(2 m, 2 H, ArCHCHCN); (100 MHz, $CDCl_3/Me_2SO$-d_6/D_2O) δ 4.70 and 4.32 (AB q, 2 H, ArCHCHCN, J = 4.0 Hz); ^{13}C NMR ($CDCl_3/Me_2SO$-d_6) 141.4, 132.4, 129.3, 127.8, 127.1, 126.4, 119.5, 119.3, 116.9, 114.5, 113.2, 55.23, 46.1 ppm.

Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.74; H, 5.54; N, 17.73.

Tetrahydroquinoxalines **4b–m** were prepared analogously.

2-Cyano-3-phenylquinoxaline (5). A suspension of 1.0 g (4.3 mmol) of **4a**, 1.75 g (8.1 mmol) of mercuric oxide, and 100 mL of absolute EtOH was stirred at reflux temperature for 1.25 h. The reaction mixture was cooled and filtered through Celite. The filtrate was concentrated in vacuo to give a reddish brown oil which was chromatographed first on silica gel ($CHCl_3$) and then on alumina (hexanes/$CHCl_3$ 1:1) to afford 630 mg (64%) of **5** as colorless plates: mp 160–163 °C (lit.[9] mp 163 °C); ^1H NMR (Me_2SO-d_6) δ 8.50–7.42 (m, Ar H).

2-Carboxamido-3-phenylquinoxaline (6). A mixture of 7.0 g (29.8 mmol) of **4a**, 7 g (80.5 mmol) of activated MnO_2, and 500 mL of toluene was stirred at 100 °C under a nitrogen atmosphere for 36 h. The reaction mixture was allowed to cool to ambient temperature, diluted with $CHCl_3$, and filtered through Celite. The filtrate was concentrated under reduced pressure to afford a colorless solid which was recrystallized from aqueous EtOH: yield 6.1 g (82%); mp 198–199 °C (lit.[11] mp 198–199 °C); IR (KBr) 3360, 3175, 1655 cm^{-1}; ^1H NMR ($CDCl_3/Me_2SO$-d_6) δ 8.10–7.20 (m, Ar H).

3-Phenyl-1,2,3,4-tetrahydroquinoxalin-2-one (8). A solution of 900 mg (5.3 mmol) of 1,1-dicyano-2-phenyloxirane,[15] 350 mg (3.1 mmol) of *o*-phenylenediamine, and 10 mL of absolute EtOH was stirred at reflux temperature under a nitrogen atmosphere for 4 h. The reaction mixture was cooled, and the resulting precipitate was collected and recrystallized from EtOH to provide 420 mg (60%) of **8** as a dark red solid: mp 196–197 °C (lit.[16] mp 201–203 °C); IR (KBr) 3300, 1660, 1595, 1500 cm^{-1}; ^1H NMR ($CDCl_3/Me_2SO$-d_6) δ 7.37–7.17 (m, 5 H, Ar H), 6.80–6.58 (m, 4 H, Ar H), 6.32–6.18 (m, 2 H, 2 NH), 4.45 (m, 1 H, PhCHN).

Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.99; H, 5.38; N, 12.49. Found: C, 74.77; H, 5.23; N, 12.35.

Registry No. 1, 54607-00-0; *cis*-**2a**, 33984-96-2; *trans*-**2a**, 33984-95-1; *cis*-**2f**, 73377-89-6; *trans*-**2f**, 73377-90-9; *cis*-**2k**, 33984-92-8; *trans*-**2k**, 33984-91-7; **3a**, 25855-20-3; **3b**, 71897-07-9; **3c**, 25187-18-2; **3d**, 49634-78-8; **4a**, 73377-91-0; **4b**, 73377-92-1; **4c**, 6-methyl derivative, 73377-93-2; **4c**, 7-methyl derivative, 73378-01-5; **4d**, 73378-32-2; **4e**, 73378-31-1; **4f**, 73377-94-3; **4g**, 73377-95-4; **4h**, 6-methyl derivative, 73377-96-5; **4h**, 7-methyl derivative, 73378-02-6; **4i**, 73378-30-0; **4j**, 73378-29-7; **4k**, 73377-97-6; **4l**, 73384-19-7; **4m**, 6-methyl derivative, 73377-98-7; **4m**, 7-methyl derivative, 73378-03-7; **5**, 59393-45-2; **6**, 73377-99-8; **7**, 33512-02-6; **8**, 23465-73-8; *o*-phenylenediamine, 95-54-5; 3-phenyl-2-(*p*-tolylsulfonyl)-1,2,3,4-tetrahydroquinoxaline, 73378-00-4; 4,5-dimethyl-*o*-phenylenediamine, 3171-45-7; 4-methyl-*o*-phenylenediamine, 496-72-0; 4-chloro-*o*-phenylenediamine, 95-83-0; 4-nitro-*o*-phenylenediamine, 99-56-9.

Supplementary Material Available: NMR and IR spectra and analytical data for quinoxalines and tetrahydroquinoxalines (6 pages). Ordering information is given on any current masthead page.

Conversion of Primary Amines into Nitrate Esters

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Received December 14, 1979

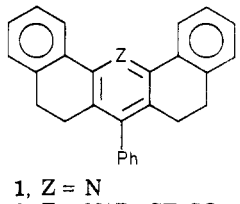
Two classical methods have been used for the preparation of nitrate esters: nitric acid esterification of the appropriate alcohol and treatment of alkyl halides with silver nitrate.[1] Recently, increased interest in these compounds has resulted in improvements in the direct esterification[2,3] and the use of mercury(I) nitrate in the preparation from alkyl halides.[4]

A general method for the conversion of amines into nitrate esters was lacking until recently. In 1970-1971, Wudl published two preliminary communications[5,6] on the conversion of amines into nitrate esters: one involved preliminary silylation[5] and the other reported four examples of which two gave yields of only 20%. No further details of this work have appeared; however, Barton and Narang[7] have shown that in the presence of excess amidine base at −78 °C, N_2O_4 can convert primary or secondary alkyl primary amines into the corresponding alkyl nitrates in good yield; the reaction proceeds with predominant retention of configuration.

We have shown[8] that the conversion of primary amines into pyridinium salts by pyryliums can be utilized as the first step in a general two-stage transformation of amino into other functionality. The displacement of the pyridinium N substituent can be carried out either by the gegen anion or by an added nucleophile. We now extend both these procedures to give nitrate esters.

Nitrate Esters by Thermolysis. 1,3,5-Triphenylpent-2-ene-1,5-dione[9] is converted by nitric acid into 2,4,6-triphenylpyrylium nitrate[10] (70%) which reacts readily with a series of alkyl- and benzylamines to give the corresponding 1-substituted 2,4,6-triphenylpyridinium nitrates (Table I); the structures of these salts are supported by their spectral features.[11] On thermolysis of these salts (Table I), using triphenylpyridine where necessary as flux, at 180–230 °C under reduced pressure, the alkyl nitrate distilled over with purity >97% as shown by ^1H and ^{13}C NMR.[11] The yields averaged 77% for the first step and 66% for the second step.

Formation of Nitrate Esters in Solution. Although mononitrates are thermally rather stable in the absence of impurities such as nitrites and nitric acid,[1] the preceding method is clearly not suitable for large-scale work or for the preparation of high molecular weight nitrates or polynitrates. Hence we sought a method in solution. 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]acridine (1) is a



1, Z = N
2, Z = N^+R, $CF_3SO_3^-$

far better leaving group than 2,4,6-triphenylpyridine.[12] We

(1) R. Boschan, R. T. Merrow, and R. W. van Dolah, *Chem. Rev.*, **55**, 485 (1955).
(2) C. D. Marken, C. E. Kristofferson, M. M. Rolond, A. P. Manzara, and M. W. Barnes, *Synthesis*, 484 (1977).
(3) G. A. Olah, S. C. Narang, R. L. Pearson, and C. A. Cupas, *Synthesis*, 452 (1978).
(4) A. McKillop and M. E. Ford, *Tetrahedron*, **30**, 2467 (1974).
(5) F. Wudl and T. B. K. Lee, *J. Chem. Soc. D*, 490 (1970).
(6) F. Wudl and T. B. K. Lee, *J. Am. Chem. Soc.*, **93**, 271 (1971).
(7) D. H. R. Barton and S. C. Narang, *J. Chem. Soc., Perkin Trans. 1*, 1114 (1977).
(8) A. R. Katritzky, *Tetrahedron Reports*, in press.
(9) R. Lombard and J. P. Stephan, *Bull. Soc. Chim. Fr.*, 1458 (1958).
(10) C. Gastaldi, *Gazz. Chim. Ital.*, **2**, 289 (1921).
(11) See paragraph on Supplementary Material at end of paper.
(12) A. R. Katritzky and S. S. Thind, *J. Chem. Soc., Perkin Trans. 1*, in press.

0022-3263/80/1945-2515$01.00/0

Table I. Preparation and Thermolysis of N-Substituted 2,4,6-Triphenylpyridinium Nitrates

N substituent	triphenylpyridinium nitrates[a,b] yield, %	mp, °C	thermolysis conditions temp, °C	pressure, mm	time, h	$RONO_2$ yield, %[c]	bp, °C	lit. bp, °C (mm)	ref
n-butyl	83	202-203	250	760	3	50	115-120	130-131 (760)	*d*
n-hexyl	85	224-227	230	15	3	68	75-80	66-70 (12)	*d*
benzyl	70	182-184	200	20	2	85	108-110	101-104 (12)	*d*
p-methylbenzyl	90	109-112	180	10	2	73	115-118	44-49 (0.015)	*e*
p-chlorobenzyl	86	124-126	180	7	3	60	108	109 (7)	*e*
phenyl	50	271-275							

[a] All from ethanol-ether. [b] Satisfactory C, H, N analyses reported. [c] Identified by IR and NMR spectra. [d] F. L. M. Pattison and G. M. Brown, *Can. J. Chem.*, 34, 879 (1956). [e] S. D. Ross, E. R. Coburn, and M. Finkelstein, *J. Org. Chem.*, 33, 585 (1968).

Table II. 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium Trifluoromethanesulfonates (2). Preparation and Conversion to Alkyl Nitrates

N substituent	2 yield,[a] %	mp, °C	yield of $RONO_2$, %
n-octyl	91[b]	147-148[c]	71
n-undecyl	92[d]	157-158[e]	72
n-dodecyl	91[d,f]	155-156	68
n-hexadecyl	92[b,g]	160	>90[h]

[a] All compounds formed yellow prisms. [b] From EtOH. [c] Mp 147-148 °C previously reported by Thind.[13] [d] Analytically pure without recrystallization. [e] Mp 157-158 °C, previously prepared by A. M. El-Mowafy (unpublished results). [f] Anal. Calcd for $C_{40}H_{46}F_3NO_3S$: C, 70.9; H, 6.9; N, 2.1. Found: C, 70.7; H, 7.0; N, 2.1. [g] Anal. Calcd for $C_{44}H_{54}F_3NO_3S$: C, 72.0; H, 7.4; N, 1.9. Found: C, 71.8; H, 7.5; N, 2.0. [h] Yield estimated by ^{13}C NMR.

prepared 1-substituted 5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium trifluoromethanesulfonates (**2**) from the corresponding amines and 5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]xanthylium trifluoromethanesulfonate[13] and reacted them with benzyltrimethylammonium nitrate in refluxing dioxane to give the alkyl nitrates[11] (Table II). The yields in the first and second steps averaged 82% and 70%, respectively.

Experimental Section

IR and NMR spectra were measured with Perkin-Elmer 257 and R12 instruments, respectively (Me_4Si as internal standard). Melting points (uncorrected) were determined on a Kofler hot-stage apparatus.

***N*-Alkylpyridinium Nitrates. General Procedure.** 2,4,6-Triphenylpyrylium nitrate (10 mmol) dried at 20 °C/0.5 mm and the appropriate amine (12 mmol) were stirred for 12 h in dry (Na) Et_2O at 20 °C. The precipitate was filtered off, washed with Et_2O (3 × 10 mL), and recrystallized from EtOH–Et_2O (Table I).

For 1-phenyl-2,4,6-triphenylpyridinium nitrate a similar procedure was used except that EtOH was used as a solvent at 100 °C and the product was precipitated by adding Et_2O after cooling.

Thermolysis of Triphenylpyridinium Nitrates. The dry (20 °C (0.5 mm) for 4 h) N-substituted triphenylpyridinium nitrate (3 g) was heated under the conditions shown in Table I. If the melting point of the pyridinium salt exceeded 130 °C, 2,4,6-triphenylpyridine (3 g) was used as flux.

***N*-Alkylpyridinium Trifluoromethanesulfonates.[11] Method A.** 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]xanthylium trifluoromethanesulfonate (2.5 g, 5 mmol) was stirred with the amine (5 mmol) in absolute EtOH (10 mL) and Et_2O (20 mL) at 20 °C for 1.5 h. The crystalline solid was filtered off and recrystallized from absolute EtOH.

Method B. The pyrylium trifluoromethanesulfonate (5.1 g, 0.01 mol) and the amine (0.02 mol) in dry (Na) Et_2O (80 mL) were stirred for 12 h at 20 °C. The precipitate (5.28 g) was filtered off and washed with Et_2O (3 × 10 mL).

Benzyltrimethylammonium Nitrate. Benzyltrimethylammonium hydroxide (40% in MeOH, 11 mL, 26 mmol) and nitric acid (1.6 mL) were stirred for 15 min. Benzene was added (30 mL) and the solvent removed at 100 °C/15 mm. The resulting hygroscopic solid, mp 152–157 °C (lit.[14] mp 151–160 °C), 5.2 g (95%), was kept under dry dioxane.

Metathesis of *N*-Alkylpyridinium Trifluoromethanesulfonates in Solution. General Procedure. 5,6,8,9-Tetrahydro-7-phenyldibenzo[*c*,*h*]acridinium trifluoromethanesulfonate (10 mmol) and benzyltrimethylammonium nitrate (20 mmol) were heated in dry dioxane (100 mL) at reflux for 24 h. After the solution was allowed to cool, water was added (80 mL) and the reaction mixture concentrated at 100 °C/15 mm to $^1/_3$ of its volume. After extraction with Et_2O (3 × 50 mL), dry HCl was passed through the dry ($MgSO_4$) extract. After filtration, the ethereal solution was neutralized and dried over $MgSO_4$. Evaporation of the solvent gave the product pure by TLC (Table II).

Acknowledgment. We thank Drs. R. C. Patel and B. Gregory for their interest in and help with this work.

Registry No. **2** (R = *n*-octyl), 73377-30-7; **2** (R = *n*-undecyl), 73377-32-9; **2** (R = *n*-dodecyl), 73377-34-1; **2** (R = *n*-hexadecyl), 73377-36-3; octyl nitrate, 629-39-0; undecyl nitrate, 73377-37-4; dodecyl nitrate, 13277-59-3; hexadecyl nitrate, 24152-77-0; 5,6,8,9-tetrahydro-7-phenyldibenzo[*c*,*h*]xanthylium trifluoromethanesulfonate, 73377-38-5; octylamine, 111-86-4; undecylamine, 7307-55-3; dodecylamine, 124-22-1; hexadecylamine, 143-27-1; 2,4,6-triphenylpyrylium nitrate, 73377-39-6; *N*-butyl-2,4,6-triphenylpyridinium nitrate, 73377-40-9; *N*-hexyl-2,4,6-triphenylpyridinium nitrate, 73377-41-0; *N*-benzyl-2,4,6-triphenylpyridinium nitrate, 73377-42-1; *N*-(*p*-methylbenzyl)-2,4,6-triphenylpyridinium nitrate, 73377-43-2; *N*-(*p*-chlorobenzyl)-2,4,6-triphenylpyridinium nitrate, 73377-44-3; *N*-phenyl-2,4,6-triphenylpyridinium nitrate, 73377-45-4; butylamine, 109-73-9; hexylamine, 111-26-2; benzylamine, 100-46-9; *p*-methylbenzylamine, 104-84-7; *p*-chlorobenzylamine, 104-86-9; aniline, 62-53-3; butyl nitrate, 928-45-0; hexyl nitrate, 20633-11-8; benzyl nitrate, 15285-42-4; *p*-methylbenzyl nitrate, 13527-05-4; *p*-chlorobenzyl nitrate, 15313-94-7; benzyltrimethylammonium nitrate, 19876-73-4; benzyltrimethylammonium hydroxide, 100-85-6.

Supplementary Material Available: ^1H NMR spectral data of N-substituted 2,4,6-triphenylpyridinium nitrates and IR, ^1H NMR, and ^{13}C NMR spectral data of alkyl and benzyl nitrates (2 pages). Ordering information is given on any current masthead page.

(13) A. R. Katritzky and S. S. Thind, *J. Chem. Soc., Perkin Trans. 1*, in press.

(14) H. R. Ing and R. Robinson, *J. Chem. Soc.*, 1666 (1926).