

14.0 g of hexamethylenetetramine (100 mmol), and 150 ml of trifluoroacetic acid was heated at reflux (83–90°) for 12 hr. The products were concentrated and combined with 600 ml of ice water; the resultant mixture was stirred for 15 min, made basic with Na₂CO₃, and extracted with ether. Evaporation of the ether solution left a yellow solid which was recrystallized from chloroform–pentane to afford 14.3 g (95% yield) of 3,5-dimethyl-4-hydroxybenzaldehyde, mp 111–112.5° (lit.⁴ mp 113–114°).

The data for a number of these transformations are summarized in Table I.

TABLE I
FORMYLATION OF AROMATICS BY HEXAMETHYLENETETRAMINE
IN TRIFLUOROACETIC ACID

| Aromatic | Hexamethylene- tetramine: aromatic | Product ^a (% yield) |
|----------------------------------|--|--|
| <i>tert</i> -Butylbenzene | 1:1 | <i>p</i> - <i>tert</i> -Butylbenzaldehyde (75) |
| <i>p</i> -Xylene | 1:1 | 2,4-Dimethylbenzaldehyde (55) |
| Toluene | 1:1 | <i>p</i> -Tolualdehyde (50) <i>o</i> -Tolualdehyde (11) |
| Benzene ^b | 1:4 | Benzaldehyde (32) |
| 2,6-Dimethylanisole | 2:1 | 3,5-Dimethyl-4-methoxybenzaldehyde (74) |
| Benzodioxane(1,4) | 1:1 | 4'-Formylbenzodioxane(1,4) (37), 3'-formylbenzodioxane(1,4) (2) |
| Diphenyl ether | 2:1 | <i>p</i> -Phenoxybenzaldehyde (29), 4,4'-diformyldiphenyl ether (25) |
| 2,6-Di- <i>tert</i> -butylphenol | 1:1 | 3,5-Di(<i>tert</i> -butyl)-4-hydroxybenzaldehyde (60) |
| 2,6-Xylenol | 1:1 | 3,5-Dimethyl-4-hydroxybenzaldehyde (95) |

^a Isolated materials exhibiting correct physical and spectroscopic properties; isomer compositions were by ¹H nmr spectroscopy. ^b Sealed tube, 125–150°.

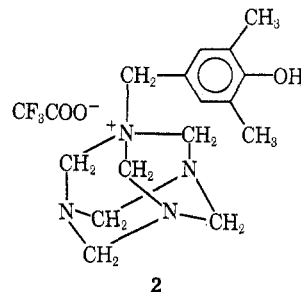
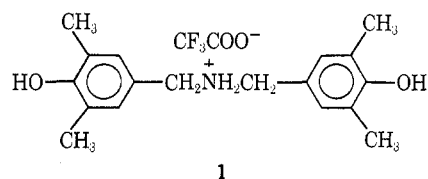
Methylimine derivatives are immediate precursors of the aldehydes. When the reaction products derived from toluene were subjected to rapid hydrolytic work-up, the *p*- and *o*-toluimines CH₃C₆H₄CH=NCH₃ were obtained in predominance to the carbonyl compounds. Whether such products are formed by rearrangement of the methyleneimines ArCH₂N=CH₂ or arise in exchange reactions involving methylamine remains to be determined.

Other kinds of intermediates are isolable when both heating and hydrolysis are avoided. Thus, the 2,6-xylenol–hexamethylenetetramine–trifluoroacetic acid system when kept below 30° for 3 hr yielded a complex mixture from which the dibenzylammonium salt⁵ **1** (41%) and the hexaminium salt⁶ **2** (15%) were isolated

(4) V. V. Ershov and G. A. Ziobina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2235 (1964).

(5) Bis(4-hydroxy-3,5-dimethylbenzyl)ammonium trifluoroacetate (**1**): mp 193–195°; ¹H nmr (DMSO-*d*₆) δ 2.30 (s, 12), 4.08 (s, 4), 7.26 (s, 4), 9.18 (br, 2), 9.80 (br, 2); Fourier transform ¹³C nmr (DMSO-*d*₆, from TMS) 153.2, 129.4, 123.8, 121.3, 48.9, 15.7 ppm. *Anal.* Calcd for C₂₆H₂₄F₃O₄N: C, 60.14; H, 6.06; F, 14.24; N, 3.51. Found: C, 60.26; H, 6.14; F, 14.36; N, 3.51.

(6) 4-Hydroxy-3,5-dimethylbenzylhexamethylenetetrammonium trifluoroacetate (**2**): mp 154° dec; ¹H nmr (DMSO-*d*₆) δ 2.27 (s, 6), 3.55 (br, 2) 4.05 (s, 2), 4.67 (s, 6), 5.20 (s, 6), 7.25 (s, 2), 9.20 (br, 1); Fourier transform ¹³C nmr (DMSO-*d*₆, from TMS) 155.4, 132.4, 125.1, 115.6, 77.7, 70.2, 59.6, 16.7 ppm. *Anal.* Calcd for C₁₈H₂₈N₆O₃F₃: C, 51.06; H, 6.16; N, 14.89; F, 15.14. Found: C, 51.27; H, 6.03; N, 14.80; F, 15.30.



after evaporation of the acid and fractional crystallization of the residue from acetonitrile–ether. No unalkylated 2,6-xylenol was recovered.

The formation of **2** makes evident the relationship of this process to the Sommelet⁷ and Delépine⁸ reactions, both of which are based on transformation of *N*-benzyl derivatives of hexamethylenetetramine. Experiments with the trifluoroacetic acid system aimed at an illumination of these mechanistically obscure⁹ facets of hexamethylenetetramine chemistry are in progress.

(7) S. J. Angyal, *Org. React.*, **8**, 197 (1954).

(8) M. Delépine, *Bull. Soc. Chim. Fr.*, **13**, 358 (1895).

(9) Methyleneimmonium¹⁰ and methylenebenzylimmonium¹¹ ions have been invoked as the oxidizing agents in the Sommelet reaction, in which aldehydes are produced on hydrolysis of hexaminium salts. Both species are likely alkylating agents in the process reported here. The seemingly high sensitivity to steric effects of substituents on the aromatic nucleus does suggest, however, that the alkylation involves bulkier electrophile(s), possibly ones more immediately derived from hexamethylenetetramine.

(10) H. R. Snyder and J. R. Demuth, *J. Amer. Chem. Soc.*, **78**, 1981 (1956).

(11) S. J. Angyal, *et al.*, *J. Chem. Soc.*, 1742 (1953).

CHEMICAL LABORATORY
GENERAL ELECTRIC RESEARCH
AND DEVELOPMENT CENTER
SCHENECTADY, NEW YORK 12301

WILLIAM E. SMITH

RECEIVED SEPTEMBER 20, 1972

Facile Thermal Rearrangements of Allyl Selenides and Diselenides. [1,3] and [2,3] Shifts

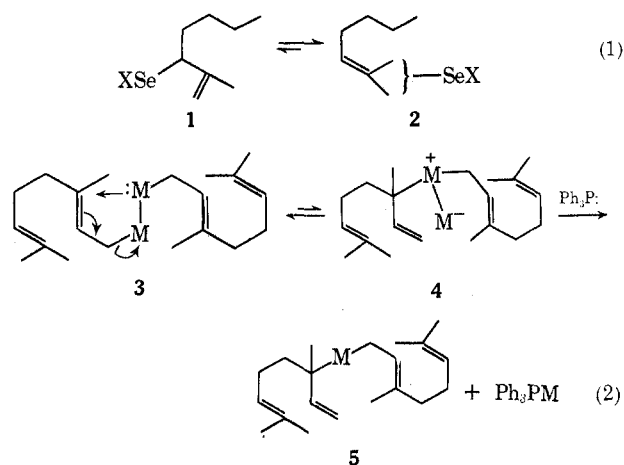
Summary: Allyl selenides and allyl diselenides undergo [1,3] and [2,3] shifts, respectively.

Sir: We wish to report the selenoallylic rearrangement^{1,2} of **1** to **2** and the [2,3] sigmatropic rearrangement–reduction³ of **3** (M = Se) to **5** (M = Se) (eq 1 and 2). The secondary allyl selenide **1** (X = Ph)

(1) The analogous thioallylic rearrangement has been studied by H. Kwart and N. Johnson, *J. Amer. Chem. Soc.*, **92**, 6064 (1970).

(2) A related [1,3] silylallylic rearrangement has also been described by H. Kwart and J. Slutsky, *ibid.*, **94**, 2515 (1972).

(3) The analogous rearrangement–reduction of allylic disulfides has been studied by G. Höfle and J. E. Baldwin, *ibid.*, **93**, 6307 (1971); the synthesis of geranyl linalyl sulfide (**5**, M = S), *via* this sequence, the exact analog of reaction 2, was reported by G. M. Blackburn and W. D. Ollis, *Chem. Commun.*, 1261 (1968).



was prepared by addition of the corresponding allyl chloride (obtained by the action of Lee's reagent⁴ on 2-methyl-1-hepten-3-ol) to a solution of PhSeNa in ethanol.⁵ Selenide **1** (X = Ph) contained, by nmr analysis, about 6% *Z-E* isomers of **2** (X = Ph). Attempted short-path distillation of selenide **1** resulted in quantitative rearrangement of **1** to **2**, proceeding with a half-life of ~ 1.3 hr in chloroform at 52°. At the same temperature in methanol the rearrangement went at a somewhat slower rate ($t_{1/2}$ 2.0 hr). Thus, the selenoallylic rearrangement occurs more readily⁶ than its thioallylic¹ partner.

All attempts to prepare the selenocyanate (X = CN) and diselenide (X = SeC₇H₁₅) analogs of **1** led only to the rearranged isomers (**2**) with selenium bound to the primary carbon. The [1,3] shift must occur

(4) T. J. Nolan and J. B. Lee, *Can. J. Chem.*, **44**, 1331 (1966).

(5) The general procedure of Cope and coworkers was used except that thiophenol was replaced by selenophenol [A. C. Cope, D. E. Morrison, and L. Field, *J. Amer. Chem. Soc.*, **72**, 59 (1950)].

(6) Admittedly, the exact comparisons have not been made, but the rate data in ref 1 and 3 for the sulfur systems clearly support our contention that the selenium systems are more reactive.

(7) T. Tarantelli and D. Leonesi, *Ann. Chim. (Rome)*, **53**, 1113 (1963).

very readily for selenocyanate **1** (X = CN). The failure to isolate the diselenide **1** (X = SeC₇H₁₅) could also be attributed to fast [1,3] shifts, but it is more likely due to double [2,3] sigmatropic rearrangement analogous to the situation for diallyl disulfides.³ Reaction of geranyl chloride (prepared from geraniol using the Lee reagent⁴) with potassium selenocyanate in acetone⁷ produced geranyl selenocyanate (**6**) in quantitative yield. Reduction of selenocyanate **6** with lithium aluminum hydride in ether gave geranyl-selenol and no geranyl amine.

Alkylation of Na₂Se₂, prepared in liquid ammonia by sodium metal reduction of metallic selenium,⁸ with geranyl chloride resulted in a 2:1 mixture of geranyl diselenide **1** (M = Se) and geranyl monoselenide (**7**). The colorless monoselenide **7** was separated from the yellow diselenide by column chromatography on silica gel eluting with hexane. When geranyl diselenide **3** (M = Se) was exposed to excess triphenylphosphine in chloroform solution at 25°, geranyl linalyl selenide⁹ (**5**, M = Se) was cleanly produced; the half-life for this process was ~ 2.5 hr. Thus, as for the [1,3] shift (reaction 1), the [2,3] shift (reaction 2) also proceeds faster⁶ for the selenium analogs.

Acknowledgment.—We gratefully acknowledge the National Science Foundation (GP-30485X), Eli Lilly and Co., and Hoffmann-La Roche for support of this research.

(8) L. Brandsma and H. E. Wijers, *Recl. Trav. Chim. Pays-Bas*, **82**, 68 (1963).

(9) All the organoselenium derivatives described in this report are new compounds and have been adequately characterized by analytical and spectral data. Some novel rearrangements occurring upon oxidation of these allyl selenium species are reported elsewhere: K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **94**, 7154 (1972).

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS 02139

K. B. SHARPLESS*
R. F. LAUER

RECEIVED SEPTEMBER 12, 1972