lithium acetylide (HC≡CH, *n*-BuLi, THF/HMPA, −78 → 0 °C, 8 h) gave the acetylene **39**. Mild acid hydrolysis of the acetal (aqueous Me_2CO, catalyst *p*-TsOH, reflux, 12 h) gave the requisite 11-dodecynal side-chain synthon **40**[20] in 69% overall yield from 10-undecenoic acid.

The enolate of ethyl (*Z*)-2-pentenoate **12** was now generated under our standard conditions. Addition of 11-dodecynal (**40**) (1.0 equiv, −78 °C, THF, 20 min) to this enolate followed by neutral workup led to the 1:1 diastereomeric pair of 3-*E* isomers **41** in 94% yield. Mesylation of this mixture (**41**), using MsCl (1.05 equiv, 1.5 equiv of Et_3N, CH_2Cl_2, 0 °C, 15 min), gave a quantitative yield of the corresponding mesylates which, in common with their precursors, showed infrared ester carbonyl absorption at 1735 cm^{-1} and a strong 970-cm^{-1} peak for the 3-*E* double bond. After a survey of less stereospecific reagents,[21] we found that elimination of MsOH could be readily performed by treatment of the mesylates with KH (2.0 equiv, THF, 0 → 25 °C, 12 h, 80%) to give exclusively the single diene ester **42**.[22] Chemoselective epoxidation was readily accomplished (1.0 equiv of MCPBA, 1.0 equiv of K_2CO_3, CH_2Cl_2, 0 °C, 2 h, 86%) to yield the epoxide **43** where the trans stereochemistry at the epoxide ring could be unambiguously confirmed by 400-MHz NMR (J = 2.4 Hz).[23] Acid-catalyzed cyclization of the epoxy ester **43** (2 N H_2SO_4, THF, reflux, 8 h), possibly with participation of the ester carbonyl,[24] proceeded smoothly to give 86% yield of (±)-litsenolide B_2 (**3b**), having IR and NMR spectra identical with those reported.[25] Semihydrogenation (H_2, 1 atm, 5% Lindlar catalyst, EtOAc, 1 h) of **3b** quantitatively gave (±)-litsenolide A_2 (**3a**),[26] with properties again identical with those described. The overall yield of (±)-litsenolide B_2 from 11-dodecynal (**40**) by this sequence was 56% over five steps.

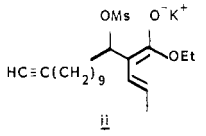
Confirmation of the stereochemical course of these reactions was obtained by an independent sequence leading to litsenolide C_2 from ethyl (*E*)-2-pentenoate (**14**). Condensation of the enolate from **14** as above with tetradecanal gave the diastereomeric pair of *Z* isomers **44** in 94% yield. Mesylation, followed by treatment with KH as described gave a single diene ester **45** having the expected 3-(*Z*) stereochemistry.[27] Osmylation at the disubstituted double bond (0.2 equiv of OsO_4, 1.05 equiv of NMO, 2 equiv of *t*-BuOH, aqueous acetone, 24 h)[28] followed by lactonization (2 N HCl, THF, room temperature, 4 h) gave in 66% yield (±)-litsenolide C_2 (**3c**), having IR, NMR, and mass spectra identical with those reported.[29] It is important to note that the osmylation/lactonization reaction sequence for the preparation of litsenolide C_2 (**3c**) could not be applied in analogous manner to the conversion of diene ester **42** to litsenolide B_2 (**3b**) because preferential osmylation at the acetylene bond took place.[30]

We conclude that the stereochemistry of deconjugative alkylation of dienolate esters is now well delineated, and that this knowledge forms the basis of a new, simple, stereospecific synthesis of AHF units from any suitable aldehyde precursor.[31]

Registry No. (±)-**3a**, 79980-79-3; (±)-**3b**, 79980-80-6; (±)-**3c**, 78340-32-6; **12**, 27805-84-1; **13a**, 3724-66-1; **13b**, 16489-03-5; **13c**, 79918-76-6; **14**, 24410-84-2; **15a**, 27829-70-5; **15b**, 58625-89-1; **15d**, 79918-77-7; **16**, 35066-42-3; **17a**, 54340-71-5; **17b**, 79918-78-8; **18**, 54340-72-6; **19a**, 79918-79-9; **19b**, 79933-08-7; **20**, 79918-80-2; **21a**, 79918-81-3; **21b**, 79918-82-4; **22**, 34993-63-0; **23**, 79918-83-5; **24**, 79918-84-6; **25**, 63860-08-2; **36**, 14811-73-5; **37**, 59014-59-4; **38**, 59014-60-7; **39**, 79918-85-7; **40**, 79918-86-8; **41** (isomer 1), 79918-87-9; **41** (isomer 2), 79918-88-0; **41** mesylate (isomer 1), 79933-09-8; **41** mesylate (isomer 2), 79918-89-1; **42**, 79918-90-4; **43**, 79918-91-5; **44** (isomer 1), 79918-92-6; **44** (isomer 2), 79918-93-7; **44** mesylate (isomer 1), 79918-94-8; **44** mesylate (isomer 2), 79918-95-9; **45**, 79918-96-0; i, 79918-97-1; iii, 79980-81-7; 10-undecenoic acid, 112-38-9; methyl 1,3-dioxolane-2-nonanoate, 79918-98-2; tetradecanal, 124-25-4.

(20) Compound **40**: IR (CCl_4) 3320 (s), 2960–2840 (s), 2710 (m), 1720 cm^{-1}; (s) NMR (400 MHz, $CDCl_3$) δ 1.24–1.70, 1.30 (m, bs, 16 H), 1.94 (t, J = 3 Hz, 1 H), 2.18 (dt, J = 3 Hz, J' = 7 Hz, 2 H), 2.41 (dt, J = 2 Hz, J' = 7 Hz, 2 H), 9.74 (t, J = 2 Hz, 1 H).

(21) In contrast to KH, Et_3N elimination of mesylate was not stereoconvergent, giving alkylidene isomers in the same proportion as the diastereomer ratio in **41**. Thus with KH a discrete enolate ii might be assumed to form which has lost its stereochemical integrity.



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(22) Compound **42**: IR (CCl_4) 3320 (s), 3025 (w), 2930 (s), 2860 (s), 1725 (s), 1650 (w), 970 cm^{-1} (s); NMR (400 MHz, $CDCl_3$) δ 1.20–1.58 (m, 17 H), 1.84 (dd, J = 7.2 Hz, J' = 1.4 Hz, 3 H), 1.94 (t, J = 2 Hz, 1 H), 2.18 (dt, J = 2.5 Hz, J' = 7 Hz, 2 H), 6.03 (qd, J = 6.8 Hz, J' = 16.2 Hz, 1 H), 6.15 (d, J = 15.9 Hz, 1 H), 6.57 (t, J = 7.4 Hz, 1 H).

(23) Booth, J. "Progress in NMR Spectroscopy"; Pergamon Press: Oxford, 1969; Vol. 5, pp 185–6.

(24) Stork, G.; Borch, R. *J. Am. Chem. Soc.* **1964**, *86*, 935.

(25) Compound **3b**: NMR (400 MHz, $CDCl_3$) δ 1.24–1.58, 1.34 (m, d, J = 7 Hz, 18 H), 1.92 (t, J = 2.5 Hz, 1 H), 2.18 (dt, J = 2.5 Hz, J' = 7 Hz, 2 H), 2.40 (m, 2 H), 4.49 (dq, J = 2.2 Hz, J' = 6.8 Hz, 1 H), 4.55 (m, 1 H), 6.98 (dt, J = 2 Hz, J' = 7.7 Hz, 1 H).

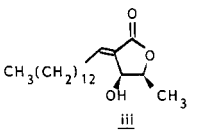
(26) Compound **3a**: NMR (400 MHz, $CDCl_3$) δ 1.18–1.78, 1.33 (m, d, J = 7 Hz, 18 H), 2.03 (bq, J = 7 Hz, 2 H), 2.40 (m, 2 H), 4.32 (dq, J = 2.3 Hz, J' = 6.5 Hz, 1 H), 4.57 (m, 1 H), 4.91–5.04 (m, 2 H), 5.93 (tdd, J = 6.5 Hz, J' = 10.3 Hz, J'' = 10.3 Hz, 1 H), 7.02 (dt, J = 1.7 Hz, J' = 7.8 Hz, 1 H).

(27) Compound **45**: IR (CCl_4) 3020 (m), 2940 (s), 2860 (s), 1725 (s), 1630 cm^{-1} (m); NMR (400 MHz, $CDCl_3$) δ 0.87 (J = 6.7 Hz, 3 H), 1.18–1.49, 1.24 (m, bs, 25 H), 1.51 (dd, J = 2 Hz, J' = 7.1 Hz, 3 H), 2.07 (dt, J = 7.3 Hz, J' = 7.3 Hz, 2 H), 4.17 (q, J = 7 Hz, 2 H), 5.75 (dq, J = 12.1 Hz, 6.5 Hz, 1 H), 5.96 (bd, J = 11.3 Hz, 1 H), 6.78 (t, J = 7.4 Hz, 1 H).

(28) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.

(29) Compound **3c**: NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 6.7 Hz, 3 H), 1.01–1.56, 1.34 (m, d, J = 6.7 Hz, 29 H), 2.39 (m, 2 H), 4.49 (dq, J = 2.1 Hz, J' = 6.4 Hz, 1 H), 4.52 (m, 1 H), 6.97 (dt, J = 1.7 Hz, J' = 7.8 Hz, 1 H).

(30) Application of our epoxidation–lactonization sequence to diene ester **45** leads in 80% yield to (±)-epilitsenolide C_2 (iii), which gave spectroscopic data identical with those reported by Katzenellenbogen (ref 6).



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(31) Support of this research by grants CA 18846 and CA 06787, awarded by the National Cancer Institute, USPH, is gratefully acknowledged.

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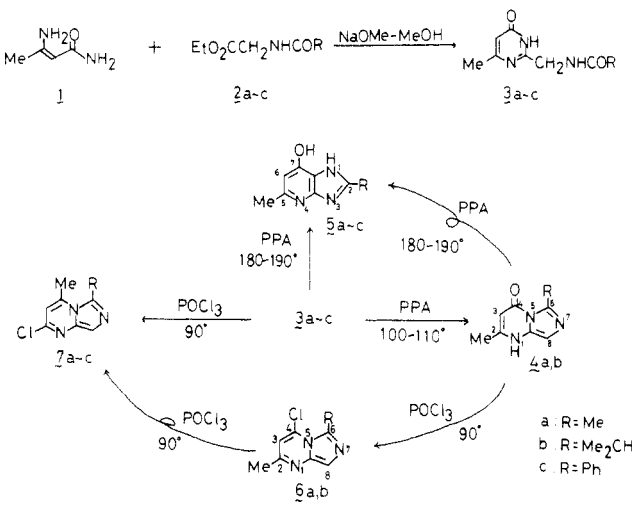
2-[(Acylamino)methyl]-6-methylpyrimidin-4(3*H*)-ones. Novel Precursors for the Synthesis of Imidazo[1,5-*a*]pyrimidines and Imidazo[4,5-*b*]pyridines

Summary: 2-[(Acylamino)methyl]-6-methylpyrimidin-4-(3*H*)-ones, which are synthesized from β-aminocrotonamide and ethyl *N*-acylglycinates, have been found to be novel and versatile precursors for the synthesis of imida-

Scheme I



zo[1,5-*a*]pyrimidines and imidazo[4,5-*b*]pyridines.

Sir: While investigating some potential uses of β-aminocrotonamide (**1**), which is most readily obtained from diketene and ammonia,[1,2] we have studied its reaction with aliphatic and aromatic acid derivatives such as acid anhydride, acid halide, ester, and nitrile to give 2-substituted 6-methylpyrimidin-4(3*H*)-ones.[3] We now report the reaction of **1** with *N*-acylglycinate (**2**) to give a good yield of 2-[(acylamino)methyl]-6-methylpyrimidin-4(3*H*)-one (**3**), which can be a useful intermediate for the synthesis of imidazo[1,5-*a*]pyrimidines (**4**, **6**, **7**) and imidazo[4,5-*b*]-pyridine (**5**).

When ethyl *N*-acetylglycinate (**2a**, 2 molar equiv) was allowed to react with **1** (1 molar equiv) under reflux in the presence of sodium methoxide (5 molar equiv) in absolute methanol for 5 h, 2-[(acetylamino)methyl]-6-methylpyrimidin-4(3*H*)-one (**3a**) was obtained in 71% yield (Scheme I): mp 196–197 °C dec (recrystallized from MeOH–AcOEt); UV (MeOH) λ_{max} 227 nm (log ε 3.91), 270 (3.70); IR (Nujol) 1690, 1660 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 2.16 (s, 3, 6-CH_3), 4.15 (d, 2, J = 6 Hz, 2-CH_2), 6.10 (s, 1, 5-H).[4]

Similarly, the reaction of **1** with ethyl *N*-isobutyrylglycinate (**2b**) and ethyl hippurate (**2c**) yielded 2-[(isobutyrylamino)methyl]-6-methylpyrimidin-4(3*H*)-one (**3b**), mp 199–201 °C dec, and 2-benzamido-6-methylpyrimidin-4(3*H*)-one (**3c**), mp 230–232 °C, in 70 and 79% yields, respectively.

Treatment of the pyrimidinone (**3a**) with polyphosphoric acid (PPA) at 100–110 °C for 3 h gave 2,6-dimethylimidazo-[1,5-*a*]pyrimidin-4(1*H*)-one (**4a**) in 58% yield: mp 200 °C dec (acetone); UV (MeOH) λ_{max} 223 nm (log ε 4.40), 227 (4.38), 261 (3.76), 334 (3.56); IR (KBr) 1683, 1636 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 2.30 (s, 3, 2-CH_3), 2.75 (s, 3, 6-CH_3), 5.17 (s, 1, 3-H), 6.60 (s, 1, 8-H).

In the ^{1}H NMR spectrum of **4a**, the signal due to methyl protons at the 2-position was observed at δ 2.30, and hence the imidazo[1,5-*a*]pyrimidin-2(1*H*)-one, an isomer of **4a**, bearing methyl group at the 4-position was ruled out.[5]

When this reaction was carried out at 180–190 °C for 10.5 h, the imidazopyrimidine (**4a**) was not detected; instead 7-hydroxy-2,5-dimethylimidazo[4,5-*b*]pyridine (**5a**) was obtained in 85% yield: mp >310 °C (H_2O); IR (Nujol) 1620, 1598 cm^{-1}; ^{1}H NMR (CF_3CO_2H) δ 2.80 (s, 3, 5-CH_3), 3.00 (s, 3, 2-CH_3), 7.18 (s, 1, 6-H).

Similarly, **3b** was treated with PPA at 100–110 °C for 5 h to give 6-isopropyl-2-methylimidazo[1,5-*a*]pyrimidin-4(1*H*)-one (**4b**), mp 202–203 °C dec, in 44% yield. Prolonged heating (10 h) of **3b** at the same temperature (100–110 °C) yielded **4b** and the imidazo[4,5-*b*]pyridine **5b**, mp >300 °C, in 31 and 43% yields, respectively. Furthermore, heating of **3b** with PPA at 180–190 °C for 2.5 h gave a 61% yield of **5b** as a sole product. On the other hand, heating of **3c** with PPA at 100–110 °C for 10 h did not give 2-methyl-6-phenylimidazo[1,5-*a*]pyrimidin-4(1*H*)-one (**4c**), but gave 7-hydroxy-5-methyl-2-phenylimidazo[4,5-*b*]pyridine (**5c**),[6] mp 217 °C, in 60% yield. In order to obtain **4c**, we heated compound **3c** with PPA at 70–80 °C for 10 h, but the starting material was recovered.

Compounds **4a** and **4b**, upon heating with PPA at 180–190 °C for 1.5–2 h, were transformed to **5a** and **5b** in 43% and 56% yields, respectively. Therefore, compounds **5a–c** would be formed by rearrangement of **4a–c**.[7] Leonard et al.[8] have reported the synthesis of imidazo[1,5-*a*]-1,3,5-triazinones by cyclization–rearrangement and proposed that the reaction may involve an isocyanate intermediate. Similarly, the rearrangement of **4a–c** to **5a–c** would occur via a ketene intermediate formed by bond cleavage between carbon (C_4) and nitrogen (N_5) of **4a–c**.

When **4a** was treated with phosphorus oxychloride (10-fold excess) at 90 °C for 10 h, 4-chloro-2,6-dimethylimidazo[1,5-*a*]pyrimidine (**6a**) and 2-chloro-4,6-dimethylimidazo[1,5-*a*]pyrimidine (**7a**) were obtained in 59% and 10% yields, respectively. **6a**: mp 191–192 °C (hexane); UV (MeOH) λ_{max} 232 nm log ε 4.65); ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3, 2-CH_3), 2.88 (s, 3, 6-CH_3), 6.23 (s, 1, 3-H), 7.16 (s, 1, 8-H). **7a**: mp 186–188 °C (benzene); UV (MeOH) λ_{max} 230 nm (log ε 4.61); ^{1}H NMR ($CDCl_3$) δ 2.77 (s, 3, 4-CH_3), 2.88 (s, 3, 6-CH_3), 6.20 (s, 1, 3-H), 7.28 (s, 1, 8-H). In the ^{1}H NMR spectrum of **6a**, the signal due to methyl protons at the 2-position was observed at δ 2.37, whereas that of **7a**, which would be affected by the imidazole ring, was observed at lower field (δ 2.77).

Similarly, **4b** was heated with phosphorus oxychloride at 90 °C for 40 min to give 4-chloro-6-isopropyl-2-methylimidazo[1,5-*a*]pyrimidine (**6b**) in 51% yield: mp 73–74 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3, 2-CH_3). Prolonged heating (5 h) at the same temperature gave **6b**

(1) Chick, F.; Wilsmore, N. T. M. *J. Chem. Soc.* **1910**, 97, 1978.
(2) Kato, T.; Yamanaka, H.; Shibata, T. *Tetrahedron* **1967**, 23, 2965.
(3) For a review on the reaction of β-aminocrotonamide (1) to give N-heterocycles, see: Kato, T.; Katagiri, N.; Daneshtalab, M. *Heterocycles* **1975**, 3, 413.
(4) Correct elemental analyses were obtained for all new compounds.
(5) It is reported that in the ^{1}H NMR spectrum (Me_2SO-d_6) of 2-methylimidazo[1,5-*a*]pyrimidin-4(1*H*)-one-8-carboxamide, the signal due to methyl protons at the 2-position is observed at δ 2.30: Novinson, T.; O'Brien, D. E.; Robins, R. K. *J. Heterocycl. Chem.* **1974**, 11, 873. Furthermore, the ^{1}H NMR spectrum of 6-isopropyl-4-methylimidazo[1,5-*a*]pyrimidin-2(1*H*)-one, prepared by hydrolysis of compound **7b** with hydrochloric acid, shows a singlet due to the methyl protons at the 4-position at δ 2.67.
(6) Chlorination of **5c** with phosphorus oxychloride, followed by reduction with hydrazide hydrate gave 5-methyl-2-phenylimidazo[4,5-*b*]-pyridine, which was identical with an authentic sample prepared according to the literature: Garmaise, D. L.; Komlossy, J. *J. Org. Chem.* **1964**, *29*, 3403.
(7) Compounds **4a,b** are regarded as nitrogen bridgehead compounds, and **5a–c** would be formed by rearrangement of the acyl group (C_4-carbonyl) to carbon (C_8) from nitrogen (N_5). Such a rearrangement had to be considered in view of the reported transformation of pyrido[1,2-*a*]pyrimidine to 1,8-naphthyridine: Hermecz, I.; Mészaros, Z.; Debreczy, L. V.; Horvath, A.; Horvath, G.; -Chsakvari, M. P. *J. Chem. Soc., Perkin Trans. 1*, **1977**, 789.
(8) Holtwick, J. B.; Golankiewicz, B.; Holmes, B. N.; Leonard N. J. *J. Org. Chem.* **1979**, 44, 3835.

and 2-chloro-6-isopropyl-4-methylimidazo[1,5-*a*]pyrimidine (**7b**) in 22% and 47% yield, respectively. **7b**: mp 88–89 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 2.82 (s, 3, 4-CH_3). Heating of **4b** for 18 h gave **7b** in 67% yield.

Compound **6b**, on treatment with phosphorus oxychloride at 90 °C for 50 h, was transformed to **7b** in 65% yield.[9]

When **3a–c** were heated with phosphorus oxychloride at 90 °C for 3 h, compounds **7a–c** were obtained in good yields: **7a** (73%), **7b** (75%), **7c** (75%). **7c**: mp 189–190 °C (benzene); ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3, 4-CH_3).[10]

Although a number of purine analogues have been synthesized, only few references are available concerning the synthesis of imidazo[1,5-*a*]pyrimidines.[4,11,12] All of them have been synthesized from imidazole derivatives. The merit of our method is that appropriate substituents can be introduced at the 6- and 8-positions of imidazo-[1,5-*a*]pyrimidines by using various N-acylated amino acid esters, and further investigations are in progress.[13]

Acknowledgment. A part of the expense for this work was defrayed by the Grant-in-Aid for Scientific Research of the Ministry of Education, which is gratefully acknowledged. Thanks are also due to Mrs. C. Koyanagi of the Central Analyses Room of this institute for elemental analyses.

Registry No. 1, 15846-25-0; **2a**, 1906-82-7; **2b**, 31766-30-0; **2c**, 1499-53-2; **3a**, 79898-99-0; **3b**, 79899-00-6; **3c**, 50850-18-5; **4a**, 79899-01-7; **4b**, 79899-02-8; **5a**, 79899-03-9; **5b**, 79899-04-0; **5c**, 79899-05-1; **6a**, 79899-06-2; **6b**, 79899-07-3; **7a**, 79899-08-4; **7b**, 79899-09-5; **7c**, 79899-10-8.

(9) The formation of **7a,b** from **6a,b** involves the ring transformation; that is, the first stage might be the bond cleavage between the nitrogen (N_5) and carbon (C_8) of **6a,b** to give the 2-substituted pyrimidine intermediate which recyclizes to **7a,b**. Details of the reaction mechanism will be discussed in our future report.

(10) The signal due to methyl group at the 4-position is shifted at higher field owing to benzene ring.

(11) Guerret, P.; Imbach, J.-L.; Jacquier, R.; Martin, P.; Maury, G. *Bull. Soc. Chim. Fr.* **1971**, 1031.

(12) Guerret, P.; Jacquier, R.; Maury, G. *Bull. Soc. Chim. Fr.* **1972**, 2481.

(13) We have observed that ester of *N*-acylalanine (or phenylalanine) reacts with 1 to give the pyrimidine-4(3*H*)-one which, on treatment with PPA or phosphorus oxychloride, is transformed to imidazo[1,5-*a*]pyrimidine.

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The Nucleophilicity of Nitranions

Summary: The nucleophilicities of carbazole, phenothiazine, and diphenylamine nitranions toward benzyl and *n*-butyl halides in dimethyl sulfoxide solution have been found to be 30–500 times less than those of carbanions of similar structure and equal basicity, depending on the substrate.

Sir: Although the alkylation of nitranions is important in synthetic chemistry and biochemistry, quantitative measurement of the nucleophilicity of these anions appears to be limited to a study of the reactions of the conjugate bases of succinimide, phthalimide, benzenesulfonamide, and *N*-methyl- and *N*-phenylbenzenesulfonamides toward methyl iodide in methanol.[1] It was concluded from this study that methoxide ion in methanol has a nucleophilicity about 50-fold less than a nitranion of the same basicity. On the other hand, comparison of the rate data for phthalimide ion with that for phenoxide ion, which have about the same basicity in MeOH (the pK_a values of their conjugate acids are 14.5[1] and 14.2,[2] respectively, in MeOH), indicates that the nitranion is slightly *less* reactive. (The n_{MeI} values are 5.4 and 5.75, respectively.[3]) Recently we have used Brønsted-type plots to compare the nucleophilicity of thianions, oxanions, and carbanions of the same basicity reacting by S_N2 pathways with alkyl halides in dimethyl sulfoxide solution.[4] This investigation has now been extended to nitranions.

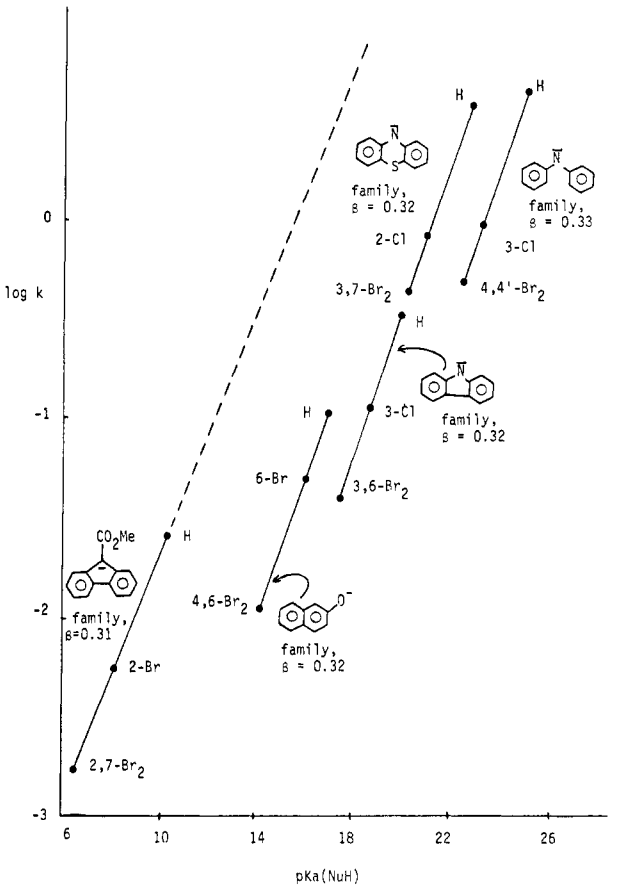

Figure 1. Plots of the log of the second-order rate constants for the reactions of substituted 9-(methoxycarbonyl)fluorenyl anions, 2-naphthoxide anions, carbazole anions, phenothiazine anions, and diphenylamine anions with benzyl chloride in Me_2SO at 25 °C vs. the pK_a values of their conjugate acids in Me_2SO.

Rates of reactions with benzyl chloride in Me_2SO solution were measured for nitranions derived from carbazoles, phenothiazines, and diphenylamines. The results are compared in Figure 1 with those for remotely substituted 9-(methoxycarbonyl)fluorenyl carbanions (9-CO_2Me-Fl$^-$) and 2-naphthoxide ions (NpO$^-$). Examination of Figure 1 reveals three noteworthy features: (1) the phenothiazine line is essentially an extension of the carbazole line, and the diphenylamine line is displaced to the right of the carbazole–phenothiazine line, (2) the slopes of the carbanion, oxanion, and nitranion lines are nearly the same, and (3) the nitranion lines are displaced to the right of the carbanion and oxanion lines.

(1) Bunnett, J. F.; Beale, J. H. *J. Org. Chem.* **1971**, *36*, 1659–1661.
(2) Rochester, C. H.; Rossall, B. *Trans. Faraday Soc.* **1968**, *65*, 1004.
(3) Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319–326.
(4) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1981**, *46*, 3570, 3571.

0022-3263/82/1947-0169$01.25/0