

TABLE V
 CYCLOHEXENE TRAPPING REACTIONS^a

Products	Retention time ^b	Reactants		
		C ₆ H ₅ CONO ₂ + LiCl ^c	NO ₂ Cl ^d	C ₆ H ₅ CO ₂ Cl ^e
<i>f</i>	4.0	m ^g	m	m
<i>f</i>	4.3	m	m	m
Cyclohexen-3-ol acetate	6.6	M ^g	M	M
1,2-Dichlorocyclohexane ^h	7.8 + 8.8	M	M	<1
1-Nitrocyclohexene	9.9	m	m	
2-Chlorocyclohexyl acetate	12.8	M	M	M
2-Chloro-1-nitrocyclohexane	13.6	M	M	
<i>f</i>	17.4	m	m	<1
2-Chlorocyclohexyl benzoate	23.3 ⁱ	<i>j</i>	<i>j</i>	M

^a Cyclohexene:LiCl:oxidizing agent = 10:0.3-2:1, acetonitrile (25 ml)-acetic acid (25 ml) solvent, 60°, 24 hr. ^b On glpc column A, 160°; see Experimental Section. ^c Similar results with LiCl:nitrate ratios of 0.67 and 1.95. ^d Similar results with LiCl:NO₂Cl = 0.38 or NO₂Cl alone. ^e Similar results with LiCl:(C₆H₅CO₂)₂ = 0.63 and 2.02. ^f Not identified. ^g m = minor product (<10%); M = major product (>10%). ^h Mixture of cis and trans. ⁱ Programmed at 170-250° at 10°/min. ^j No higher boilers noted upon programming to 250°.

chloride. Apparently, benzoyl hypochlorite is not formed in the nitrate reduction; if it had been produced, 2-chlorocyclohexyl benzoate (a major product from the benzoyl hypochlorite-cyclohexene control, Table V) would have been noted.

Experimental Section

Reactions involving benzoyl nitrate were carried out using freshly prepared stock solutions in acetonitrile as described elsewhere.^{9,12} Nitryl chloride was prepared according to a published procedure,²³ and also used as a stock solution in acetonitrile as was dinitrogen pentoxide.⁹ In all reactions, the oxidant solution was added last to a solution of all the other components at the temperature desired. Although all reactions involving benzoyl nitrate-halide ion gave instantaneous indication of molecular halogen formation, they were allowed to react at the designated temperature until halogen decomposition was complete. At the end of the reactions the mixtures were analyzed directly by gas chromatography.

Varian Models 1400 and 600D (with flame ionization detectors) were used with the following columns: (A) 10 ft × 0.125 in. 20% SE-30/Chromosorb W-DMCS, 60/80 mesh; (B) 10 ft ×

0.125 in. 10% OV-225/Suprelcoport, 80/100 mesh; (C) 6 ft × 0.125 in. 20% DEGS/Chromosorb W, 60/80 mesh.

Reaction product yields were determined by adding a known quantity of marker (*p*-chloroanisole, *p*-bromoanisole, or *p*-bromotoluene) to a one-tenth portion of the reaction mixture and analyzing by glpc (column A, 160-180°). The appropriate correction factors were used to convert area ratios to molar ratios and ultimately to product yields.³ Yields were based on moles of product/mole of benzoyl nitrate (benzoyl peroxide, halogen, or nitryl chloride), and in all cases the table entries represent an average of at least duplicated runs in close agreement. Benzoic acid yields were determined in a number of representative reactions by titration, and were found to be quantitative based on starting aryl nitrate.

Bromo- and chlorotoluene isomers were analyzed on glpc column B (100-150°) and column C (100°).

The products from the cyclohexene reactions were collected by way of preparative glpc (Varian Model 90-P, thermal conductivity detector, 6 ft × 0.25 in. 3% SE-30/Chromosorb W, 60/80 mesh) on concentrated reaction mixtures. Ir and nmr spectra were used to identify the products with comparison to authentic spectra performed where available. Semiquantitative amounts of each product (Table V) were obtained using glpc column A at 160°, with programming to higher temperatures in some cases.

Registry No.—Benzoyl nitrate, 6786-32-9; chloride ion, 16887-00-6; bromide ion, 24959-67-9; nitryl chloride, 13444-90-1.

(23) M. J. Collis, F. P. Gintz, D. R. Goddard, E. A. Hebron, and G. J. Minkoff, *J. Chem. Soc.*, 438 (1958).

The Stereochemistry and Ultraviolet Spectra of Simple Nitrate Esters^{1a}

V. M. CSIZMADIA, S. A. HOULDEN, G. J. KOVES, J. M. BOGGS, AND I. G. CSIZMADIA*^{1b}

Lash Miller Chemical Laboratory, Department of Chemistry, University of Toronto, Toronto 5, Ontario

Received November 13, 1972

Eight simple representative nitrate esters (methyl nitrate, ethyl nitrate, *n*-propyl nitrate, isopropyl nitrate, *n*-butyl nitrate, *tert*-butyl nitrate, benzyl nitrate, and β -phenethyl nitrate) have been investigated by the extended Hückel molecular orbital (EHMO) method. The uv spectra of this set of compounds were recorded in heptane and resolved into a number of component bands as suggested by the EHMO calculations. The charge distributions of these molecules were calculated by an iterative charge consistency method.

Nitrate esters are used as propellants and explosives and as drugs for the relief of hypertension and *angina pectoris*. In synthetic work, the nitrate group (ONO₂) is frequently employed for blocking hydroxyl groups in molecules while the manipulation of other functional groups is carried out.

(1) (a) Presented in part at the 50th Canadian Chemical Conference of the Chemical Institute of Canada, June 4-7, 1967, Toronto. (b) On leave during 1971-1972 at the Department of Chemistry, University of York, Heslington, York, England.

The physical and chemical properties of this interesting π -electron system have so far, however, received only brief attention in the literature.² We report here theoretical and experimental investigations of the stereochemistry and uv spectra of methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *tert*-butyl, benzyl-, and β -phenethyl nitrates.

(2) L. D. Hayward, "The Chemistry of Nitrate Esters," in preparation; J. Honeyman and J. W. W. Morgan, *Advan. Carbohydr. Chem.*, **12**, 117 (1957).

The well-known extended Hückel molecular orbital (EHMO) method³ was applied to the above compounds; the input data consisted of the geometrical parameters of the molecules together with the exponents and matrix elements for the atomic orbitals. The bond lengths for the *C*-nitrate group (*C*-ONO₂) measured on methyl nitrate⁴ were used (*C*-O = 1.43 Å, O-N = 1.36 Å, and N-O = 1.26 Å) and the data for alkyl and aryl groups were taken from published tables.⁵ Bond angles were taken as either tetrahedral or 120° with the exception of the CON angle and the apical angle of the NO₂ portion of the nitrate group which were varied to calculate optimum values. The orbital exponents were estimated by Slater's rule⁶ as H(1s) = 1.000, C(2s,sp) = 1.625, N(2s,2p) = 1.950, and O(2s,2p) = 2.275, and the matrix elements were taken as the negative of reported^{7,8} ionization potentials (Table I). The results obtained by the EHMO method

TABLE I
ATOMIC ORBITAL IONIZATION POTENTIALS (eV) AS
DIAGONAL MATRIX ELEMENTS

H	C ^a	N ^b	O ^b
1s, -13.60			
2s	-21.40	-26.00	-32.30
2p	-11.40	-13.40	-14.80

^a Reference 6. ^b Reference 7.

were then used in the conformational and spectroscopic calculations. To obtain chemically meaningful net charges and dipole moments a previously proposed⁹ charge iteration technique was employed.

The eight compounds were prepared according to published techniques.^{10a} The uv spectra of the carefully purified samples were recorded from 30,000 to 47,500 cm⁻¹ on 10⁻², 10⁻³, and 10⁻⁴ molar solutions in heptane with a UNICAM SP. 800 spectrophotometer. The spectra were digitalized at 100-cm⁻¹ intervals and then resolved into Gaussian component bands by a least-squares technique suggested by Stone.^{10b} The number and to some degree the positions and intensities of the component bands were suggested by the EHMO results.

Results and Discussion

Stereochemistry.—To conserve computer time, complete potential surfaces were not calculated. Instead, the conformation of minimum energy was determined by the sequence of variations. For methyl nitrate the CON angle, β , was varied in conjunction with the ONO apical angle α and the rotation of the NO₂ group by the angle ϕ . A minimum was obtained with $\alpha = 122.8^\circ$, $\beta = 130.2^\circ$, the methyl group stag-

gered, and the plane of the NO₂ group in the plane of the molecule. This predicted conformation of methyl nitrate is in agreement with that proposed by Dixon and Wilson.¹¹ The barrier to rotation of the nitrate group (ϕ) by 180° is 3.23 kcal/mol and the barrier to rotation of the methyl group (ϕ) by 120° is 0.20 kcal/mol.

For ethyl nitrate, θ_1 , describing the rotation of the C-O bond, was also varied in addition to α , β , and ϕ . The terminal methyl group was assumed to be staggered ($\theta_2 = 60^\circ$). A minimum was obtained for a completely staggered molecule with the nitrate group again in the plane of the C-C-O chain and $\alpha = 122.8^\circ$, $\beta = 130.8^\circ$. The barrier to rotation of the nitrate group (ϕ) by 180° is 3.53 kcal/mol.

On the basis of the results for methyl and ethyl nitrates the NO₂ group was assumed to be coplanar for *n*-propyl and *n*-butyl nitrates, α was assumed to be 122.8°, and β was taken to be the average of the results for methyl and ethyl nitrates, 130.5°. The methyl groups were assumed to be fully staggered. Only two isomers were considered for these two nitrates, the *trans* form ($\theta_2 = 0^\circ$) and the *gauche* form ($\theta_2 = 120^\circ$). The *trans* form was lower in energy by 0.36 kcal/mol for *n*-propyl nitrate and by 3.66 kcal/mol for *n*-butyl nitrate.

To select the minimum energy conformation of isopropyl nitrate the CON angle θ was again varied and the O-N and C-O bonds were rotated by ϕ and θ , respectively. The ONO apical angle was again assumed to be 122.8° and the methyl groups were staggered. The minimum was found for the NO₂ group coplanar with the C-O bond and the C-O bond rotated 29.5° out of a fully staggered conformation with $\beta = 133^\circ$. The barrier to rotation of the nitrate group by 180° is 3.20 kcal/mol. The minimum with $\theta_1 = 29.5^\circ$ is 0.08 kcal/mol below the energy for $\theta_1 = 0^\circ$.

Only the CON angle β and rotation about the C-O bond were considered for *tert*-butyl nitrate. The conformation of minimum energy is a fully staggered molecule with the nitrate group coplanar and $\beta = 140^\circ$.

The optimum value for the CON angle β increases with the size of the nitrate ester when varied. However, an increase or decrease in the optimum value for β by 2° raises the energy less than 0.05 kcal/mol.

Benzyl nitrate and β -phenethyl nitrate were considered in this study as examples of aryl nitrates and as phenyl-substituted methyl and ethyl nitrates, respectively. With increasing size of the molecule the computation becomes lengthy; hence calculations of only individual extreme conformations were performed, with $\alpha = 122.8^\circ$ and $\beta = 130.5^\circ$. For benzyl nitrate four conformations were considered, two with the benzene ring coplanar with the C-C-O-N chain and the nitrate group either coplanar or perpendicular to the plane of the C-C-O-N chain. The conformation of minimum energy was found to be that with the benzene ring and the nitrate group coplanar with the C-C-O-N chain. The two conformations with the plane of the benzene ring perpendicular to the plane of the nitrate group were at nearly the same energy and were 3.3 kcal/mol above the minimum. The maximum occurred when the plane of the benzene ring and the plane of the nitrate group were perpendicular to

(3) (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); (b) G. Blyholder and C. A. Coulson, *Theor. Chim. Acta (Berlin)*, **10**, 316 (1968).

(4) L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.*, **59**, 13 (1937).

(5) H. J. M. Bowen, et al. (compilers), "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., London, Spec. Publ.*, **No. 11** (1958); *Suppl.*, **No. 13** (1965).

(6) C. A. Coulson, "Valence," Oxford University Press, London, 1952, p 40.

(7) H. A. Skinner and H. O. Pritchard, *Chem. Rev.*, **55**, 754 (1955).

(8) R. Hoffmann, *J. Chem. Phys.*, **40**, 2745 (1964).

(9) M. Zerner and M. Gouterman, *Theor. Chim. Acta (Berlin)*, **4**, 44 (1966).

(10) (a) R. Boschan, R. T. Merron, and R. W. van Dolah, *Chem. Rev.*, **55**, 486 (1955); (b) H. Stone, *J. Opt. Soc. Amer.*, **52**, 998 (1962).

(11) W. B. Dixon and E. B. Wilson, *J. Chem. Phys.*, **35**, 191 (1961).

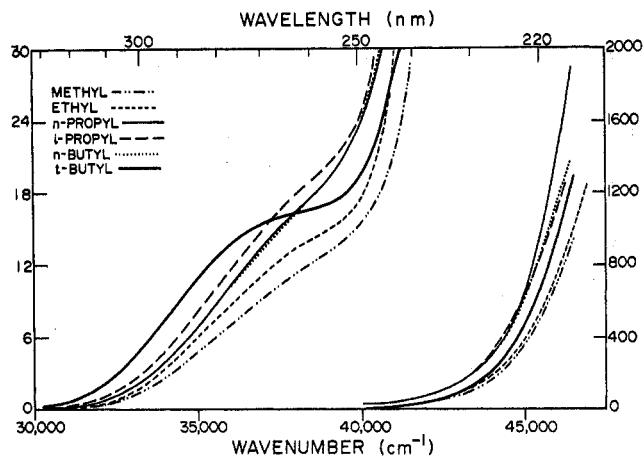


Figure 1.—Uv spectra of alkyl nitrate esters in heptane.

the plane of the C-C-O-N chain and was 6.9 kcal/mol above the minimum.

In the case of β -phenethyl nitrate it was assumed that the nitrate group was coplanar and two conformations were considered, one with the plane of the benzene ring perpendicular to the plane of the C-C-C-O-N chain and one with it coplanar. The conformation with the benzene ring perpendicular was lower in energy by 9.7 kcal/mol.

For the optimum conformations of all eight compounds as well as the sequence of geometrical optimization, see footnote 12.

Electronic Spectra.—The uv spectra of the six alkyl nitrates studied are presented in Figure 1. On inspection, a number of characteristics become apparent: (1) a progression can be seen with increasing *n*-alkyl chain length with the curves for *n*-propyl and *n*-butyl nitrates almost superimposable; (2) with increasing substitution on the α carbon (*i.e.*, methyl, ethyl, isopropyl, and *tert*-butyl nitrates) progression occurs for the first three compounds but the spectrum of *tert*-butyl nitrate is quite different from the others. This effect is easily explained if we assume the presence of a low intensity band progressively shifted to lower energy through the series methyl, ethyl and isopropyl nitrates. This would have the effect of increasing the intensity of the "bump" on the high intensity band and for *tert*-butyl nitrate the shift would be sufficient to appear as a band separation, with decreased intensity in the intermediate region.

The uv spectra of the two aralkyl nitrates studied (not shown in Figure 1) have the added complication that a benzenoid absorption possessing vibrational fine structure is superimposed on the excitation pattern associated with the nitrate group.

To analyze the spectra, the molecular orbital energy levels were used to construct theoretical spectra. Estimates of the relative intensities of the transitions were made from inspection of the coefficient matrices. All of these compounds except isopropyl nitrate possess a plane of symmetry in the plane of the carbon chain and nitrate

(12) Optimized conformations, net atomic charges, and geometry variations (Figures A and B) as well as band parameters resolved from the experimental uv spectra of selected nitrate esters (Tables A-F) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-73-2281.

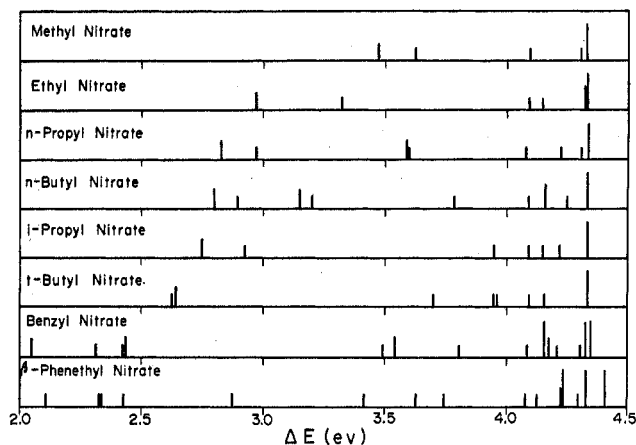


Figure 2.—Theoretical spectra of eight nitrate esters. Four classes of intensity are used. The lowest corresponds to $\pi_N^* \leftarrow \sigma$ excitations, the next highest to $\pi_N^* \leftarrow \pi'$, the 3rd highest to $\pi_N^* \leftarrow \pi$ or $\phi^* \leftarrow \phi$.

group. The MO's can be classified as σ or π with respect to this plane. Among the π MO's several different types could be distinguished; those localized on the nitrate group were designated as π_N , those delocalized over the molecule as a whole but with larger coefficients on the nitrate group were classified as π , those delocalized over the whole molecule but with larger coefficients on the carbon atoms as π' , and those localized on the benzene ring were designated by ϕ . Some MO's localized on the nitrate group were also identified as being similar to *n* type MO's of the nitrate ion¹³ and hence were classified as *n*. Other MO's which were delocalized over the entire molecule were classified as σ MO's.

The theoretical spectra of the eight nitrate esters, presented schematically in Figure 2, were calculated by taking all possible differences of the MO energy levels listed in Table II. The intensity scale shown is arbitrary; however, three classes of intensities were selected on the basis of MO type (σ , n , π_N , π , π' , or ϕ). The highest corresponds to $\phi^* \leftarrow \phi$ or $\pi_N^* \leftarrow \pi$ type excitations, the medium to $\pi_N^* \leftarrow \pi'$, and the lowest to $\pi_N^* \leftarrow \sigma$, $\pi_N^* \leftarrow n$, or $\phi^* \leftarrow n$ excitations.

The resolved spectra of the six aliphatic nitrates are shown in Figure 3. The first $\pi_N^* \leftarrow \pi$ excitation was assumed to correspond to the high intensity absorption at the high energy end of the spectra and hence the bands used to resolve the spectra were cut off at this point. The resolution of the spectra of the aralkyl nitrates was considerably more complex owing to the vibrational structure in the benzenoid absorption. For this reason the vibrational bands of the corresponding alcohols plus a high energy electronic band probably corresponding to a $\phi^* \leftarrow \phi$ type excitation were resolved as shown in the two upper diagrams of Figure 4 and the band parameters are summarized elsewhere.¹²

The same number of vibrational bands was then assumed for the corresponding aralkyl nitrates in addition to the electronic bands suggested by the MO pattern (Table II). The first predicted $\phi^* \leftarrow \phi$ excitation for the nitrates was assumed to give rise to

(13) S. J. Strickler and M. Kasha, in P. O. Löwdin and B. Pullman, "Molecular Orbitals in Chemistry, Physics and Biology," Academic Press, New York, N. Y., 1964, p 241.

TABLE II
 EXCITATION ENERGIES OF NITRATE ESTERS (UP TO 5 eV) PREDICTED FROM THE EHMO ENERGY LEVELS^a

Methyl		Ethyl		Benzyl		β -Phenethyl	
Transition	ΔE , eV	Transition	ΔE , eV	Transition	ΔE , eV	Transition	ΔE , eV
$2\pi_N^* \leftarrow 3\pi'$	3.40	$2\pi_N^* \leftarrow 4\pi'$	2.969	$3\pi_N^* \leftarrow \phi_{+1}$	2.051	$3\pi_N^* \leftarrow \phi_{+1}$	2.112
$2\pi_N^* \leftarrow 9\sigma$	3.622	$2\pi_N^* \leftarrow 12\sigma$	3.319	$3\pi_N^* \leftarrow 19\sigma$	2.315	$3\pi_N^* \leftarrow 21\sigma$	2.330
$2\pi_N^* \leftarrow 2n$	4.095	$2\pi_N^* \leftarrow 1n$	4.087	$3\pi_N^* \leftarrow 18\sigma$	2.424	$3\pi_N^* \leftarrow \phi_{-1}$	2.333
$2\pi_N^* \leftarrow 1n$	4.313	$2\pi_N^* \leftarrow 11\sigma$	4.141	$3\pi_N^* \leftarrow \phi_{-1}$	2.431	$3\pi_N^* \leftarrow \phi_0$	2.431
$\pi_N^* \leftarrow 1\pi_N$	4.336	$2\pi_N^* \leftarrow 3\pi$	4.319	$3\pi_N^* \leftarrow 17\sigma$	3.493	$3\pi_N^* \leftarrow 20\sigma$	2.869
$2\pi_N \leftarrow 8\sigma$	5.057	$2\pi_N^* \leftarrow 1\pi_N$	4.337	$3\pi_N^* \leftarrow 3\pi$	3.540	$3\pi_N^* \leftarrow 19\sigma$	3.415
		$2\pi_N^* \leftarrow 10\sigma$	4.524	$3\pi_N^* \leftarrow 16\sigma$	3.807	$3\pi_N^* \leftarrow 18\sigma$	3.632
		$2\pi_N^* \leftarrow 9\sigma$	4.611	$3\pi_N^* \leftarrow 3n$	4.087	$3\pi_N^* \leftarrow 17\sigma$	3.741
				$\phi_{-2} \leftarrow \phi_{+1}$	4.157	$3\pi_N^* \leftarrow 3n$	4.077
				$3\pi_N^* \leftarrow 2\pi'$	4.173	$3\pi_N^* \leftarrow 2n$	4.128
				$3\pi_N^* \leftarrow 15\sigma$	4.210	$3\pi_N^* \leftarrow 1\pi'$	4.224
				$3\pi_N^* \leftarrow 2n$	4.308	$\phi_{-2} \leftarrow \phi_{+1}$	4.224
				$3\pi_N^* \leftarrow 2\pi_N$	4.335	$3\pi_N^* \leftarrow 1n$	4.296
				$\phi_{+2} \leftarrow \phi_{+1}$	4.396	$3\pi_N^* \leftarrow 2\pi_N$	4.336
				$\phi_{-2}^* \leftarrow 19\sigma$	4.421	$\phi_{+2} \leftarrow \phi_{+1}$	4.409
				$\phi_{-2}^* \leftarrow 18\sigma$	4.530	$\phi_{-2} \leftarrow 21\sigma$	4.442
				$\phi_{-2}^* \leftarrow \phi_{-1}$	4.537	$\phi_{-2}^* \leftarrow \phi_{-1}$	4.445
				$3\pi_N^* \leftarrow 1n$	4.577	$3\pi_N^* \leftarrow 2\pi$	4.470
				$\phi_{+2}^* \leftarrow 19\sigma$	4.660	$\phi_{-2}^* \leftarrow \phi_0$	4.543
				$\phi_{+2}^* \leftarrow 18\sigma$	4.769	$\phi_{+2} \leftarrow 21\sigma$	4.627
						$\phi_{+2}^* \leftarrow \phi_{-1}$	4.036

<i>n</i> -Propyl		<i>n</i> -Butyl	
Transition	ΔE , eV	Transition	ΔE , eV
$2\pi_N^* \leftarrow 5\pi'$	2.831	$3\pi_N^* \leftarrow 5\pi'$	2.793
$2\pi_N^* \leftarrow 13\sigma$	2.970	$3\pi_N^* \leftarrow 14\sigma$	2.889
$2\pi_N^* \leftarrow 4\pi'$	3.537	$3\pi_N^* \leftarrow 4\pi'$	3.151
$2\pi_N^* \leftarrow 12\sigma$	3.592	$3\pi_N^* \leftarrow 13\sigma$	3.195
$2\pi_N^* \leftarrow 2n$	4.079	$3\pi_N^* \leftarrow 12\sigma$	3.788
$2\pi_N^* \leftarrow 11\sigma$	4.216	$3\pi_N^* \leftarrow 3n$	4.089
$2\pi_N^* \leftarrow 1n$	4.309	$3\pi_N^* \leftarrow 3\pi$	4.160
$2\pi_N^* \leftarrow 1\pi_N$	4.337	$3\pi_N^* \leftarrow 2n$	4.255
$2\pi_N^* \leftarrow 3\pi$	4.770	$3\pi_N^* \leftarrow 2\pi_N$	4.336
$2\pi_N^* \leftarrow 10\sigma$	4.982	$3\pi_N^* \leftarrow 1n$	4.547
		$3\pi_N^* \leftarrow 11\sigma$	4.959

Isopropyl		<i>tert</i> -Butyl	
Transition	ΔE , eV	Transition	ΔE , eV
$3\pi_N^* \leftarrow 1\pi'$	2.776	$3\pi_N^* \leftarrow 19\sigma$	2.628
$3\pi_N^* \leftarrow 16\sigma$	2.928	$3\pi_N^* \leftarrow 1\pi'$	2.637
$3\pi_N^* \leftarrow 15\sigma$	3.947	$3\pi_N^* \leftarrow 18\sigma$	3.705
$3\pi_N^* \leftarrow 2n$	4.090	$3\pi_N^* \leftarrow 17\sigma$	3.951
$3\pi_N^* \leftarrow 1n$	4.152	$3\pi_N^* \leftarrow 16\sigma$	2.963
$3\pi_N^* \leftarrow 14\sigma$	4.221	$3\pi_N^* \leftarrow 2n$	4.098
$3\pi_N^* \leftarrow 2\pi_N$	4.338	$3\pi_N^* \leftarrow 1n$	4.164
$3\pi_N^* \leftarrow 13\sigma$	4.338	$3\pi_N^* \leftarrow 2\pi_N$	4.336
$3\pi_N^* \leftarrow 12\sigma$	4.699	$3\pi_N^* \leftarrow 15\sigma$	4.487
$3\pi_N^* \leftarrow 11\sigma$	4.930	$3\pi_N^* \leftarrow 14\sigma$	4.551
		$3\pi_N^* \leftarrow 13\sigma$	4.949

^a Only those modes of excitation which are above the rules were included in the spectral resolution.

 TABLE III
 DIPOLE MOMENTS (DEBYE) OF EIGHT NITRATE ESTERS

Registry no.	Compd	Calcd ^a				Exptl ^b M
		M_x	M_y	M_z	M	
598-58-3	Methyl nitrate	-4.58	0	2.29	5.12	2.88 ^{c,d}
625-58-1	Ethyl nitrate	-5.02	0	2.03	5.42	2.96 ^e
627-13-4	<i>n</i> -Propyl nitrate	-5.07	0	2.20	5.53	2.98 ^d
928-45-0	<i>n</i> -Butyl nitrate	-5.10	0	2.13	5.53	2.99 ^d
1712-64-7	Isopropyl nitrate	-5.18	-0.22	2.04	5.57	
926-05-6	<i>tert</i> -Butyl nitrate	-5.12	0	2.22	5.58	
15285-42-4	Benzyl nitrate	-4.42	0	2.15	4.91	
39835-32-0	β -Phenethyl nitrate	-4.42	0	2.08	5.43	

^a Calculated from the point charges which in turn were obtained by the charge iteration technique. ^b Measured in benzene. ^c Dixon and Wilson¹¹ measured a value of 3.10 D in the gaseous phase. ^d Reference 17. ^e Reference 18.

the vibrational structure and so was not included in the resolution as a separate electronic transition. The second predicted $\phi^* \leftarrow \phi$ excitation which occurs after the first $\pi_N^* \leftarrow \pi$ excitation was thought to be the electronic transition which was assumed to be present in the alcohol spectra. Thus the high intensity of the high energy absorption of the aralkyl nitrates is due to both the $\pi_N^* \leftarrow \pi$ and the $\phi^* \leftarrow \phi$ excitations. The vibrational bands of the nitrate esters after optimization are given in the two lower diagrams of Figure 4. The broken lines on these spectra correspond to the gross absorption minus that of the vibrational bands. The component Gaussian bands associated with the absorp-

tion of the nitrate chromophore (the broken lines in Figure 4) are reproduced in Figure 5. A schematic representation of all the spectral resolution work is shown in Figure 6 and the detailed characteristics of the spectral components are listed elsewhere.¹²

It cannot, of course, be conclusively demonstrated in this manner that the simple-looking experimental curves (Figure 1) have indeed such unique complex structures as shown (Figures 3 and 5) (*e.g.*, that *tert*-butyl nitrate has eight bands). However, conversely, we do demonstrate that a complex band pattern can have a simple envelope curve. The error curves (observed-calculated curve) were less than 0.5 intensity unit for the curve

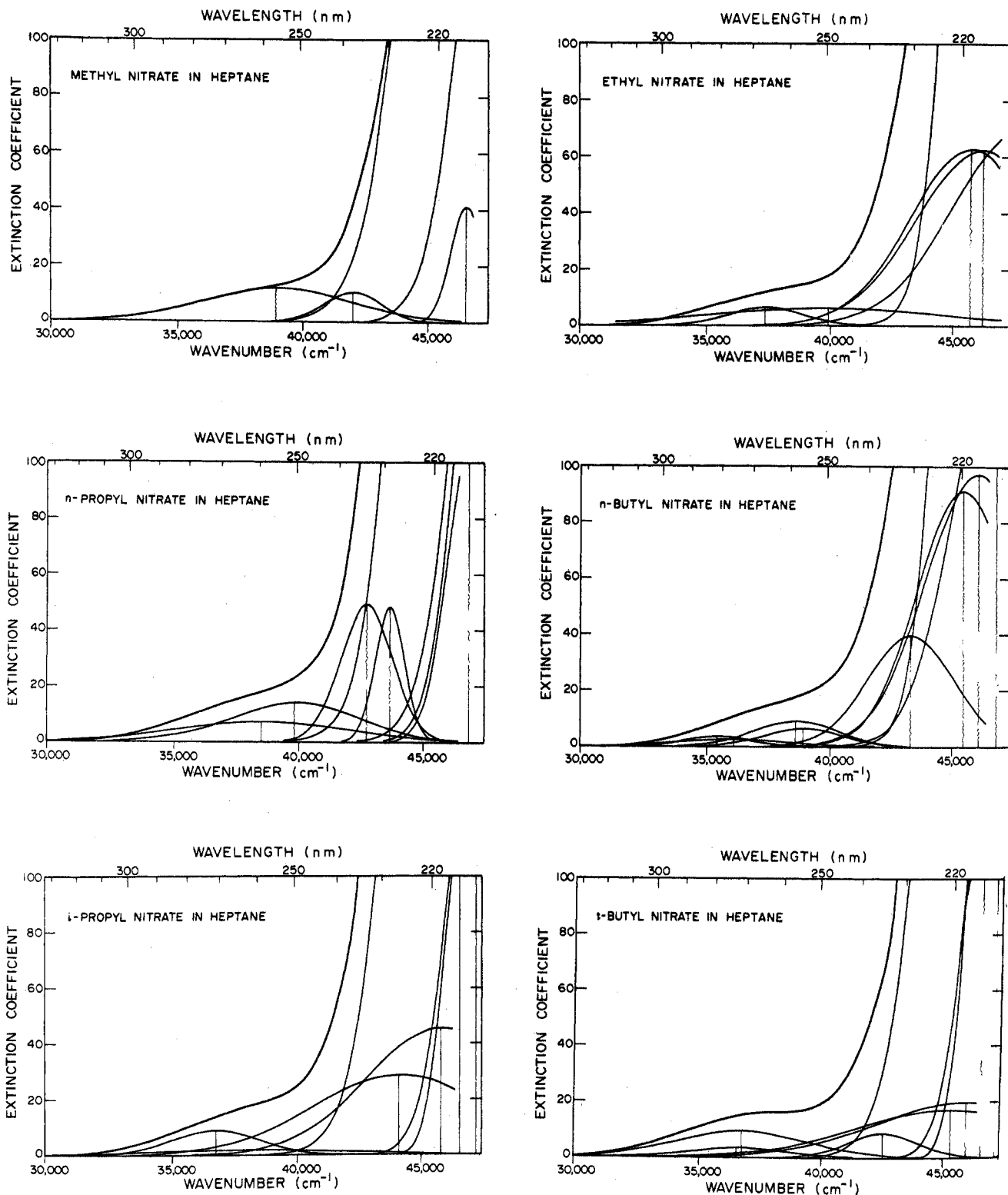


Figure 3.—Uv spectra of the aliphatic nitrate esters resolved to Gaussian component bands corresponding to the individual modes of excitation.

with $\epsilon < 200$ and not more than 5 intensity units for the entire curve up to ϵ 1400–2000.

As previously stated the number of bands was chosen to agree with the number predicted by the EHMO calculation keeping in mind the previous success of the EHMO method in this area.^{14–16}

(14) K. S. Sidhu, I. G. Csizmadia, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **88**, 2412 (1966).

(15) S. A. Houlden and I. G. Csizmadia, *Tetrahedron*, **25**, 1137 (1969).

(16) I. G. Csizmadia, S. A. Houlden, O. Meresz, and P. Yates, *Tetrahedron*, **25**, 2121 (1969).

Charge Distribution.—The total electron distributions, which are of the same shape as the molecules, are of no particular interest. However the net charges, as obtained by Mulliken's population, have been computed and they are in agreement with expectations.¹²

The numerical values of the dipole moments (calculated from the point charges) are summarized in Table III. As might be expected the computed dipole moments are systematically larger than the experi-

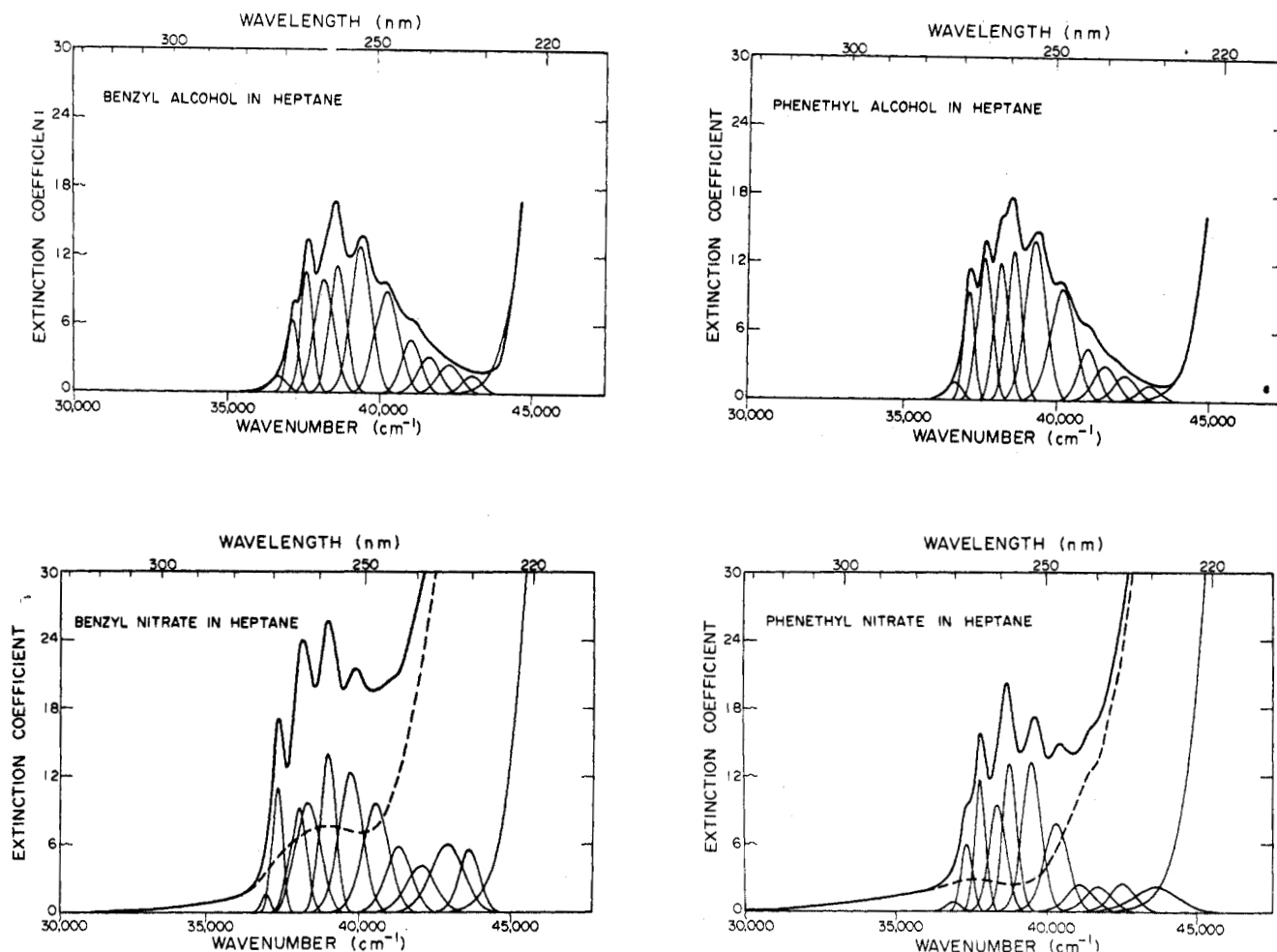


Figure 4.—Vibrational structure plus an electronic band of the benzenoid absorption in aryl alcohols and their corresponding nitrates. The broken line represents the total absorption associated with the nitrate group.

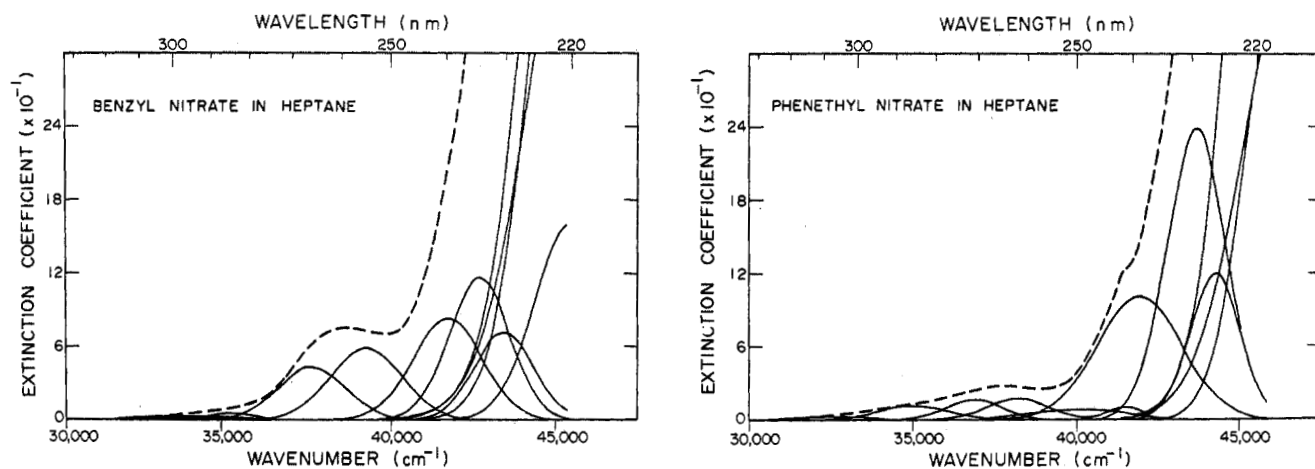


Figure 5.—Gaussian component bands of the nitrate absorption in aralkyl nitrates.

mental values;^{17,18} nevertheless they show the same tendency to increase with the length of the alkyl chain as is apparent in the experimentally measured values.

Conclusions

A number of problems have been raised and possible answers have been offered in this paper.

One question concerns the preferred conformation of

nitrate esters. For some time it was established^{4,19-21} that the α -carbon atom in nitrate esters lies in a plane perpendicular to the nitrate group. Later Dixon and Wilson¹¹ suggested that the α carbon in methyl nitrate is coplanar with the ONO_2 moiety. The present results are in agreement with the latter observations.

Secondly it has been suggested that the tail of the long wavelength absorption in the uv spectrum is due to

(17) E. G. Cowley and J. R. Pastington, *J. Chem. Soc.*, 1252 (1933).

(18) A. R. Lawrence and A. J. Matuszko, *J. Chem. Phys.*, **65**, (1961).

(19) A. D. Booth and F. J. Llewellyn, *J. Chem. Soc.*, 837 (1947).

(20) F. Rogowski, *Ber.*, **75**, 244 (1942).

(21) T. C. W. Mak and J. Trotter, *Acta Crystallogr.*, **17**, 367 (1964).

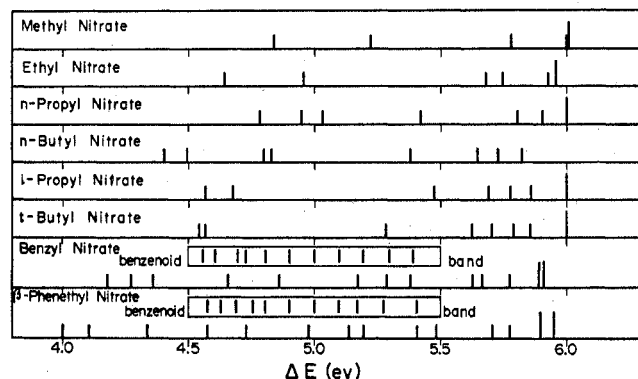


Figure 6.—A schematic representation of the nitrate absorption in aralkyl nitrates. High intensity bands correspond to $\pi_N^* \rightarrow \pi_N$ and $\phi^* \leftarrow \phi$ excitations.

the $\pi_N^* \leftarrow n$ mode of excitation.^{22,23} Very recently the discovery of a second, higher energy, $\pi_N^* \leftarrow n$ band in the circular dichroism spectrum has been reported.²⁴ The present work indicates the presence of still more low intensity bands in this region, some of which are associated with a charge transfer from the alkyl or aryl group to the nitrate π_N^* orbitals. From this viewpoint the photochemical reactions^{25–28} of nitrate esters (RONO_2) may be associated with an excited dipolar species $\text{R}^\delta + \text{ONO}_2^{\delta-}$, the chemical behavior of

(22) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

(23) C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworths, London, 1961, p 21.

(24) L. D. Hayward and S. Claesson, *Chem. Commun.*, 302 (1967).

(25) J. A. Gray and D. W. G. Style, *Trans. Faraday Soc.*, **49**, 52 (1953).

(26) S. Claesson, G. Palm, and G. Wettermark, *Ark. Kemi*, **17**, 579 (1961).

(27) L. D. Hayward, R. A. Kitchen, and D. J. Livingstone, *Can. J. Chem.*, **40**, 434 (1962).

(28) I. G. Csizmadia and L. D. Hayward, *Photochem. Photobiol.*, **4**, 657 (1965).

which must be more than a mere superimposition of the properties of the cation (R^+ONO_2) generated in the mass spectrometer and the anion (RONO_2^-) generated by electrolytic or chemical reductions. It is hoped that the information provided here will aid in the interpretation of the photochemical reactions.

Finally the electron distribution which indicated a net positive charge on nitrogen and carbon as well as α and β hydrogens is in agreement with the reaction mechanistic conclusions^{29–32} of base-catalyzed reactions while the net negative charge on the three oxygen atoms predicts the sites of protonation which occur during acid catalyzed reactions.

Registry No.—Benzyl alcohol, 100-51-6; β -phenethyl alcohol, 60-12-8.

Acknowledgments.—The authors would like to thank Professor L. D. Hayward for stimulating discussions and valuable suggestions during the preparation of the manuscript. Thanks are also due to Dr. Hoffman and Dr. Stone for making their computer programs available to us. A research grant provided by the Ontario Department of University Affairs and the continuous financial support of the National Research Council are gratefully acknowledged. One of us (S. A. H.) would like to thank the Province of Ontario for a graduate fellowship (1965–1966) and the National Research Council of Canada for a studentship (1966–1968). The authors wish to express their appreciation to the Institute of Computer Science at the University of Toronto for making its computer facilities available for this work.

(29) L. D. Hayward and I. G. Csizmadia, *Tetrahedron*, **19**, 2111 (1963).

(30) E. Buncl and A. N. Bourne, *Can. J. Chem.*, **38**, 2457 (1960).

(31) M. Jackson and L. D. Hayward, *Can. J. Chem.*, **38**, 496 (1960).

(32) J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952).

Reactions of Enaminonitriles with Phosgene. Synthesis of Enaminocarboxylic Acid Chlorides

MASATAKA OHOKA,* KATSUHIKO ASADA, SHOZO YANAGIDA, MITSUO OKAHARA, AND SABURO KOMORI

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-ka, Suita, Osaka, Japan

Received January 3, 1973

Reactions of enaminonitriles with phosgene have been investigated. Enaminonitriles with an α hydrogen or α halogen gave enaminocarboxylic acid chlorides in moderate to good yields together with low yields of isocyanates. Reactions of enaminonitriles with an α -cyano or α -ethoxycarbonyl group resulted in the quantitative recovery of the starting materials. The acid chlorides obtained were characterized by spectral analyses and by conversion to derivatives such as esters and amides.

Halleux and Viehe¹ have recently reported the formation of enaminocarboxylic acid chlorides from reactions of tertiary enamines with phosgene in the presence of triethylamine. However, isolation of the acid chlorides was unsuccessful because of their instability, and therefore they were identified by conversion to derivatives such as esters and amides.

In the course of our studies on the reactions of enaminonitriles with phosgene,² we have found that enaminonitriles possessing an α halogen gave relatively stable enaminocarboxylic acid chlorides. We have

succeeded in their isolation and have characterized them by spectral analyses and by conversion to esters or amides.

Results and Discussion

Treatment of enaminonitriles **1a–f** with phosgene in refluxing ethyl acetate gave enaminocarboxylic acid chlorides **2a–d** in moderate to good yields (Table I). It is of much interest that in addition to **1a** enaminonitriles **1e** and **1f** possessing an α halogen also gave acid chloride **2a**. However, reactions of **1i** and **1j** with phosgene resulted in the quantitative recovery of the starting materials. The acid chlorides **2a–d** are either

(1) A. Halleux and H. G. Viehe, *J. Chem. Soc. C*, 881 (1970).

(2) M. Ohoka, S. Yanagida, and S. Komori, *J. Org. Chem.*, **37**, 3030 (1972).