Experimental Section

Preparation of Dimethyl Chloroacetylenephosphonate.—Dichloroacetylene diethyl ether azeotrope was prepared by the procedure described in detail by Wotiz, *et al.*,[8] from 0.5 mol each of trichloroethylene and diethyl ether and distilled [bp 32° (760 mm)] into a 250-ml three-necked flask cooled to −78° and equipped with a magnetic stirring assembly, a gas inlet tube, and an exit tube leading to a bubbler. To the flask then was added under nitrogen 0.1 mol of trimethyl phosphite. The reaction mixture was warmed slowly to 0° and, after 1 hr, to room temperature. The evolution of a gas (methyl chloride) was observed. The reaction mixture was kept at room temperature overnight. Subsequently the unconverted dichloroacetylene and the ether were evaporated in a stream of dry nitrogen, the flask being warmed to 30–35°. A brown liquid residue (17.19 g) remained. Distillation gave 14.7 g of colorless liquid: bp 55° (2.2 mm); n^{25}D 1.4569; nmr spectrum, 3.71 ppm (d, J = 12.4 cps);[9] ir spectrum (neat liquid), 3000 (w), 2975 (m), 2850 (m), 2250 (sh), 2180 (vs), 2130 (w), 2060 (w), 1460 (s), 1280 (vs), 1185 (s), 1040 (vs), 950 (s), 840 (s), 795 (sh), 775 (s) cm^{-1}.

Anal. Calcd for $C_4H_6O_3ClP$: C, 28.51; H, 3.51; Cl, 21.05. Found: C, 28.27; H, 3.61; Cl, 21.15.

Preparation of Tetramethyl Acetylenediphosphonate.—Dimethyl chloroacetylenephosphonate (25 mmol) and 30 mmol of trimethyl phosphite were mixed at 0° in a reaction assembly as described in the previous experiment. The mixture was warmed slowly to 10–15° and stirred at this temperature for 15 hr. Evolution of a gas was noticed. Finally, the reaction mixture was heated at 30° for 1 hr. (Rapid heating from 0° to room temperature can result in an exothermic, uncontrollable reaction.) The brown liquid mixture was then heated at 1 mm while the external oil-bath temperature was raised slowly to 100°; 0.55 g of trimethyl phosphite distilled into the cooled trap, leaving 6.1 g of brown liquid. The latter was distilled to give 4.35 g (72%) of colorless liquid: n^{25}D 1.4476; bp 155–156° (1.5 mm), solidifying at 13–15°; nmr spectrum, 3.83 ppm (d, J = 12.3 cps); ir spectrum (liquid film), 2995 (w), 2950 (m), 2895 (sh), 2845 (m), 2160 (vw), 2020 (vw), 1890 (w), 1455 (s), 1290 (vs), 1185 (s), 1040 (vs), 845 (vs), 805 (sh), 795 (sh), 755 (m) cm^{-1}.

Anal. Calcd for $C_6H_{12}O_6P_2$: C, 29.76; H, 4.99. Found: C, 29.54; H, 4.98.

Diels–Alder Reactions.—The acetylene and the diene in equimolar quantities either were heated together without solvent under nitrogen with stirring using an oil bath heated to *ca.* 140–150° for 2–4 hr or, in the case of the tetramethyl acetylenediphosphonate–cyclopentadiene reaction, were heated in benzene solution for 10.5 hr. Distillation or, in the case of IV, crystallization gave the product.

Dimethyl 2-chloronorbornadiene-3-phosphonate (IIIa) was obtained in 64% yield: bp 85° (0.02 mm); n^{25}D 1.4996; nmr spectrum, 3.63 ppm (d, J = 11.2 cps), 2.2, 3.7, and 6.93 ppm (m, 2 H each).

Anal. Calcd for $C_9H_{12}O_3ClP$: C, 46.07; H, 5.16; Cl, 15.11. Found: C, 46.30; H, 5.12; Cl, 15.26.

Tetramethyl norbornadiene-2,3-diphosphonate (IIIb) was obtained in 72% yield: bp 137° (0.01 mm); n^{25}D 1.4947; nmr spectrum, 3.66 ppm (d, J = 11 cps), 2.0, 4.03, and 6.78 ppm (m, 2 H each).

Anal. Calcd for $C_{11}H_{18}O_6P_2$: C, 42.87; H, 5.88. Found: C, 42.65; H, 6.07.

Dimethyl *o*-chlorobenzenephosphonate was obtained in 22% yield: bp 87–88° (0.01 mm); n^{25}D 1.5209; nmr spectrum, 3.75 ppm (d, J = 12 cps), 7.22 (m), and 8.0 ppm (m).

Anal. Calcd for $C_8H_{10}O_3ClP$: C, 43.55; H, 4.57; Cl, 16.07. Found: C, 43.67; H, 4.86; Cl, 16.23.

Tetramethyl *o*-phenylenediphosphonate was obtained in 93.5% yield: mp 82–84° (from benzene–heptane) (lit.[7] mp 80–81° (the *meta* isomer was a high-boiling liquid; the *para* isomer melted at 100–101°);[7] nmr spectrum, 3.80 ppm (d, J = 11.8 cps), 7.62 (m), and 8.1 ppm (m).

Anal. Calcd for $C_{10}H_{16}O_6P_2$: C, 38.99; H, 5.48. Found: C, 39.15; H, 5.48.

Reaction of Tetramethyl Acetylenediphosphonate with Diazomethane.—To a stirred and cooled solution of the acetylene (10 mmol) in 20 ml of diethyl ether was added dropwise a solution of diazomethane in ether until the yellow color of the diazomethane no longer was discharged. A white crystalline solid formed immediately upon addition of the first drops of diazomethane solution. Filtration gave 2.80 g (95% yield) of white crystals, mp 130°. These were insoluble in ether, carbon tetrachloride, benzene, and hexane and soluble in chloroform, ethanol, and water. Recrystallization from chloroform–hexane gave pure material: mp 131.5°; white needles; nmr spectrum (in $CDCl_3$), 3.76 and 3.82 ppm (d, J = 11.8 cps), 8.25 ppm (s), and 11.9 ppm (s, broad); ir spectrum (Nujol), 3115 (s, broad), 2978 (m), 2940 (s), 2845 (m), 1560 (w), 1455 (s), 1374 (w), 1326 (w), 1240 (vs), 1040 (vs), 944 (m), 895 (w), 840 (s), cm^{-1}.

Anal. Calcd for $C_7H_{14}O_6N_2P_2$: C, 29.45; H, 4.97; N, 9.85. Found: C, 29.21; H, 5.00; N, 9.75.

(8) J. H. Wotiz, F. Huba and R. Vendley, *J. Org. Chem.*, **26**, 1626 (1961).

(9) Nmr spectra were measured using a Varian Associates T-60 nmr spectrometer in carbon tetrachloride solution. Chemical shifts are given in parts per million downfield from internal tetramethylsilane.

Registry No.—I (R = Me), 19519-59-6; II (R = Me), 19519-58-5; IIIa, 19581-55-6; IIIb, 19519-61-0; V, 19519-63-2; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; diazomethane, 334-88-3; dimethyl *o*-chlorobenzenephosphonate, 15104-43-5.

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Nitrogen Inversion in N-Benzoylaziridines

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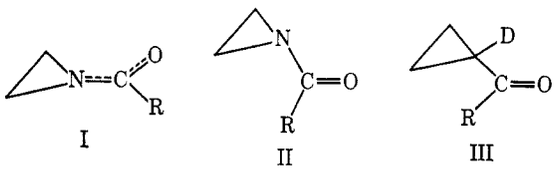
The molecular architecture of an N-acylaziridine is expected to be intermediate between two possible structures I and II. In form I, delocalization of the



I II III

a, R = CH_3O
b, R = $(CH_3)_2N$
c, R = CH_3
d, R = C_6H_5

nitrogen lone-pair electrons is significant and the atoms of the aziridine ring and the carbonyl group tend to lie in a common plane. This delocalization is minimal in structure II and the aziridine nitrogen is in a trihedral state. A competition between the tendency toward electron delocalization and the unfavorable effects of incorporation of an sp^2 nitrogen atom into a three-membered ring leads to a compromise structure between these two extremes.

Each of these limiting forms for an N-acylaziridine has distinctive kinetic features as regards either rotational isomerism about the nitrogen–acyl carbon bond or lone-pair inversion at the nitrogen atom. Structure I should exhibit a high barrier to rotation but, because

(1) Abstracted from the M.A. Thesis of G. R. B., University of California at Santa Barbara, Santa Barbara, Calif., Aug 1968.

the system is planar or nearly so, will have a low energy barrier to inversion. On the other hand, nitrogen inversion should be the dominant rate process for molecules close to structure II.

Anet and Osyany have studied several N-acylaziridines and have shown how it is possible to distinguish between these two kinetic processes by means of the spin-coupling pattern of the aziridine ring protons when the processes occur slowly on the nmr time scale.[2] These workers determined that when the substituent R was N,N-dimethylamino or methoxy—groups capable of strong resonance interaction with the carbonyl group—nitrogen inversion is the prevalent rate process. If this substituent is methyl, however, no change in the pmr spectrum was found down to −160°, a result consistent with a much smaller energy barrier to inversion than that found with the previously mentioned derivatives. These results are in line with the expected conjugative ability of N,N-dimethylamino or methoxy relative to methyl.

The conjugative ability of a phenyl group should be intermediate between that of the methyl group and the methoxy or dimethylamino groups; N-benzoylaziridine (Id) would thus be expected to have a lower barrier to inversion than Ia or Ib but a barrier higher than that for Ic. More importantly, the energy barrier to rotation about the carbon–nitrogen bond of the amide group may be large enough to produce additional effects in the pmr spectrum of this molecule. An X-ray crystallographic investigation of *p*-bromobenzoylaziridine shows that the nitrogen atom of this molecule is, in fact, strongly trihedral.[3] The angle between the plane of the ethylenimine ring and the nitrogen–carbonyl bond is 122°. From the magnitude of the carbon–nitrogen, carbon–oxygen, and carbon–carbon interatomic distances in the amide portion of the molecule, it was concluded that an appreciable resonance interaction is present in *p*-bromobenzoylazindine which increases the proclivity of this molecule for a structure closely resembling form II.[3] With the hope that we could obtain kinetic data for the inversion of nitrogen in N-benzoylaziridine, we have examined the pmr spectrum of this material as a function of temperature in a variety of solvents. The solvents used and the lowest temperature reached in each solvent are recorded in Table I. The aziridine ring protons appeared as a singlet and in no case were any changes beyond viscosity effects observed in these spectra as the temperature was decreased.

TABLE I

SOLVENTS USED IN N-BENZOYLAZIRIDINE EXPERIMENTS

Solvent	T_c,[a] °C	$\Delta\nu$,[b] ppm	$\Delta F^{\ddagger}$, kcal/mol
Acetone-d_6	−75	0.08	<11
50% acetone-d_6–50% toluene-d_3	−80	0.22	<10
Chloroform-d_1	−55	0.24	<11
Freon-11	−118	0.28	<8
Freon-22	−155	0.16	<6

[a] Lowest temperature that could be reached in the solvent before solubility or viscosity problems precluded further work. [b] Chemical shift difference for cyclopropyl phenyl ketone-d_1 in each solvent.

We have also prepared *p*-dimethylamino-, *p*-methoxy-, and *p*-nitrobenzoylaziridine and determined their pmr spectra in these solvents or various mixtures of these solvents, but with essentially the same results.

These observations are equally consistent with two interpretations. It may be that the dominant contributor to the ground state of these benzoylaziridines is structure I, in spite of the observation that *p*-bromobenzoylaziridine is nonplanar in the solid state. Alternatively, the nitrogen inversion process expected for structure II could be rapid at all temperatures. A comparison of the infrared spectra of the various aziridines in both a potassium bromide matrix and in chloroform solutions shows no consistent, pronounced shift of the carbonyl absorptions to lower frequency as might be expected if form I became more important in solution.[4] However, these vibrational frequencies in reality reflect molecular properties rather than properties of individual bonds so that changes in these quantities need not be related exclusively to variations in the hybridization of the amide nitrogen as the molecule is transferred from the solid state to the solution state.

If one presumes that these molecules are nonplanar, then the lowest temperature reached in these experiments must be above the coalescence temperature, as far as the kinetic dependence of the nmr spectra are concerned. If the chemical shift difference between the *syn* and the *anti* protons in the slowly inverting aziridine were available, it would be possible to estimate at least an upper limit for the free energy of activation for nitrogen inversion. Cyclopropyl phenyl ketone-d_1 (III) was chosen as a reasonable structural model for the noninverting aziridine and, therefore, we have obtained the approximate chemical shift difference between the *syn* and *anti* protons in this compound. (These spectra are of the AA′BB′ type and the chemical shift difference was taken as the frequency difference between the center of the two multiplets in the spectra.) These data are also recorded in Table I, along with the estimated upper limit for the free energy barriers to inversion of the aziridine in each of the solvents.

While we recognize the approximate nature of this procedure and the relative insensitivity of the calculated free energy barriers to the magnitude of $\Delta\nu$, our results suggest that the energy barrier to inversion in N-benzoylaziridine is less than 6 kcal/mol. This energy is less than the values of 10.3 and 7.6 kcal/mol found for *n*-(N′,N′-dimethylcarbamyl)aziridine (Ib) and N-carbomethoxyaziridine (Ia), respectively, as would be expected on the basis of the relative conjugative efficiencies of these groups, as discussed above. It also seems reasonable to infer that the barrier in the N-acetyl compound (Ic) is significantly lower than 6 kcal/mol.

Experimental Section

N-Benzoylaziridine was prepared according to the procedure of Goldberg and Kelly.[5]

N-(*p*-Dimethylaminobenzoyl)aziridine was prepared by a mixed anhydride method. Triethylamine (10 g, 0.099 mol) was added to a stirred solution of 7.5 g (0.046 mol) of *p*-dimethylaminobenzoic acid in 50 ml of dimethylformamide. The solution was cooled to 5° while 4.83 g (0.046 mol) of ethyl chloroformate was

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(4) H. L. Spell, *Anal. Chem.*, **39**, 185 (1967).
(5) A. A. Goldberg and W. Kelly, *J. Chem. Soc.*, 1919 (1948).

added. After 3 hr, the triethylamine hydrochloride was filtered from the solution and the filtrate was added dropwise to a solution of 5 g (0.12 mol) of aziridine in 25 ml of dimethylformamide at 5° with stirring. The reaction mixture was stirred for an additional 4 hr and then poured into ice water. The resulting white solid (5.7 g, 67%) was recrystallized from ethanol–water and was found to melt over the range 98–101°. The mass spectrum exhibited a molecular ion at *m/e* 190 (relative abundance, 35) and fragments at *m/e* 149 and 42 (relative abundances 100 and 11, respectively) which are assigned to the ions $(CH_3)_2NC_6H_4CO^+$ and $C_2H_4N^+$. The pmr spectrum of a 10% solution of the material in deuteriochloroform showed a sharp singlet at 2.28 ppm (relative area 4), a singlet at 3.00 ppm (relative area 6), and an apparent quartet centered at 7.4 ppm (relative area 4), downfield from tetramethylsilane. Prominent infrared bands at 1670, 1625, 1360, 1190, and 820 cm^{-1} were observed for the compound in a KBr matrix while absorptions at 1690, 1625, 1370, 1172, and 840 cm^{-1} were found with a 1% chloroform solution. These infrared features are quite consistent with the proposed acylaziridine structure.[4]

N-(*p*-Methoxybenzoyl)aziridine was prepared by the reaction of aziridine with anisoyl chloride. A stirred solution of 5 g (0.12 mol) of aziridine and 100 ml (0.72 mol) of triethylamine was treated with 17.1 g (0.1 mol) of anisoyl chloride in anhydrous ether over the course of 15 min. The mixture was stirred for a few minutes after the addition of the acid chloride was completed and then poured into water. The ether layer was washed with water and cooled until the crystallization occurred. The white product (mp 76–77°) was obtained in 80% yield. The pmr spectrum of the material showed sharp singlets at 2.32 (area 4) and 3.32 ppm (area 3) and a quartet at 7.1 ppm relative to TMS. The mass spectrum consisted of a molecular ion at *m/e* 177 (relative abundance 100) and peaks at *m/e* 135, 107, and 42 (relative abundances 40, 40, and 40, respectively) which are assigned to the ions $CH_3OC_6H_4CO^+$, $CH_3OC_6H_4^+$, and $C_2H_4N^+$, respectively. The infrared spectrum evidenced absorption at 1680, 1650, 1360, 1250, and 850 cm^{-1} in a KBr matrix and absorption at 1650, 1590, 1350, and 845 cm^{-1} in chloroform solution.

N-(*p*-Nitrobenzoyl)aziridine was prepared in a manner analogous to that used for the methoxy-substituted compound except that the product was insoluble in ether and was isolated by filtration in 60% yield. After recrystallization from acetone–water the pale yellow material melted over the range 170–172°. The nuclear magnetic resonance spectrum of the compound exhibited a singlet at 2.48 (area 4) and a broad singlet at 8.28 ppm (area 4) downfield from TMS. The mass spectrum showed a molecular ion at *m/e* 192 (relative abundance 36) and peaks at *m/e* 150 and 42 (relative abundance 100 and 56) which are assigned to the ions $NO_2C_6H_4CO^+$ and $C_2H_4N^+$, respectively. The infrared spectrum in a KBr matrix consisted of bands at 1675, 1620, 1355, 1228, and 807 cm^{-1} while in chloroform solution absorptions at 1648, 1620, 1355, 1150, and 810 cm^{-1} were noted. The pmr, ir, and mass spectral data were in complete accord with the assigned structure.

Cyclopropyl phenyl ketone-d_1 was prepared by dissolution of cyclopropyl phenyl ketone (Aldrich Chemical Co.) in a 2 *M* solution of NaOD in deuterium oxide. An equivalent volume of dioxane was added to help solubility and the mixture was heated under reflux for 2 or 3 days. The mixture was poured into water and extracted with ether. The ether extracts were washed with water, dried over sodium sulfate, and concentrated *in vacuo*. The residue was vacuum distilled to afford a product which showed essentially complete incorporation of deuterium into the position α to the carbonyl group, as determined by pmr spectroscopy.

The nuclear magnetic resonance spectra were taken with a JEOL C60-H spectrometer at 60 MHz and/or a Varian Associates HA-100 instrument at 100 MHz. Samples were 4–6% solute. Spectra of the cyclopropyl phenyl ketone-d_1 were recorded at 100 MHz with decoupling of the deuterium nucleus by means of an NMR Specialties, Inc., HD-60A spin decoupler. The standard variable-temperature accessory for each spectrometer was used; temperatures were determined with a Digitec Model 560 digital thermocouple and are believed to be accurate to at least 1°.

Registry No.—N-Benzoylaziridine, 7646-66-4; N-(*p*-dimethylaminobenzoyl)aziridine, 19614-27-8; N-(*p*-methoxybenzoyl)aziridine, 15269-50-8; N-(*p*-nitrobenzoyl)aziridine, 19614-29-0; IIId, 19614-30-3.

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Proton Nuclear Magnetic Resonance, Infrared, and Electronic Spectral Properties of the Cyanide Ion–1,3,5-Trinitrobenzene σ Complex

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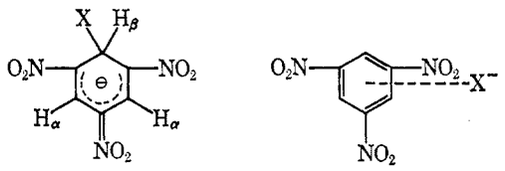
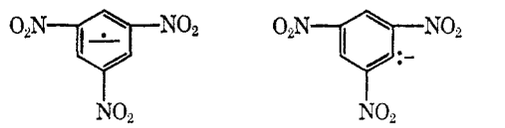
In recent years the ^1H nuclear magnetic resonance (nmr), infrared, and visible absorption spectra characteristic of the interactions of 1,3,5-trinitrobenzene and a variety of anions have been used to support the formulation of the resulting anionic species as σ complexes (I) rather than π complexes (II), radical anions (III), or aryl carbanions (IV).[1]



I II



III IV

X = OH, OCH_3, OC_2H_5, SO_3^-, CN, CH_2COCH_3, CH_3NH, and $C_5H_{10}N$

The spectra have been obtained, however, under quite different experimental conditions: nmr data from solutions approximately 0.50–1.0 *M* in both anion and nitro compound;[2-5] visible absorption data[6-8] from solutions whose concentration in either component may vary from 10^{-5} to 10^{-3} *M;* and infrared data, with one exception,[9] from the solids precipitated from concentrated solutions containing the two components.[10-13] As a result, there is some question whether the spectroscopic data refers to the same species in all cases.

We have now succeeded in obtaining nmr, infrared, and visible absorption data for the 1,3,5-trinitroben-

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