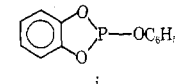
(22) (a) See ref b, Table V; (b) T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, **97**, 2947 (1975).
(23) (a) H. Goetz, F. Nerdel, and K.-H. Wiechel, *Justus Liebigs Ann. Chem.*, **665**, 1 (1963); (b) H. Goetz, H. Juds, and F. Marschner, *Phosphorus*, **1**, 217 (1972); (c) B. J. Walker, "Organophosphorus Chemistry", Penguin Books, Middlesen, England, 1972, pp 32–40.
(24) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, pp 430–436.
(25) Although no other Hammett type studies of the nucleophilicities or basicities of arenesulfinates show correlations with σ^+ constants,[1] others have observed a better correlation of ir stretching frequency intensities of S–O bonds in aryl sulfones with σ^+ constants than with normal σ values.[26]
(26) M. C. Cutress, T. B. Grindley, A. R. Katritsky, M. Shome, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 268 (1974).
(27) σ constants are mean values, and so a natural spread in these numbers is to be expected: O. Exner in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Ed., Plenum Press, New York, N.Y., 1972, p 1.
(28) M. P. Naan, R. I. Powell, and C. D. Hall, *J. Chem. Soc. B*, 1683 (1971).
(29) A plausible reaction pathway might be that depicted below. However, it is difficult to rationalize (1) the abnormally high σ values (ca. +6) associated

$$RX + Ar_3P \longrightarrow R{\cdot}X^- + Ar_3\dot{P}{\cdot}^+ \xrightarrow[-HX]{H_2O} R{\cdot} + Ar_3\dot{P}OH \longrightarrow$$

$$R{:}^- + Ar_3\dot{P}OH \longrightarrow RH + Ar_3PO$$

with the reactions of TPP with **1** and (2) why R· and $Ar_3P{\cdot}^+$ (or $Ar_3\dot{P}OH$) would not combine and lead to stable and isolable quaternary phosphonium salt (not observed). No evidence through use of free-radical initiators or inhibitors could be obtained for a free-radical chain reaction.
(30) Reduction of an α-bromo sulfone with TPP has been shown to take place with retention of configuration at the α-sulfonyl carbon atom: F. G. Bordwell and E. Doomes, *J. Org. Chem.*, **39**, 2298 (1974).
(31) W. G. Bentrude in "Free Radicals", Vol. 2, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 652.
(32) I. J. Borowitz, K. C. Kirby, P. E. Rusek, and E. W. Casper, *J. Org. Chem.*, **36**, 88 (1971).
(33) See entries 3 and 6 in Table VI.
(34) R. Hiatt, C. McColeman, and G. R. Howe, *Can. J. Chem.*, **53**, 559 (1975).
(35) Typical amines also prove to be very poor agents for dehalogenation reactions. Highly polarizable amines (e.g., the bicyclic amidines) are useful in certain dehalogenation reactions,[36,37] and 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN) reacts with **1a** (X = Br and I) in aqueous DMF to give the reduced sulfone **5**.
(36) E. Baciocchi and C. Lillocci, *J. Chem. Soc., Perkin Trans. 2*, 802 (1975).
(37) T. L. Ho and C. M. Wong, *Synth. Commun.*, **5**, 87 (1975).
(38) (a) B. Miller, *Top. Phosphorus Chem.*, **2**, 133 (1965); (b) P. A. Chopard, *Chimia*, **20**, 429 (1966).
(39) I. J. Borowitz, D. Weiss, and R. K. Crouch, *J. Org. Chem.*, **36**, 2377 (1971).
(40) This difference in rate is reflected almost entirely in the $\Delta H^{\ddagger}$ parameters rather than in the $\Delta S^{\ddagger}$ factors.
(41) M. Leblanc, E. Corre, M. Soenen-Sullarich, M. F. Chasle, and A. Foucand, *Tetrahedron*, **28**, 4431 (1972).
(42) The relative order of reactivity for the trialkyl phosphites, *i*-Pr < Et < *n*-Bu, in reaction 4 follows no clear relationship with σ^* or steric factors. The observed order of reactivity probably is due to a combination of steric and electronic effects.
(43) M. Charton, *J. Am. Chem. Soc.*, **97**, 3691, 3694 (1975).
(44) The O–P–O bond angle in phosphites is ca. 100° [L. V. Vilkov, P. A. Akishin, and G. E. Salova, *Zh. Strukt. Khim.*, **6**, 355 (1965)], whereas this angle increases to ca. 110° in the tetracoordinate intermediate (J. J. Daly in "Perspectives in Structural Chemistry", J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N.Y., 1970, p 175).
(45) (a) R. G. Harvey and E. R. DeSombre, *Top. Phosphorus Chem.*, **1**, 57 (1964); (b) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus", Elsevier, New York, N.Y., 1967, p 38.
(46) Although no quantitative data are available, tri-*tert*-butyl phosphite appears to be far more reactive in the Arbuzov reaction than are the other trialkyl phosphites. This has been attributed to both steric and electronic effects, but in view of our results is most certainly due primarily to a steric effect: V. Mark and J. Van Wazer, *J. Org. Chem.*, **29**, 1006 (1964).
(47) (a) Reference e, Table V; (b) R. D. Temple and J. E. Leffler, *Tetrahedron Lett.*, 1893 (1968).
(48) In the deoxygenation of pyridine *N*-oxides, triaryl phosphites are more reactive than trialkyl phosphites. However in these reactions, organophosphorus compounds appear to be functioning as electrophiles rather than nucleophiles: A. R. Katritsky and J. M. Lagowski, "Chemistry of the Heterocyclic N-Oxides", Academic Press, New York, N.Y., 1971, pp 195–196.
(49) In a private communication, Professor A. Foucaud informs us that he also has observed that triphenyl phosphite is more reactive than trimethyl phosphite toward α-bromo-α-cyano esters [ref 41; see also M. Svilarich-Soenen and A. Foucaud, *Tetrahedron*, **28**, 5149 (1972)]. However, phosphite i is less reactive than trimethyl phosphite, which is not unexpected based on the steric argument presented.



i

(50) (a) F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 529 (1937); (b) H. Fritzsche, U. Hasserodt, and F. Koste, *Chem. Ber.*, **97**, 1988 (1964); (c) Reference e, Table V.
(51) L. Maier in "Organic Phosphorus Compounds", Vol. 1, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 1.
(52) This compound was reported earlier, ref 47, but no physical data were given.
(53) K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).

2-Thenyl Group as Terminus *and* Migrating Moiety in the Stevens and Sommelet Rearrangements of a Quaternary Ammonium Ion[1]

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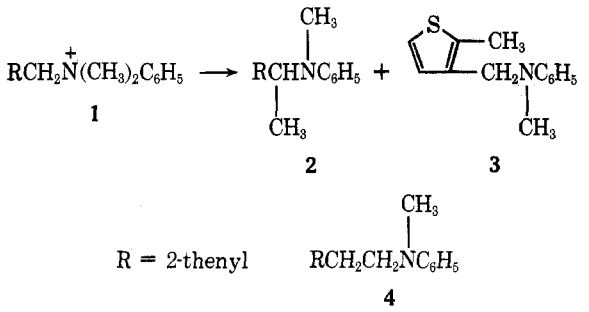
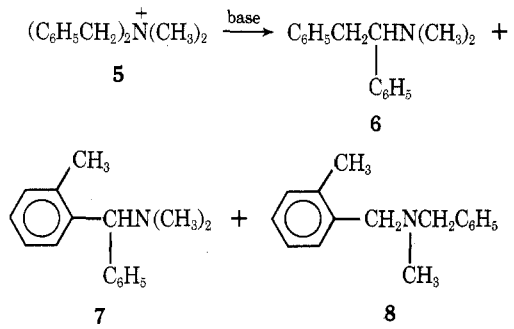
The presence of two thenyl groups as substituents on nitrogen in the ammonium salt **9** gave base-initiated rearrangements producing high yields of amines **13** and **14**. The absence of other rearrangement products and the relatively good linear fit of all log (**13**/**14**) values vs. $1/T$ which is independent of concentrations, base, or solvent system was taken as indicative of a common ylide precursor **16** but subsequently different reaction routes in the Stevens and the Sommelet rearrangement processes. Synthesis of a variety of compounds, including others which might be anticipated in such a reaction, ensured adequate knowledge of separation and spectroscopic characteristics to allow clear distinction of structures.

Much research has been done in recent years to broaden the scope and to unveil the mechanistic features of the Stevens and the Sommelet rearrangements of quaternary ammonium ions.[2] However, few papers[3–5] have appeared concerning heterobenzyl quaternaries, which, like the benzyl analogues, are potentially apt to yield both types of migration.

We have recently shown[5] that a 1,2-methyl shift to the α position of a 2-thenyl moiety may be induced by base to yield **2**. In this reaction, hints that the 2-thenyl group may also function as a migrating radical came from traces of rearranged amines **3** and **4** wherein the heterobenzyl moiety has undergone Sommelet and Stevens shifts, respectively.[4,5] Since a previous report[3] stated that no rearranged product could be detected from 2-thenyltrimethylammonium ion, which is in sharp contrast to our 2-thenyldimethylanilinum (**1**) results,[4,5] we felt that it was important to determine whether 2-thenyl

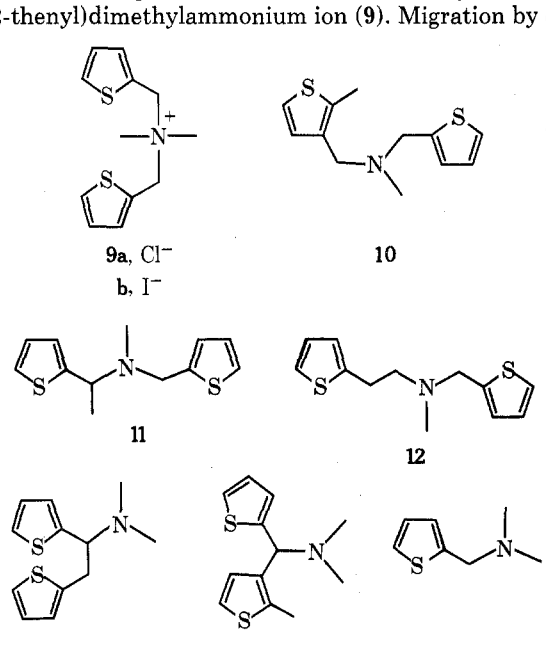


migrations were limited to anilinium as opposed to alkylammonium systems. An excellent candidate for this determination was the "heterolog" of dibenzyldimethylammonium ion, **5**, since the base-induced rearrangements of **5** to amines have been extensively studied.[6-14]



Three rearrangement products, **6**, **7**, and **8**, have been reported from the base-induced reaction of **5**. The relative amounts of Stevens product, **6**, or *o*-benzyl to α-benzyl (**7**) and *o*-benzyl to methyl (**8**) shift Sommelet products was strongly dependent on the base employed, the base concentration (base–salt ratio), the solvent, and the temperature.[2] Displacement resulting in predominant formation of benzyldimethylamine together with **6–8** resulted under one set of conditions.[12]

By analogy with the reactions of **5** and **1**, a variety of products were anticipated for our chosen heterlog of **5**, *N,N*-di(2-thenyl)dimethylammonium ion (**9**). Migration by or to



a methyl group of the Sommelet or the Stevens type, which from **1** gave **3** or **2** and **4**, would lead from **9** to **10** or **11** and **12**, respectively. The rearrangements of **5** via Stevens or Sommelet routes to **6** or **7** and **8** would find parallels in respective formation of **13** or **14** and **10** from **9**. Displacement or cleavage would re-form the synthetic precursor of **9**, *N,N*-dimethyl-*N*-(2-thenyl)amine (**15**). Synthesis of di(2-thenyl) starting materials and anticipated products is discussed in Part B.

Part A

Rearrangement of the chloride (**a**) or iodide (**b**) of **9** resulted in the exclusive production of the Stevens amine **13** and the Sommelet amine **14** accompanied by only minute traces of **15**.

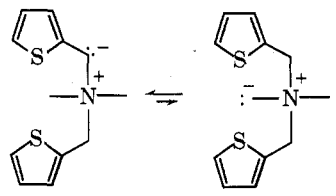
$$9 \rightarrow 13 + 14 (+ 15)$$

Although details of the conclusive identification of these products are presented in Part B, the marked changes in product distribution with a variety of basic conditions (Table I) and comparisons with analogous systems are of immediate interest. No attempt was made to optimize conditions to produce maximum yields in these reactions.

The absence of **10–12** clearly distinguishes the dithenyl system **9** from its thenyl–anilinium counterpart **1**. Even if consideration is taken of the very limited amounts of **3** and **4** seen under any conditions from **1** and the maximization of **2** when KOH was used,[5] the mono- and dithenyl systems are quite distinct. However, KOH does give the highest observed yields of Stevens rearrangement products **2** and **13** from **1** and **9**, respectively. Yet 23% cumulative yield of all rearranged products[5] from **1** is significantly less impressive than 35–95% in the current study, or 50–70% if the comparison is limited to the same base, KOH. Thus, contrary to the situation with **1** the cleavage and polycondensation reactions of **9** are minimal.

The dibenzyl homologue **5** poses fewer contrasts, with the formation of **6** and **8** directly correlating with **13** and **14**, respectively, from **9**. Both systems gave higher yields of Stevens migration, **6**[13] or **13**, when heated with KOH but greatly predominating Sommelet shifts, **7**[8,9] or **14**, with alkali amides in liquid ammonia. The best material balance in rearranged products also occurred in liquid ammonia with 92–95% from **5**[8,9] and 95% from **9**. However, **10**, which is analogous to **8**, the major Sommelet rearrangement product when *n*-butyllithium was used with **5**, was not detected under comparable conditions, but might account for the low material balance in that reaction. The two benzylic type positions of thenyl groups in **10**, as opposed to the more acidic methine locations in **13** and **14**, account for greater basicity, and thus continued reactivity in the anions derived from **10** which would lead to its own demise. Even less selectivity between **13** and **14** formation was evident with methylsulfinyllithium[15] than with *n*-butyllithium. These data are an aid in selecting between the several options available for detailed reaction pathways.

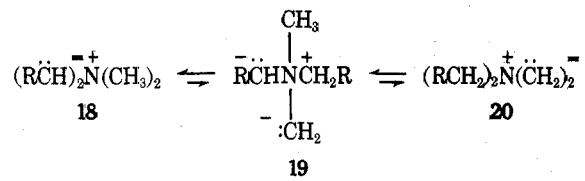
Mechanistically, the attack of base on **9** either displaces a group from nitrogen with the liberated tertiary amine acting as the "anion" equivalent in this pseudohalide substitution, or abstracts a proton. The predominant ylide produced when **9** acts as an acid due to charge support from the ammonium cation depends on resonance stabilization. This favors **16** to the virtual exclusion of **17** because proton exchange between



the two benzyl groups is greatly preferred over conversion to the methyl ylide despite the statistical ratio of available protons of 6:4 for **17**:**16**. However, from the point of reactivity, any **17** which is not rapidly converted to **16** has a higher probability (lower activation energy) of conversion to rearrangement

Table I. Reactions of *N,N*-Di(2-thenyl)dimethylammonium Ions (9) with Bases

Anion	Base	Solvent	Base–salt ratio	Temp, °C	Time, min	% yield 13 + 14	Ratio 13/14
Cl^-	KOH		18.5	180	120	71	3.7
Cl^-	KOH		20.0	160	180	70	4.0
Cl^-	KOH		20.0	130	180	65	3.3
I^-	KOH		17.8	120	240	50	3.2
Cl^-	MeONa	Me_2SO	12.7	25	900	51	1.7
I^-	$NaNH_2$	NH_3	3.8	−60	90	35	0.46
Cl^-	$NaNH_2$	NH_3	2.6	−45	45	95	0.32
CL^-	*n*-BuLi	*n*-C_6H_{14}	2.3	20	30	46	1.7
I^-	$MeSOCH_2Li$	Me_2SO	2.1	−15	120	47	0.88
Cl^-	$MeSOCH_2Li$	Me_2SO	2.3	−10	60	60	0.77



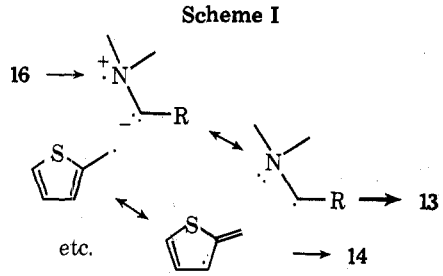
18 19 20

products. Similar reasoning dictates the virtually exclusive formation of **18** rather than **19** or **20**, if 2 mol of a very strong base, higher ratios of a weaker base, or more vigorus reaction conditions favor formation from **16** of its conjugate base.

The isolation of ylides in other reaction systems producing Sommelet[16] and Stevens[17] migration products and the extensive recent studies[18-20] on the latter rearrangement mechanism strongly support ylide participation. However, the subsequent involvement of monoanions derived from ylides[11,21] is less well characterized.

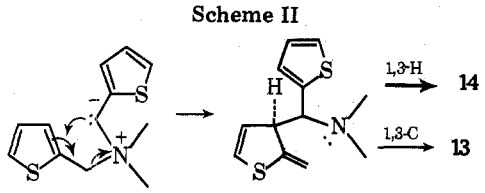
The best understood path for ylide conversion to products involves radical intermediates extensively[20,22] or perhaps exclusively.[19] Applied to **16** (Scheme I), homolytic cleavage

Scheme I



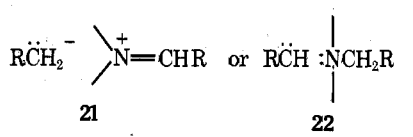
of the nonylidic 2-thenyl–N bond forms a 2-thenyl and ylide radical pair which has a variety of resonance contributors. The Stevens product **13** then is formed when the α-2-thenyl radical couples with its partner α-dimethylamino-α-2-thenyl radical. Most of the other possible products **10–12** and **14** can also be derived from the several locations of maximum unpaired electron density as represented by various resonance contributors but since electron density considerations indicate at least 2:1 predominance to the α–α' coupling, only a form which might produce the Sommelet product is shown as an alternative route in Scheme I. By contrast, support for the Sommelet process via an exo-methylene intermediate has been thoroughly studied by Hauser's group and is covered by extensive reviews.[2,23] Application of this approach to **16** in Scheme II involves a $4\pi + 2\sigma$ electron concerted process to

Scheme II



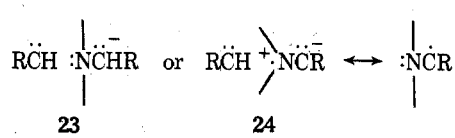
produce the exo-methylene species in a $2_{N-C},3_C$ shift. Subsequent conversion to **14** requires a 1,3-sigmatropic hydrogen migration (or equivalent solvent exchange) route. The alternative 1,3-carbon migration of the bulky carbon moiety attached at the same point as the hydrogen would give **13** but could only become relevant at high temperatures,[18,24] which would agree with the greater conversion to the Stevens product observed with heated reactions (Table I).

Although the anion–ammonium ion pair **21** or carbene–amine pair **22** can be envisaged as intermediates in the con-



21 22

version of **16** to **13** and/or **14**, exchange studies on benzylic systems[14] dictate against **21** while the limited product distribution is not in keeping with a predominant pathway involving a singlet carbene intermediate. The same argument holds for the carbene anion pair **23** possible from **18** but an



23 24

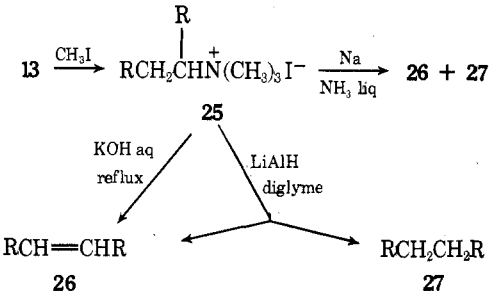
interesting radical anion–radical pair **24** could result from **18**. While it is not completely obvious where intermediates such as **24** would lead, if a tight, short-lived, radical pair as in Scheme I is the principal route to **13** and if Scheme II is used to account for **14**, then a temperature shift from **14** to **13** gives a good qualitative fit of the observed results. In fact a quantitative linear least-squares comparison of log (ratio **13/14**) to $1/T(K)$, using all reactions in which rearrangement occurred, provides $\Delta(\Delta S^{\ddagger})$ of 7.3 ± 0.6 cal deg mol^{-1} and $\Delta(\Delta H^{\ddagger})$ of 2.0 ± 0.2 kcal mol^{-1}. The remarkably small scatter despite the wide variety of bases, base/salt concentration ratios, anion, and solvents employed is indicative of a common intermediate generated by attack of base on **9**, for which we propose **16**, with the subsequent control of the destiny in **13** or **14** being essentially independent of variables other than temperature. The entropy term is reasonable for differences in an unimolecular process, the structurally more flexible Stevens form with the anticipated larger two particle activation volume being favored. The calculated equivalence temperature (yield **13** = yield **14**) of 270 ± 10 K is consistent with the observations.

Part B

The determination of rearrangement products was accomplished by separation and physical analysis, reactions of the material mixture to generate known compounds, and independent syntheses of predicted structures. This extended approach was essential because the rearranged products could

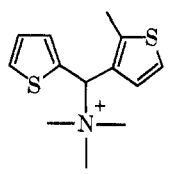
not be separated by conventional distillation, but pure analytical samples were obtained by preparative gas–liquid chromatography (GLC), by thin layer chromatography, and by absorption chromatography on silica gel.

Amine **13** was eluted faster than **14** in all types of chromatography. It was a liquid, which upon treatment with excess methyl iodide gave the corresponding quaternary salt **25.** This



salt upon treatment with hot aqueous potassium hydroxide gave 1,2-di(2′-thienyl)ethylene (**26**) and when treated with lithium aluminum hydride 1,2-di(2′-thienyl)ethane (**27**) together with **13** and **26.** Reduction of **25** with sodium in liquid ammonia yielded **26** and **27.** The identification of **26** was based upon its mass (M^+ at *m/e* 192), ^1H NMR, and ir (ν_{al-C-H} at 3020 cm^{-1}, no $\nu_{al-C=C}$ due to trans isomerism, δ_{oop} 1-CH at 851, 827, and 697 cm^{-1} for 2-substituted[25] thiophene) spectra and its melting point.[26] The saturated compound **27** had physical properties (GLC and MS) identical with those of a sample prepared via a Wolff–Kishner reduction of the corresponding ketone with hydrazine and potassium hydroxide.[5]

A quaternary salt **28** could also be obtained from the Sommelet amine **14** with methyl iodide but **28** did not react with



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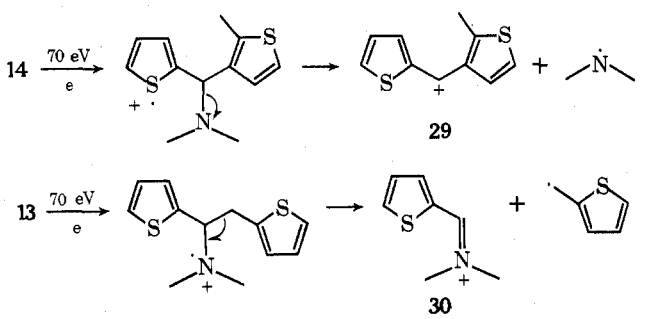
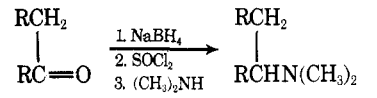
any of the reagents used on **25.** Amine **14** was a low-melting (mp 40–42 °C), colorless solid, whose ^1H NMR at 60 MHz showed the presence of three singlets at δ 2.16 (6 H), 2.41 (3 H), and 4.54 ppm (1 H), the integration values and chemical shifts of which agree with the presence of two methyl groups on nitrogen,[12] a methyl group on the 2 position of thiophene,[27] and a methine attached to two (hetero)aromatic rings and a nitrogen atom.[12] Unfortunately, the "aromatic" region of the spectrum was not adequately resolved to allow detailed NMR evaluation. However, by use of the shift reagent[28] Eu(fod)$_3$, this region was well resolved over a 2-ppm range, giving a spectrum in agreement with **14.**

The mass spectrum of **14** was dominated by the peak at *m/e* 193 (**29**), corresponding to the loss of the dimethylamino



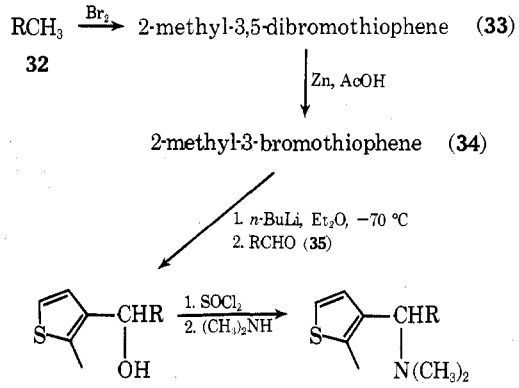
group; this behavior differentiated the amine sharply from the isomer **13,** whose parent ion lost a thenyl group with great ease to give the base peak at *m/e* 140 (**30**).



The structures of the rearranged amines from **9** were confirmed by preparing the postulated products by independent routes. Ketone **31** was reduced with sodium borohydride to the alcohol, which was transformed into its chloride by the action of thionyl chloride. Reaction of this chloride with dimethylamine gave a poor yield of **13,** identical in every respect with the corresponding amine separated from the reaction mixture on rearrangement of **9.**

Production of **14** required an elaborate multistep synthesis, Scheme III. 2-Methylthiophene (**32**) was brominated to

Scheme III



3,5-dibromo-2-methylthiophene (**33**), then reduced with zinc to 3-bromo-2-methylthiophene (**34**).[29] The bromine of **34** was exchanged with lithium and then condensed with 2-thenaldehyde (**35**) to the alcohol **36.** In turn **36** was converted to its chloride with thionyl chloride before reaction with dimethylamine to give the desired amine **14.** Thus, cumbersome synthesis with very poor conversions was necessary to arrive at the same product which the anionic rearrangement of **9** produced in excellent and controllable yields. The easy access to a 2,3-disubstituted thiophene is particularly remarkable. The propensity of **9** to yield the Sommelet rearrangement product **14** contrasts markedly with the earlier heteronuclear cases,[3–5] particularly since cleavage and polycondensation are minimal.

In order to be absolutely certain that other possible products were not present in small amounts which might be obscured by overlapping peaks in GLC analyses of **13** and **14,** amines **11, 12,** and **41** were prepared (Scheme IV) and their

Scheme IV

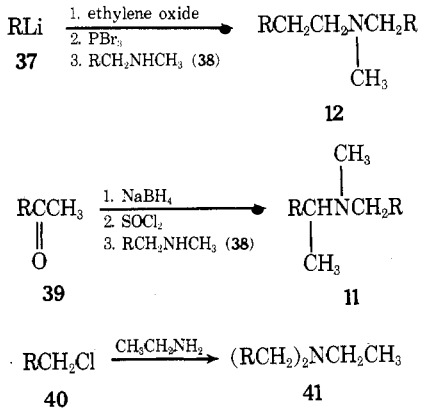


Table II. GLC Properties[a] of Amines Related to the Reactions of 9 with Bases

Amine	Column 1[b]	Column 2[c] 100 °C	Column 2[c] 180 °C	Column 3[d]
N,N-Diphenylamine				1.00
N,N-Dibenzylmethylamine			1.00	
N-[α-(2′-Thenyl)-2-thenyl]dimethylamine (**13**)	1.46		1.77	1.70
N-[α-(2′-Thienyl)-2-(3-thenyl)]dimethylamine (**14**)	1.00		1.19	1.42
N-(2-Thenyl)-*N*-methyl-β-(2′-thienethyl)amine (**12**)	2.06		2.40	2.01
N-(2-Thenyl)-*N*-methyl-α-(2′-thienethyl)amine (**11**)	1.61		1.51	1.79
N,N-Di(2-thenyl)methylamine (**42**)			1.89	1.37
N-(2-Thenyl)dimethylamine (**15**)		1.78		

[a] Retention time ratios vs. a known standard are given. [b] 2 m by 0.25 mm packed with Igepal CO 880 5% on Chromosorb W, 60–80 mesh, 180 °C, flow rate 6–8 ml/min nitrogen. [c] 2 m by 0.25 mm, packed with FFAP 4% on Chromosorb W, 80–100 mesh, 100 or 180 °C, flow rate 25–30 ml/min nitrogen. [d] 2 m by 0.25 mm, packed with SF96 5% on Chromosorb P, 80–100 mesh, 180 °C, flow rate 30–35 ml/min nitrogen.

mass spectra recorded. No evidence for any of these compounds was found in the GLC–MS analysis for the several experiments of Table I.

Experimental Section

Chemicals. Thiophene, dimethylamine, methylamine, ethylene oxide, sodium borohydride, and solvents were purchased from J. T. Baker. Lithium wire, silica gel for absorption and TLC, bromine, thionyl chloride, phosphorus tribromide, lithium aluminum hydride, GLC stationary phases, and inert supports were obtained from C. Erba. 2-Thenoic acid was commercially available from SIO, Italy.

Instrumental Methods. Mass spectra were recorded with a Perkin-Elmer 270 double focusing gas chromatograph–mass spectrometer at 10–70 eV (nominal energy) and ca. 100 μA with GLC and direct (solids) inlets; *m/e* values for each compound, followed by relative abundances, are reported for the ten highest peaks and any other significant ions. Gas–liquid chromatographs (GLC) were obtained with a Perkin-Elmer 900 equipped with a flame ionization detector. Retention time ratios were reproducible to 0.5%, and are compiled for the rearranged amines in Table II together with column packing and conditions used. Yields were determined by using internal standards and precalibrated weight/area responses.

Infrared spectra (ir) were measured on a Perkin-Elmer 21 for neat liquids or KBr pellets of solids, and are reported relative to polystyrene calibration in cm^{-1} with intensities relative to the strongest peak as 100%: strong (s) 100–75%, medium (m) 75–50%, weak (w) 50–25%, very weak (vw) 25–5%. Proton magnetic resonance (^1H NMR) spectra were recorded with a JEOL 60 and a Perkin-Elmer R12B at 60 MHz. Chemical shifts are reported as δ values in parts per million relative to Me_4Si; *J* values are in hertz.

2-Thenaldehyde (35). Using a variant on the procedure of King and Nord,[30] $POCl_3$ (1 mol) was carefully poured into dimethylformamide (1 mol) which gave a red solution. Thiophene (1 mol) was added in one lot. The mixture was kept at room temperature for 4 days before pouring onto ice, making neutral to slightly basic with solid NaOH, and extracting with ether. Distillation of the dried (Na_2SO_4) ether solution gave 66% yield of the aldehyde, bp 83–85 °C (13 Torr).

***N*-(2-Thenyl)dimethylamine (15).** The reaction between dimethylformamide (DMF), formic acid (FA, 80%), and **35** gave practically none of the expected product,[31] but when DMF (0.96 mol) was refluxed with FA (21 ml) and water (20 ml) for 3 h and then the aldehyde was added and refluxed for 6 h, workup of the mixture and distillation gave **15** in 52% yield, based on reacted **35**: bp 71 °C (14 Torr); ir 3050 vw, 2950 m, 2850 s, 2770 s, 1660 m, 1440 m, 1362 vw, 1343 w, 1305 m, 1277 w, 1258 m, 1230 s, 1215 m, 1188 m, 1129 w, 1098 w, 1038 s, 1008 w, 888 m, 855 w, 823 w, 766 m, 710 m, 704 s, 663 cm^{-1} m; ^1H NMR (CCl_4) δ 7.04 (m, 1 H), 6.77 (m, 2 H), 3.53 (s, 2 H), 2.16 (s, 6 H); MS (70 eV) *m/e* 97 (100, $C_5H_5S^+$), 141 (36, M^+), 140 (29), 58 (28, $C_2H_2S^+$), 42 (24, $CH_2{=}N{=}CH_2^+$), 45 (19, $HNMe_2^+$), 53 (17), 98 (16), 39 (15, $C_3H_3^+$), 44 (13, NMe_2^+), 99 (9), 27 (7, $C_2H_3^+$) and 41 (7); doubly charged ion at 70.5, metastable ions at 15.5 (58 → 30) and 66.8 ($M^+ \rightarrow C_5H_5S^+$).

***N,N*-Di(2-thenyl)dimethylammonium Chloride (9a).** A solution of **40**[5] (68 mmol) and **15** (70 mmol) in 50 ml of anhydrous ether was refluxed for 3 h, then left standing overnight before filtering (9.1 g of **9a**). The solution gave some 3.1 g more of **9a** after standing for 5 days. The salt, recrystallized from ethyl acetate–ether and 1-butanol–*n*-hexane, was dried under vacuum (P_2O_5, 0.15 Torr, 100 °C): mp 187–189 °C, white crystals; ir (KBr) 3070 vw, 2980 m, 2910 m, 1750 vw, 1630 vw, 1505 vw, 1480 m, 1440 m, 1425 m, 1382 m, 1360 w, 1333 vw, 1300 vw, 1240 m, 1214 m, 1187 w, 1173 w, 1115 w, 1064 vw, 1043 w, 1008 m, 989 m, 924 w, 862 m, 851 s, 835 s, 806 w, 751 s, 738 s (broad), 725 s, 712 cm^{-1} m; ^1H NMR (D_2O, δ from Me_4Si) 7.65 (m, 2 H), 7.28 (m, 4 H), 4.74 (s, 4 H), and 3.03 (s, 6 H).

2-Thenyl Iodide. To a solution of sodium iodide (114 mmol) in 160 ml of dry acetone was added **40** (98 mmol) dropwise while stirring at 20 °C. A precipitate of NaCl was formed at once. Fifteen minutes after the end of the addition, the decanted solution was used as such. The strongly lachrymatory compound appeared to be very sensitive to air and light (formation of iodine).

***N,N*-Di(2-thenyl)dimethylammonium Iodide (9b).** To a fresh solution of 2-thenyl iodide (98 mmol) in acetone (160 ml) was added **15** (98 mmol); the mixture was refluxed for 90 min while excluding oxygen and light. The yellow precipitate was filtered, washed with dry acetone, and recrystallized from 1-propanol. The iodide, which was not hydroscopic, was vacuum dried as was **9a**, mp 150–152 °C (80%). Extensive drying at 100 °C caused some retro-Menschutkin reaction[32] to occur with production of lachrymatory 2-thenyl iodide.

Alternatively, **9b** was prepared by room temperature reaction of methyl iodide (90 mmol) and *N,N*-di(2-thenyl)methylamine (**42**, 90 mmol, vide infra) in acetonitrile (70 ml) for 15 h. The salt precipitated on dilution of the solution with ether. Recrystallization from 1-propanol gave a slightly yellow crystalline solid: mp 151–152 °C (55%); ir (KBr) 3098 w, 3050 w, 3038 vw, 3005 vw, 2960 w, 2930 w, 2870 vw, 2720 vw, 2340 vw, 1822 vw, 1670 vw, 1600 vw, 1524 w, 1475 s, 1470 s, 1448 s, 1440 s, 1430 s, 1408 m, 1380 w, 1360 vw, 1340 s, 1280 w, 1242 s, 1238 s, 1185 m, 1165 w, 1120 m, 1070 w, 1053 w, 1010 m, 980 m, 941 w, 918 w, 858 s, 844 m, 810 s, 750 s, 715 cm^{-1} s; ^1H NMR ($CDCl_3$) δ 7.48 (m, 2 H), 7.11 (m, 4 H), 5.38 (s, 4 H), and 3.26 (s, 6 H).

General Procedure for the Reaction of Salts 9a and 9b with Bases. The dry salt was treated with the appropriate base under the selected conditions; the reaction mixture was then quenched with cold water and extracted with ether. The ether solution was analyzed by temperature programmed GLC with different columns up to their maximum operating temperature (260–300 °C). The amines were extracted with cold concentrated hydrochloric acid and freed into ether with sodium hydroxide. The neutral and the amine extracts were again checked by GLC, to ascertain that the separation procedure was efficient and did not produce any artifacts. The best GLC conditions for the separations of the amines were then sought and, after addition of a suitable standard (diphenylamine), the quantitative determination was performed. GLC–MS and GLC peak enhancement with authentic samples, prepared by independent routes, allowed preliminary identification of the components of the amine mixture. Rearranged amines were separated collectively by conventional vacuum distillation from the extracts and then isolated individually by preparative GLC and/or absorption chromatography on silica gel (benzene–ethyl acetate, 80/20 v/v). TLC was also of help in the determination of the purity of obtained samples; the R_f values were respectively 0.165 and 0.37 for the Stevens amine **13** and the Sommelet amine **14** on silica gel (benzene–ethyl acetate, 80/20 v/v). Spectroscopic methods (vide supra) were employed for the definitive structural confirmation of the obtained products.

Reaction of 9 with KOH. Pellets of potassium hydroxide (85% titer, 15% H_2O) were crushed into a fine powder out of the contact with air and mixed with the pulverized salt **9** in an Erlenmeyer flask kept at the desired temperature by immersion in an oil bath. When the chosen reaction time elapsed, the mixture was cooled to room temperature and chilled brine was added.

Reaction of 9 with Sodium Methoxide in Me_2SO. A saturated solution of sodium methoxide in anhydrous Me_2SO was taken to the selected temperature, then the solid salt **9** was added in one lot while stirring. The mixture was quenched with ca. four volumes of water.

Reaction of 9 with *n*-Butyllithium. *n*-Butyllithium (ca. 1 M in *n*-hexane) was added dropwise with a syringe to a stirred suspension of the pulverized salt **9** in *n*-hexane with accurate temperature control (exothermic reaction) under argon. The reaction mixture was quenched by pouring it carefully onto crushed ice.

Reaction of 9 with Methylsulfinyllithium. The salt **9** was dissolved in the least amount of anhydrous Me_2SO, the solution was thermostated at the desired temperature, and *n*-butyllithium (ca. 1 M in *n*-hexane) was added slowly while stirring under argon. Alternatively, *n*-butyllithium was added to Me_2SO at −15 °C to give a concentration of about 0.6 atom/l. of Li. This solution was added with due caution while stirring to a saturated solution of **9** at the desired temperature. The reaction mixture was quenched by pouring into four volumes of ice.

Reaction of 9 with $NaNH_2$ in Liquid Ammonia. Ammonia dried by passage through a KOH scrubber was liquefied and sodamide (ca. 1 M) was prepared by addition of Na and a few crystals of anhydrous $FeCl_3$. The pulverized salt **9** was added in one lot to this solution at the desired temperature. The reaction was quenched by addition of an excess of NH_4Cl and dry ether. Ammonia was evaporated and the products were recovered by addition of excess 10% aqueous sodium hydroxide and ether.

2-Thenyl-2′-thienylcarbinol. 2-Thenyl 2′-thienyl ketone (**31**,[5] 11.5 mmol) in methanol (30 ml) was reduced to the alcohol by addition of sodium borohydride (8 g) while stirring at 10 °C during 20 min. The solution was poured into ice, extracted with ether, and dried over sodium sulfate. The alcohol was obtained by distillation: bp 187–189 °C (13 Torr); yield 36%; ir 3450 s, 3100 w, 2980 w, 1790 vw, 1630 vw, 1540 vw, 1446 m, 1397 w, 1362 vw, 1325 w, 1250 m, 1200 w, 1177 w, 1126 w, 1082 m, 1043 s, 855 s, 834 s, 697 cm^{-1} s (broad); MS (70 eV) *m/e* 113 (100, $M^+ - C_5H_5S^+$), 98 (96, M^+ − 2-ThCHO, McLafferty-type rearrangement), 97 (57), 45 (40), 192 (18, $M^+ - H_2O$), 39 (17), 147 (16), 191 (15), 53 (12), 99 (12), 111 (11, 2-ThC≡O$^+$), 115 (10), 114 (9), 58 (8), 69 (8), 100 (7), 193 (6), . . . , 210 (3, M^+).

***N*-[α-(2′-Thenyl)-2-thenyl]dimethylamine (13).** 2-Thenyl-2′-thienylcarbinol (1.5 g) was treated with thionyl chloride (5.5 ml), then the excess reagent carefully evaporated under vacuum. The residue was taken up with *tert*-butyl alcohol and reconcentrated under vacuum. Dimethylamine (10 ml) was added to this crude chloride solution at −10 °C and allowed to warm to room temperature (30 min), and the dimethylamine was evaporated. Acid–base separation followed by distillation gave **13:** bp 113–116 °C (0.15 Torr); yield 11%; ir 3030 vw, 2890 w, 2833 w, 2770 w, 2740 w, 1790 vw, 1590 vw, 1535 vw, 1470 vw, 1438 w, 1425 w, 1356 vw, 1312 vw, 1252 w, 1225 w, 1219 w, 1170 vw, 1150 vw, 1103 vw, 1095 vw, 1086 vw, 1070 vw, 1034 m, 1004 w, 945 vw, 875 vw, 850 m, 822 w, 777 vw, 742 vw, 695 cm^{-1} s (broad); ^1H NMR (CS_2) δ 6.70 (m, 6 H), 3.88 (pseudo-t, 1 H, 6.5 Hz), 3.26 (m, 2 H); MS (70 eV) *m/e* 140 (100, M^+ − 2-ThCH$_2$), 97 (11), 192 (11), 42 (11), 141 (10), 191 (9), 45 (8), 147 (8), 142 (6), 124 (6), . . . , 237 (2, M^+).

2′-Thienyl-2-(3-thenyl)carbinol (36). 2-Methylthiophene, obtained by Wolff–Kishner reduction[33] in 50% yield, was treated with bromine to get **33**,[34] in 57% yield: bp 101–103 °C (15 Torr); MS (70 eV) *m/e* 125 (100), 45 (67), 111 (57), 39 (36), 210 (34, M^+), 97 (33), 193 (30, M^+ − OH·), 85 (29), 73 (29), 147 (26, $M^+ - C_5H_3$·); MS (25 eV) 125 (100), 210 (41, M^+), 126 (27), 193 (19), 192 (18), 111 (17), 99 (9), 194 (9), 85 (8) and 177 (8); doubly charged ions at *m/e* 46.5, 47.5, 87.5, and 88.5.

The dibromo derivative **33** (32.6 g, 125 mmol) was rapidly added to a refluxing solution of water (40 ml), acetic acid (20 ml), and powdered zinc (15 g) to obtain **34**:[29] bp 173–174 °C; yield 49%; ^1H NMR (CCl_4) δ 6.93 (d, 1 H, J = 6 Hz), 6.67 (d, 1 H, *J* = 6 Hz), and 2 33 (s, 3 H); MS (70 eV) *m/e* 96 (100, $C_5H_4S^+$), 45 (29, HCS^+), 178 (25, M^+ + 2), 176 (24, M^+), 53 (20), 177 (14, M^+ + 1), 175 (13, M^+ − 1), 69 (10), 51 (10), 63 (6); MS (20 eV) 96 (100), 176 (52, M^+), 178 (51), 177 (14), 175 (14), 53 (5), and 45 (4). Compound **34** (2.5 g, 14.2 mmol) in anhydrous ether (40 ml) was added dropwise while stirring under argon to a solution of *n*-butyllithium in *n*-hexane (1.75 N, 15.0 mmol) at −60 °C. Ten minutes after completion of the addition the mixture was poured into **35** (3.2 g, 28.6 mmol) at −40 °C. The slurry was stirred at −40 °C under argon for 30 min, then allowed to warm up to room temperature and left standing overnight. The mixture was then poured into aqueous sodium bicarbonate, the organic product extracted with ether, and extracts dried over sodium carbonate. GLC–MS analysis (SF96 5% on Chromosorb W, 160 °C) revealed the presence of 2-thenyl alcohol, **36**, and 2′-thienyl 2-(3-thenyl) ketone with the relative retention times 1.0:2.72:2.99. The whole mixture was then reduced with lithium aluminum hydride at 25 °C; the ketone peak was thus greatly reduced. No further purification nor isolation of the product was attempted owing to the thermal and acid sensitivity of benzhydrol type compounds to ether formation. Mass spectra (70 eV) *m/e* (carbinol) 85 (100, $C_4H_5S^+$), 114 (86, M^+), 97 (77, $C_5H_5S^+$), 45 (67, HCS^+), 113 (36, M^+ − 1), 81 (35), 39 (34, $C_3H_3^+$), 53 (22), 58 (17), and 57 (12); (ketone) 111 (100), 39 (99), 208 (86, M^+), 45 (75), 125 (61), 53 (58), 96 (38), 97 (32), 69 (25), and 193 (23).

***N*-[α-(2′-Thienyl)-2-(3-thenyl)]dimethylamine (14).** Alcohol **36** in ether, cooled to −50 °C, was treated with thionyl chloride (7 ml, *very* slow addition!, precooled to −20 °C). The extremely violent reaction was accompanied by tarring. Five minutes after the end of the addition, the whole mixture was added with extreme caution to dimethylamine (ca. 30 ml) kept at −40 °C. After the addition, the temperature was allowed to rise until all dimethylamine evaporated (20 °C). The residue was taken up with hydrochloric acid and ether, and the aqueous solution was filtered through Celite, then made strongly alkaline with solid KOH. **14** was extracted with ether and distilled: 31 mg, bp 109–113 °C (0.15 Torr); mp 40–41 °C; ir 3070 vw, 2960 m, 2830 m, 2770 m, 2720 m, 1674 w, 1595 vw, 1480 vw, 1420 m, 1405 m, 1360 w, 1298 w, 1233 m, 1190 w, 1143 m, 1108 w, 1075 w, 1038 m, 1005 m, 888 vw, 867 vw, 851 w, 824 m, 764 w, 741 m, 725 m, 695 cm^{-1} s (broad); ^1H NMR (CCl_4) δ 6.90 (m, 5 H), 4.54 (s, 1 H), 2.41 (s, 3 H), and 2.16 (s, 6 H); ^1H NMR [CCl_4 + Eu(fod)$_3$] δ 8.86 (pseudo-d, 1 H, 5.5 Hz), 7.88 (pseudo-s, 1 H), 7.39 (m, 2 H), 7.06 (d of d, 1 H, *J* = 3.5 Hz), 6.29 (s, 1 H), 4.30 (s, 3 H), and 2.91 (s, 6 H); MS (70 eV) *m/e* 193 (100, $M^+ - {}^{\cdot}NMe_2$), 194 (28), 192 (22), 195 (19), 160 (15), 147 (12), 134 (7), 140 (7), 115 (7), 59 (7), . . . , 237 (3, M^+); MS (20 eV) *m/e* 193 (100), 192 (24), 194 (15), 195 (7), 222 (3, M^+ − Me), 237 (2, M^+).

Methoiodides of 13 and 14. Salt **25** was prepared by heating methyl iodide (9 ml) and the amine at 70 °C for 45 min while protecting the mixture from light. The precipitate was washed with ether and recrystallized from acetonitrile: yield 26%; mp 173–175 °C; ^1H NMR (Me_2SO-d_6) δ 7.76 (m, 1 H), 7.27 (m, 3 H), 6.91 (m, 2 H), 5.41 (pseudo-q, 1 H), 3.92 (pseudo-t, 2 H), 3.22 (s, 9 H).

Salt **28** was prepared analogously, yield 30%. It decomposed at 205°; ^1H NMR (Me_2SO-d_6) δ 7.66 (m, 2 H), 7.22 (m, 2 H), 6.96 (m, 1 H), 3.69 (s, 1 H), 3.34 (s, 3 H), 3.22 (s, 9 H).

1,2-Di(2′-thienyl)ethylene (26). Salt **25** (0.4 mmol) in distilled water (4 ml) was heated with potassium hydroxide (1.5 g) at 110 °C for 60 min. Trimethylamine developed at once. Workup and recrystallization from 95% EtOH of the neutral compound obtained gave **26:** mp 126–129 °C; yield 89%; ir 3095 vw, 3063 vw, 3020 vw, 2960 w, 2930 w, 2854 vw, 2430 vw, 1788 vw, 1730 w, 1620 vw, 1595 vw, 1465 vw, 1436 w, 1408 vw, 1384 vw, 1283 m, 1262 w, 1241 vw, 1220 vw, 1184 w, 1165 vw, 1118 vw, 1075 w, 1040 w, 945 s, 852 m, 827 m, 810 w, 744 w, 698 cm^{-1} s; MS (70 eV) *m/e* 192 (100, M^+), 191 (63), 147 (55, M^+ − HCS·), 45 (35, HCS^+), 135 (23, $M^+ - C_2HS$·), 69 (22), 115 (20), 39 (19), 63 (15), and 108 (12); ^1H NMR (CCl_4) δ 7.10 (m, 8 H).

1,2-Di(2′-thienyl)ethane (27). A. Salt **25** (1.2 mmol) and lithium aluminum hydride (0.6 g) in anhydrous diglyme (10 ml) were heated at 100 °C for 18 h while stirring. Moist ether was added to the chilled solution with caution. Isothermal (190 °C) GLC analysis with a 2-m column packed with 5% Apiezon L on Chromosorb P revealed the presence of three compounds (relative retention times, relative area): **27**, (0.52, 38),[35] **13** (1.00, 36), and **26** (1.12, 26). The solvent was then evaporated under vacuum and the organic material taken up with ether.

B. Salt **25** (0.14 g) was added to a solution of sodium (21.6 mmol) in liquid ammonia at −40 °C and allowed to react for 60 min. Workup gave an ether solution containing **27** and **26** in a 15:85 ratio.

***N*-(2-Thenyl)methylamine (38) and *N,N*-Di(2-thenyl)amine (42).** Chloride **40** (98 g, 0.75 mol) was added during 30 min to a stirred solution of ca. 150 ml of methylamine and 94.5 g of sodium hydrogen carbonate at −10 °C. The mixture was allowed to warm to room temperature and then stirred vigorously for 90 min. Vacuum evaporation of the volatile amine followed by conventional acid–base separation and distillation gave 35% of **38** [bp 81–83 °C (13 Torr); ir 3280 m (broad), 3050 m, 2790 m (broad), 1780 vw, 1590 vw, 1532 vw, 1460 m, 1435 s, 1360 m, 1325 m, 1255 w, 1218 m, 1160 m, 1122 s, 1090 s, 1075 m, 1032 m, 955 w, 845 s, 824 s, 768 s, 685 cm^{-1} s; ^1H NMR (CCl_4) δ 7.01 (m, 1 H), 6.74 (m, 2 H), 3.83 (s, 2 H), 2.39 (s, 3 H), and 1.09 (s, 1 H); MS (70 eV) *m/e* 97 (100, $C_5H_5S^+$), 127 (59, M^+), 126 (40), 42 (35, $CH_2{=}N{=}CH_2^+$), 44 (22, NMe_2^+), 98 (18, $C_5H_6S^+$), 45 (18, HCS^+), 53 (10), 39 (9, $C_3H_3^+$), and 43 (7, $CH_2{=}NCH_3^+$)] and 22% of **42** [bp 169 °C (13 Torr); ir 3040 w, 2910 m, 2750 s, 1775 w, 1540 w, 1445 m, 1368 m, 1330 m, 1280 m, 1265 m, 1225 m, 1165 m, 1120 m, 1075 w, 1020 s, 965 m, 850 m, 828 m, 775 m, 750 m, 695 cm^{-1} s (broad); ^1H NMR (CCl_4) δ 7.02 (m, 2 H), 6.78 (m, 4 H), 3.70 (s, 4 H), and 2.27 (s, 3 H); MS (70 eV) *m/e* 97 (100), 42 (17), 98 (17), 126 (16, ThNMe$^+$), 45 (16), 223 (12, M^+), 53 (10), 139 (8, $M^+ - C_4H_4S$·), 39 (8), and 99 (7)].

Methyl 2-Thienyl Ketone (39). This ketone was prepared in 67% yield by iodine-catalyzed acetic anhydride acylation of thiophene:[36] ir 3050 w, 2940 vw, 1650 s, 1500 w, 1410 s, 1350 m, 1265 s, 1225 w, 1080

vw, 1060 w, 1032 w, 1015 w, 965 vw, 920 w, 875 vw, 854 m, 769 vw, 722 cm^{-1} m (broad); MS (70 eV) *m/e* 111 (100, $ThCO^+$), 39 (64, $C_3H_3^+$), 126 (38, M^+), 43 (32, CH_3CO^+), 45 (19, HCS^+) 83 (19, $C_4H_3S^+$), 15 (17), and 38 (10). Doubly charged ions: 55.5 and 41.5. Metastable ion: 98 (126 → 111).

Methyl-2-thienylcarbinol (43). Ketone **39** (0.44 mol) dissolved in 300 ml of ethanol–methanol (1:1 v/v) was treated at room temperature with sodium borohydride (0.66 mol). After 30 min, water and ice were added and the mixture was extracted with ether. Distillation afforded 84% of **43:** bp 98–99 °C (13 Torr) [lit.[37] 91–93 °C (11 Torr)]; ir 3300 s (v broad), 2900 s (broad), 1950 vw, 1884 vw, 1810 vw, 1760 vw, 1670 vw, 1600 m, 1495 s, 1450 s, 1370 s (broad), 1280 s (broad), 1205 m, 1075 s, 1010 s, 900 s, 845 w, 760 s, 700 cm^{-1} s (broad); MS (70 eV) *m/e* 110 (100, $M^+ - H_2O$), 85 (48, $C_4H_6S^+$), 109 (41), 65 (37), 113 (35, $M^+ - CH_3\cdot$), 84 (30, $C_4H_5S^+$), 45 (28), 39 (22), 128 (19, M^+), and 111 (16, $M^+ - OH$).

1-Chloro-1-(2′-thienyl)ethane (44). Alcohol **43** (0.41 mol) was poured slowly into 75 ml of thionyl chloride at −10 °C under stirring. Vacuum evaporation removed most excess $SOCl_2$, then residual reagent was destroyed by careful treatment with ethanol at −10 °C. Distillation gave **44** in 91% yield: bp 70–72 °C (13 Torr); ir 3080 vw, 2960 w, 2820 w, 1790 vw, 1725 vw, 1665 vw, 1620 vw, 1580 w, 1440 s, 1375 s, 1328 w, 1300 m, 1200 s (broad), 1079 m, 1045 s, 1115 s, 995 s, 964 m, 948 m, 900 s, 872 s, 850 s, 830 m, 700 cm^{-1} s (broad); ^1H NMR (neat) δ 7.09 (m, 1 H), 6.84 (m, 2 H), 5.23 (q, 1 H, J = 7 Hz), 1.74 (d, 3 H, J = 7 Hz).

***N*-(2-Thenyl)-*N*-methyl-α-(2′-thienethyl)amine (11).** Chloride **44** (52 mmol) was added to a mixture of **38** (50 mmol), sodium hydrogen carbonate (55 mmol), and water (10 ml) while stirring at room temperature. After 15 min, workup and distillation gave 14% of **11:** bp 162–165 °C (13 Torr); ir 3040 w, 2950 m, 2850 m, 2810 m, 2760 m, 1790 vw, 1660 vw, 1600 vw, 1530 vw, 1455 m, 1427 w, 1365 s, 1328 m, 1316 w, 1277 w, 1235 m, 1205 m, 1160 m, 1117 m, 1075 m, 1049 m, 1038 m, 1004 m, 971 w, 918 w, 892 vw, 853 s, 826 s, 799 w, 748 w, 694 cm^{-1} s (broad); ^1H NMR (CCl_4) δ 7.01 (m, 2 H), 6.76 (m, 4 H), 4.02 (q, 1 H, J = 7 Hz), 3.65 (s, 2 H), 2.11 (s, 3 H), and 1.43 (d, 3 H, J = 7 Hz); MS (70 eV) *m/e* 97 (100), 111 (60), 222 (42), 45 (12), 237 (9, M^+), 110 (10), 98 (8), 42 (7), 223 (7), and 39 (6).

2-(2′-Thienyl)ethanol (45). Ethylene oxide was bubbled through an ether solution of 2-thienyllithium (**37**) (prepared from *n*-butyllithium and thiophene[38] with stirring while cooling so that a gentle reflux was allowed). The thick mixture was diluted with 95% ethanol, then poured onto ice and filtered from Celite. Extraction with ether (Na_2SO_4) and distillation gave **45:** bp 111–115 °C (13 Torr); 50% yield on the basis of starting thiophene; ir 3300 s, 3050 w, 2880 m, 2720 m, 1505 vw, 1470 vw, 1445 w, 1315 vw, 1265 vw, 1238 w, 1185 vw, 1135 w, 1140 s (broad), 847 w, 818 w, 695 cm^{-1} s (broad); ^1H NMR (CCl_4) δ 6.95 (m, 1 H), 6.74 (m, 2 H), 3.68 (t, 2 H, J = 7 Hz), 2.93 (t, 2 H, J = 7 Hz), and 2.83 (s, 1 H, D_2O exchangable); MS (70 eV) *m/e* 97 (100, $C_5H_5S^+$), 128 (39, M^+), 96 (22), 45 (17, HCS^+) and 31 (4, $CH_2{=}OH^+$); MS (10 eV) 128 (100, M^+), 97 (50), 98 (47, $M^+ - CH_2O$, McLafferty rearrangement), and 110 (7, $M^+ - H_2O$).

1-(2′-Thienyl)-2-bromoethane (46). Phosphorus tribromide (80 mmol) was added quickly at 60 °C to a stirred solution of **45** (74 mmol) in 30 ml of carbon tetrachloride. The mixture was kept at 65 °C for 20 min. After cooling to room temperature, water was added, the organic phase was separated, washed with aqueous sodium hydrogen carbonate, dried over Na_2SO_4, and distilled to give 47% of **46:** bp 97–99 °C (14 Torr); ir 3100 w, 2960 w, 1790 vw, 1595 vw, 1533 w, 1440 s, 1360 w, 1320 w, 1274 s, 1234 s, 1210 s, 1165 m, 1110 w, 1074 m, 1035 m, 955 w, 905 w, 848 s, 824 s, 745 w, 690 cm^{-1} s (broad); ^1H NMR (CCl_4) δ 6.97 (m, 1 H), 6.75 (m, 2 H), 3.36 (pseudo-t, 4 H, J = 6 Hz); MS (70 eV) *m/e* 97 (100, $C_5H_5S^+$), 192 (20, M^+), 190 (19), 111 (19, $ThCH_2^+$), 45 (15, HCS^+), 39 (10, $C_3H_3^+$), 77 (8, $C_6H_5^+$), and 110 (7).

***N*-(2-Thenyl)-*N*-methyl-β-(2′-thienethyl)amine (12).** Bromide **46** (15.5 mmol) was added to 15.5 mmol of **38** and kept at 100 °C for 30 min. Workup recovered unreacted **38** and gave 43% of **12:** bp 177–179 °C (13 Torr); ir 3070 w, 2920 m, 2840 m, 2800 m, 1785 vw, 1600 vw, 1535 vw, 1505 vw, 1460 m, 1443 m, 1368 m, 1339 m, 1274 w, 1223 m, 1155 w, 1118 w, 1075 w, 1039 m, 1014 m, 970 vw, 868 w, 850 m, 832 m, 746 w, 690 cm^{-1} s; ^1H NMR (CCl_4) δ 6 63 (m, 6 H), 3.49 (s, 2 H), 2.61 (m, 4 H, J = 6 Hz), and 2.16 (s, 3 H); MS (70 eV) *m/e* 97 (100, $C_5H_5S^+$), 140 (37, $CH_2{=}NMeTh^+$), 45 (12, HCS^+), 53 (10, $C_4H_5^+$), 42 (9), 98 (6), 44 (3), 41 (3), 91 (3), and 84 (2); no molecular ion.

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Registry No.—9a, 58703-12-1; **9b,** 58703-13-2; **11,** 58703-14-3; **12,** 58703-15-4; **13,** 58703-16-5; **14,** 58703-17-6; **15,** 26019-17-0; **25,** 58703-18-7; **26,** 15332-30-6; **27,** 7326-80-9; **28,** 58703-19-8; **31,** 53119-26-9; **33,** 29421-73-6; **34,** 30319-05-2; **35,** 15022-15-8; **36,** 58703-20-1; **37,** 2786-07-4; **38,** 58255-18-8; **39,** 88-15-3; **40,** 765-50-4; **42,** 58703-21-2; **43,** 2309-47-9; **44,** 28612-98-8; **45,** 5402-55-1; **46,** 26478-16-0; 2-thenyl iodide, 58703-22-3; KOH, 1310-58-3; MeONa, 124-41-4; BuLi, 109-72-8; $MeSOCH_2Li$, 10543-35-8; $NaNH_2$, 7782-92-5; 2-thenyl-2′-thienylcarbinol, 58703-23-4; 2-methylthiophene, 554-14-3.

References and Notes

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(2) A. R. Lepley and A. G. Giumanini in "Mechanisms of Molecular Migrations", Vol. 3, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N.Y., 1971, p 297.
(3) R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, 2134 (1968).
(4) A. G. Giumanini and S. Grassi, *Chem. Ind. (London)*, 1567 (1970).
(5) A. G. Giumanini and G. Lercker, *Gazz. Chim. Ital.*, **104,** 415 (1974).
(6) T. Thompson and T. S. Stevens, *J. Chem. Soc.*, 1932 (1932).
(7) G. Wittig, H. Tenhaeff, W. Schoch, and G. Koenig, *Justus Liebigs Ann. Chem.*, **572,** 1 (1951).
(8) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73,** 4122 (1951).
(9) C. R. Hauser, R. M. Manzik, W. R. Brasen, and P. L. Bayless, *J. Org. Chem.*, **20,** 1119 (1955).
(10) M. G. Indzhikyan and A. T. Babazan, *Izv. Akad. Nauk Arm. SSR, Ser. Khim. Nauk*, **10,** 411 (1957); *Chem. Abstr.*, **52,** 16256*f* (1958).
(11) K. P. Klein, D. N. Van Eenam, and C. R. Hauser, *J. Org. Chem.*, **32,** 1155 (1967).
(12) A. R. Lepley and A G. Giumanini, *J. Org. Chem.*, **32,** 1706 (1967).
(13) A. G. Giumanini, *Chem. Ind. (London)*, 1140 (1967).
(14) E. Grovenstein and G. Wentworth, *J. Am. Chem. Soc.*, **89,** 1852 (1967).
(15) K. P. Klein and C. R. Hauser, *J. Org. Chem.*, **31,** 4276 (1966).
(16) W. H. Puterbaugh and C. R Hauser, *J. Am. Chem. Soc.*, **86,** 1105 (1964).
(17) R. W. Jemison, S. Mageswaran, W. D. Ollis, S. E. Potter, A. J. Pretty, and I. O. Sutherland, *Chem. Commun.*, 1201 (1970).
(18) S. H. Pine and J. Cheney, *J. Org. Chem.*, **40,** 870 (1975).
(19) W. D. Ollis, M. Ray, I. O. Sutherland, and G. L. Closs, *J. Chem. Soc., Chem. Commun.*, 543 (1975).
(20) U. H. Dolling, G. L. Closs, A. H. Cohen, and W. D. Ollis, *J. Chem. Soc., Chem. Commun.*, 545 (1975).
(21) A. R. Lepley and A. G. Giumanini, *J. Org. Chem.*, **36,** 1217 (1971).
(22) A. R. Lepley in "Chemically Induced Magnetic Polarization", A. R. Lepley and G. L. Closs, Ed, Wiley-Interscience, New York, N.Y., 1973, p 323.
(23) S. H. Pine, *Org. React.*, **18,** 403 (1970); *J. Chem. Educ.*, **48,** 99 (1971).
(24) J. E. Baldwin, J. E. Brown, and R. W. Cordell, *Chem. Commun.*, 31 (1970).
(25) A. R. Katritzky and A. P. Ambler in "Physical Methods in Heterocyclic Chemistry", Vol. II, A. R. Katritzky, Ed., Academic Press, New York, N.Y., 1963, p 161.
(26) R. E. Miller and F. F. Nord, *J. Org. Chem.*, **16,** 1380 (1951).
(27) S. Gronowitz and B. Gestblom, *Ark. Kemi*, **18,** 513 (1961).
(28) B. C. Mayo, *Chem. Soc. Rev.*, **2,** 49 (1973).
(29) S. Gronowitz, P. Moses, A. B. Hörnfeld, and R. Håkansson, *Ark. Kemi*, **17,** 165 (1961).
(30) W. J. King and F. F. Nord, *J. Org. Chem.*, **13,** 635 (1948).
(31) H. D. Hartough, S. L. Meisel, E. Koft, and S. W. Schick, *J. Am. Chem. Soc.*, **70,** 4013 (1948).
(32) A. G. Giumanini, S. Roveri, and D. Del Mazza, *J. Org. Chem.*, **40,** 1677 (1975).
(33) W. J. King and F. F. Nord, *J. Org. Chem.*, **14,** 638 (1949).
(34) M. G. Reinecke, H. W. Adickes, and C. Pim, *J. Org. Chem.*, **36,** 2690 (1971).
(35) Identified by comparison with authentic compound, available from previous work.[5]
(36) H. D. Hartough and A. I. Kosak, *J. Am. Chem. Soc.*, **68,** 2639 (1946).
(37) D. T. Mowry, M. Renoll, and W. F. Huber, *J. Am. Chem. Soc.*, **68,** 1105 (1946).
(38) G. Van Zyl, R. J. Langerberg, H. H. Tan, and R. N. Schut, *J. Am. Chem. Soc.*, **78,** 1955 (1956).