous; *m/e* 375.0726 (calcd for $\mathrm{C_{22}H_{17}NOS_2}$, 375.0752); nmr τ 2.10–2.90 (14 H, m), 7.60 (3 H, s). That phenyl migration occurs in this reaction as well was strongly indicated by the similar uv spectra of 5 and 10: 5, $\lambda_{\max}$ 228 nm (ϵ 3483), 296 (1711); 10, 232 (2970), 295 (1543). While 5 and 10 give expected ir, nmr, mass



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[1] NRCC Scholarship Recipient, 1967–1970.

[2] D. N. Harpp and P. Mathiaparanam, *Tetrahedron Lett.*, 2089 (1970).

[3] Analogous compounds are formed in the reaction of α-chloro ketones and KSCN; see A. Hantzsch and L. Aripides, *Justus Liebigs Ann. Chem.*, **249**, 18 (1888).

[4] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp 561–617.

[5] K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966, pp 93–95. It should be noted that a sharp singlet was observed in a variety of solvents: $\mathrm{C_6H_6}$, $\mathrm{CDCl_3}$, $\mathrm{CD_3OD}$, and $\mathrm{(CD_3)_2SO}$ at τ 6.00, 5.77, 5.77, and 5.67, respectively. Strong AB coupling is observed in 2 as well as other similar derivatives (see ref 2).

[6] Reference 4, p 636.