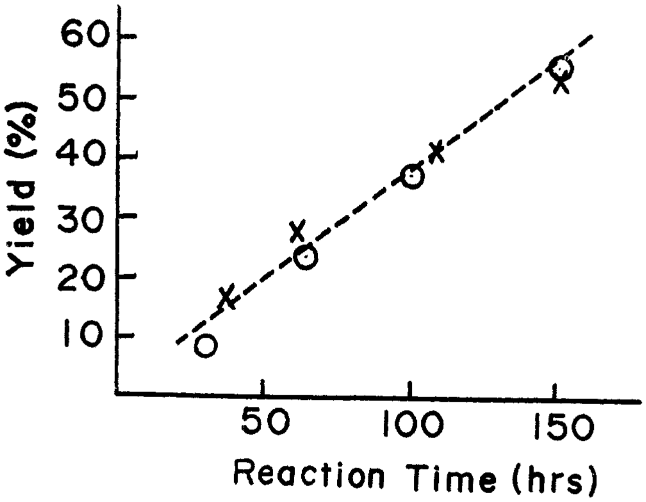

Figure 1.—Comparison of the reactivity to phosgene of acetamide hydrochloride with that of acetonitrile in the presence of hydrogen chloride: O, acetamide, 60–65°, $(CH_3CONH_2)_2$-HCl (0.5 g, 3.23 mmol) and $COCl_2$ (2.6 g, 26.2 mmol) molar ratio 1:8, nitrobenzene (17 g); ×, acetonitrile, 60–65°, CH_3CN (0.266 g, 6.48 mmol) and $COCl_2$ (1.93 g, 19.5 mmol) molar ratio 1:3:2.6, nitrobenzene (15 g).

similar reactivity. On the other hand, the reaction of primary amides with phosphorus pentachloride is well known to give imidoyl chloride hydrochloride (I) as an intermediate,[5,6] but the addition of phosphorus pentachloride to the reaction mixture did not affect the yield of the pyrimidone hydrochloride. In view of these facts, it is clear that the formation of imidoyl chloride hydrochloride (I) is not rate determining in the formation of pyrimidone hydrochlorides (II).

The reaction of amides with phosgene in the presence of hydrogen chloride has been extended to propionamide, butyroamide, caproamide, and lauroamide, the products being the corresponding pyrimidone hydrochlorides (II) and nitriles (Table I). Glpc analysis of the reaction mixture showed the formation of a small amount of 4,6-dichloro-2,5-dialkylpyrimidines as in the reaction of nitriles with phosgene in the presence of hydrogen chloride.[3]

Experimental Section

Acetamide hydrochloride $[(CH_3CONH_2)_2HCl]$ was prepared by the method of Strecker.[7] The other amides were purchased and purified by boiling.

Procedure.—*Caution. Because carbon dioxide and hydrogen chloride are evolved during the reaction, the reaction should be conducted on a small scale to avoid any dangerous explosion of the glass tube. The reaction temperature should also be kept below 70°.*

In a 50-ml glass tube were placed acetamide hydrochloride (0.003 mol) and 15 ml of phosgene solution (0.02–0.03 mol of phosgene). The tube was stoppered, cooled in Dry Ice–acetone, sealed carefully, and heated to 60–65° in a water bath. After the usual reaction period (*ca.* 200 hr), the reaction tube was chilled in Dry Ice–acetone and opened carefully. After removal of phosgene and hydrogen chloride, the resulting precipitate was separated by filtration, washed with ether, and dried *in vacuo.* It was identified as 6-chloro-2-methyl-4(3H)-pyrimidone hydrochloride by direct comparison with the ir spectrum of the authentic sample.[3]

Since the hydrochlorides of other amides were found too hygroscopic to isolate, they were prepared *in situ* by introducing dry hydrogen chloride into a solution of the amide and then allowing the mixture to react with phosgene in the same manner as mentioned above (0.01 mol of amide and hydrogen chloride, and 0.03 mol of phosgene in 15 g of nitrobenzene). The yield of nitriles was determined by glpc [on a column of silicone DC 550 10% on Diasolid L (60–80 mesh), 1 m × 4 mm]. The pyrimidone hydrochlorides except that from caproamide were identified by direct comparison with authentic samples.[3] 6-Chloro-2-pentyl-5-butyl-4(3H)-pyrimidone prepared from caproamide was recrystallized from acetonitrile and identified on the basis of its elemental analysis and ir spectrum: mp 109.5–111.0°; ir (mull) 1690 and 1590 cm^{-1}.

Anal. Calcd for $C_{13}H_{21}N_2ClO$: C, 60.80; H, 8.24; N, 10.90. Found: C, 61.10; H, 8.47; N, 10.88.

Registry No.—Phosgene, 75-44-5; hydrogen chloride, 7647-01-0; 6-chloro-2-pentyl-5-bentyl-4(3H)-pyrimidone, 21691-18-9.

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Rotational Isomerism in Vinylethylene Oxide

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In recent years, various spectroscopic methods have been employed to determine the electronic interactions of three-membered rings with unsaturated systems. Thus, with respect to benzene, cyclopropane is electron donating whereas oxirane and thiirane are electron withdrawing.[1] Recently, a large number of uv[2] and nmr[3] data have suggested a stereochemical requirement for maximum interaction between the cyclopropyl group and an adjacent p orbital. Maximum overlap occurs when the plane of the three-membered ring is parallel to the axis of the p orbital, *i.e.*, the bisected conformation.

Two bisected conformations exist for vinylcyclopropane, the *s-trans* and *s-cis* conformations.[4] However nmr evidence has been presented for a three-well torsonial potential for vinylcyclopropane.[5,6] It appears that the lower energy conformer is the *s-trans* form with two upper state forms corresponding to dihedral angles of *ca.* 80°, *i.e.*, the two *gauche* conformations. The energy separation between the *s-trans* and *gauche* conformations has been determined by nmr[6] and electron diffraction[7] to be *ca.* 1.0 kcal/mol. It is of interest to compare the results obtained for vinylcyclopropane with those obtained for the similar molecule, vinylethylene oxide (I). We wish to report our studies on the temperature variation of the nmr spectrum of

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[1] L. A. Strait, D. Jambotkar, R. Ketcham, and M. Hrenoff, *J. Org. Chem.*, **31**, 3976 (1966), and references cited therein.

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[3] (a) C. U. Pittman, Jr., and G. Olah, *J. Amer. Chem. Soc.*, **87**, 2998 (1965); (b) G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965); (c) N. C. Deno, H. G. Richey, J. S. Lin, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965); (d) T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966).

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vinylethylene oxide along with their implications concerning the conformations of this molecule.

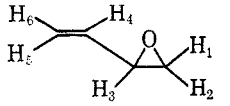
Spectra were analyzed in terms of chemical shifts and coupling constants with the aid of the computer program LAOCN3.[8] Results obtained from the analysis of vinylethyleneoxide (I) are given in Table I. Assuming I to be similar to vinylcyclopropane, the likely conformers of I are the *s-trans* and two *gauche* forms. Over the temperature range studied, there is rapid equilibrium between all the possible conformers, and a mean value for J_{34} is observed. This mean value of J_{34} is given by eq 1, where J_t and J_g are the *trans* and *gauche* coupling constants in individual conformers and p is the population of the *s-trans* conformer. If one assumes reasonable values for the individual coupling

$$J_{34} = pJ_t + J_t + (1 - p)J_g \tag{1}$$

constants[6] and that the conformers are of equal energy, a value of 6.3 Hz is obtained for J_{34}.[9] The observed value of J_{34} indicates that $p > 0.33$, and furthermore, the increase in J_{34} on lowering the temperature also suggests that the *s-trans* conformer is the lower energy form. Using reasonable values for the individual couplings,[9] p is calculated to be 0.49 with an energy difference between the rotamers of 400 cal/mol.

TABLE I

NMR PARAMETERS FOR VINYLETHYLENE OXIDE AT VARIOUS TEMPERATURES



	$+45^a$	$+27$	$+16$	-17	-45
$V_1{}^b$	2.619	2.635	2.653	2.697	2.744
V_2	2.932	2.946	2.962	2.999	3.040
V_3	3.319	3.332	3.345	3.376	3.410
V_4	5.544	5.538	5.530	5.515	5.502
V_5	5.492	5.503	5.517	5.549	5.584
V_6	5.274	5.285	5.298	5.329	5.361
$J_{12}{}^c$	5.36	5.28	5.29	5.12	5.08
J_{13}	2.60	2.63	2.62	2.67	2.67
J_{23}	4.09	4.01	4.09	4.08	4.13
J_{34}	7.58	7.69	7.83	8.06	8.40
J_{35}	−0.64	−0.62	−0.63	−0.55	−0.46
J_{36}	−0.61	−0.63	−0.59	−0.58	−0.64
J_{45}	17.24	17.17	17.22	17.11	17.06
J_{46}	10.54	10.40	10.42	10.44	10.30
J_{56}	1.28	1.22	1.28	1.28	1.30

[a] Temperature, °C. [b] In parts per million downfield from TMS. [c] In hertz.

In the vinyl coupling, the existence of a relationship between the coupling constants and substituent electronegativity has been adequately demonstrated.[10] All three couplings exhibit an approximately linear decrease as the electronegativity increases. Therefore, in I, as the population of the *s-trans* conformer increases, the electron-withdrawing effect of the ethylene oxide substituent should increase and the vinyl coupling should decrease. Examination of Table I shows that J_{45} and J_{46} do indeed decrease by 0.2 Hz, indicating a slightly greater electron-withdrawing effect of the ethylene oxide ring at lower temperatures (*i.e.*, an increased population of the *s-trans* conformer).

All chemical shifts are deshielded at lower temperatures, with the expection of V_4, which shows increased shielding (Table I). Similar results have been reported for vinylcyclopropane[5] and were interpreted in terms of the anisotropic diamagnetic polarizability of the cyclopropane ring, which has the large component normal to the ring. It has been suggested that the factors influencing the shifts in epoxides are similar to those in cyclopropane.[11,12] Therefore, the higher shielding of H_4 at low temperatures suggests that the location of H_4 is near the symmetry axis of the ring polarizability tensor (*i.e.*, the *s-trans* conformation). Therefore, the temperature variation of both chemical shifts and coupling constants indicates that the *s-trans* conformer is the lower energy conformation of vinylethylene oxide.

Experimental Section

Vinylethylene oxide, of commercial origin, was used without further purification. Samples were made up gravimetrically to 10 mol % in chloroform-*d* solution containing *ca.* 3% TMS as internal reference and lock signal source. Samples were degassed and sealed under vacuum.

Proton spectra were obtained using a Varian Associates HA-100 spectrometer with a probe temperature of 29°. Calibration of spectra was by the usual frequency difference technique. Line positions were obtained by averaging the results of two upfield and two downfield scans with a scan rate of 0.05 Hz/sec. Temperatures for the variable-temperature experiments were calibrated using the standard methanol and ethylene glycol samples.

Registry No.—Vinylethylene oxide, 930-22-3.

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[9] Calculated assuming J_t = 12.0 Hz and J_g = 3.5 Hz. The value of J_{34} will change slightly depending upon the values choosen for J_t and J_g.

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Structure of the Indenylacetic Acids

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The reported literature on the 1-indenylacetic acids and their esters is ambiguous with regard to the α,β *vs.* β,γ position of the double bond in the various synthetic species prepared. The earlier workers[1,2] were not in a position to make completely unequivocal assignments, whereas in more recent times an incomplete analysis of the pertinent systems has left uncertainty in this area.[3-5] Since these systems provide intermediates of potential synthetic consequence, we undertook a clarification of the question of the relative double-bond position.

Ahmed and Campbell[3] had described the structure of the unsaturated acid derived from Reformatsky reaction of indanone-1 (**1**) with ethyl bromoacetate followed by saponification to be entirely the *endo* product,

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