Nucleophilic displacement of NHCOR by ${}^{-}$ OH is in agreement with the finding that the yellow compound can be derived from either 5 (R = H) or 5 (R = Me).

Experimental Section

Microanalyses were performed by the Australian Microanalytical Service, CSIRO, Melbourne. The nmr spectra were recorded on a Varian Associates A-60D instrument; ir spectra were recorded on a Perkin-Elmer 225 spectrometer. Mass spectra were recorded by courtesy of Dr. G. Wunderlich, CSIRO Division of Organic Chemistry, Melbourne.

4-Acetyl-2,5-dimethyloxazole (1, $R = CH_3$) was prepared according to the procedure of Treibs and Sutter,⁷ mp 49.0-49.5° (lit.⁷ mp 49°).

2,5-Dimethyl-4-(β , β -dicyano- α -methylvinyl)oxazole (2, **R** = **CH**₃).—4-Acetyl-2,5-dimethyloxazole (0.35 g, 0.0025 mol), malononitrile (0.165 g, 0.0025 mol), and dry potassium acetate (0.01 g) were refluxed in dry benzene (20 ml) for 44 hr. Removal of the solvent *in vacuo* afforded a brown oil which was chromatographed on an aluminum oxide (BDH) column using benzene-petroleum spirit (bp 60-80) (1:1) as elutent. Unreacted 4-acetyl-2,5-dimethyloxazole (0.15 g) and 2 (R = CH₃) (0.1 g), mp 130-131°, were obtained as colorless needles: ir 2240 (CN), 1621 cm⁻¹ (C=N); mass spectrum M+187, 187 \rightarrow 91 [loss of (CN)₂C=C(CH₃)₂].

Anal. Calcd for $C_{10}H_9N_8O$: C, 64.17; H, 4.81; N, 22.46. Found: C, 64.30; H, 4.80; N, 22.34.

3-Amino-5-cyano-6-(dicyanomethyl)-2,4-dimethylpyridine (4).

—To 4-acetyl-2,5-dimethyloxazole (0.7 g, 0.005 mol) in ethanol (10 ml) and aqueous sodium hydroxide (3 ml, 2 N) was added malononitrile (0.66 g, 0.01 mol) in water (10 ml). The resulting red solution was heated on a steam bath for 20 min, cooled in ice, filtered, and washed with water. 3-Amino-5-cyano-6-(dicyanomethyl)-2,4-dimethylpyridine (4) (0.32 g, 33%) crystallized from aqueous DMF (1:1) as red needles, mp >300° dec.

Anal. Calcd for $C_{11}H_9N_5$: C, 62.56; H, 4.26; N, 33.17. Found: C, 62.34; H, 4.25; N, 33.65.

Reaction of 2,5-Dimethyl-4-(β , β -dicyano- α -methylvinyl)oxazole with Malononitrile.—2,5-Dimethyl-4-(β , β -dicyano- α -methylvinyl)oxazole (0.09 g, 0.0001 mol) in ethanol (5 ml) and aqueous sodium hydroxide (1 ml, 2 N) were treated at 25° with malononitrile (0.007 g, 0.0001 mol) in water (1 ml). After heating the red solution on a steam bath for 20 min, the solvent was removed, water (2 ml) was added, and the precipitate was collected, washed

with water, and recrystallized from aqueous DMF (1:5) to yield material (0.01 g) identical (mass spectrum, ir) with 4.

5-Acetyl-4-methyloxazole (5, R=H).—This was prepared according to the method of Dornow and Hell, 4 bp 68-74° (10-12 mm) [lit. 4 bp 74-75° (15 mm)].

5-Acetyl-2,4-dimethyloxazole (5, $R = CH_3$) was prepared according to the procedure of Dornow and Hell⁴ as colorless needles from petroleum spirit (bp 60-80°), mp 58-59° (lit.⁴ mp 61°).

Anal. Calcd for C₇H₉NO₂: C, 60.48; H, 6.53; N, 10.08. Found: C, 60.52; H, 6.61; N, 10.31.

2,4-Dimethyl-5- $(\beta,\beta$ -dicyano- α -methylvinyl)oxazole (6, $\mathbf{R}=\mathbf{CH_3}$).—5-Acetyl-2,4-dimethyloxazole⁴ (1.39 g, 0.01 mol), malononitrile (0.66 g, 0.01 mol), dry potassium acetate (0.01 g), and dry benzene (25 ml) were refluxed for 26 hr with water removal (Dean and Stark apparatus). Removal of the solvent in vacuo followed by addition of water (20 ml) to the residue and extraction with ethyl acetate gave after drying (MgSO₄) and evaporation of the solvent a brown oil. This was dissolved in benzene (10 ml) and petroleum spirit (bp 40-60°) was added dropwise to turbidity. After 5 days at 0° the crystals that deposited were collected, washed with petroleum spirit (bp 40-60°), and recrystallized twice (charcoal) from water to afford 6 ($\mathbf{R}=\mathbf{CH_3}$) (0.2 g) as colorless needles: mp 88-89°; ir 2200 cm⁻¹ (CN); nmr δ 2.55 (s, 6, 2 CH₃), 2.46 (s, 3, CH₃).

Anal. Calcd for C₁₀H₀N₂O: C, 64.22; H, 4.85; N, 22.47. Found: C, 64.28; H, 4.80; N, 22.29.

2-Acetyl-5-amino-4-cyano-1,1-dicyano-3-methylcyclopentadiene (10).—5-Acetyl-4-methyl- or 5-acetyl-2,4-dimethyloxazole (5) (0.01 mol) in ethanol (25 ml) and aqueous sodium hydroxide (5 ml, 2 N) was treated at 20° with malononitrile (0.02 mol) in water (5 ml). The red solution was heated on a steam bath for 15 min (NH₃ evolved), cooled to 20°, and neutralized with hydrochloric acid (12 N), water (100 ml) was added, and the yellow precipitate was collected and washed with water and then aqueous alcohol (1:1). 10 (60%) crystallized from aqueous DMF (1:3) as yellow needles mp = 300° dec

DMF (1:3) as yellow needles, mp = 300° dec. Anal. Calcd for $C_{11}H_8N_4O$: C, 62.26; H, 3.77; N, 26.41. Found: C, 62.48; H, 4.04; N, 26.17.

2-Acetyl-4-cyano-1,1-dicyano-5-dimethylamino-3-methylcyclopentadiene.—The yellow compound 10 (0.1 g), silver oxide (0.1 g), and methyl iodide (30 ml) were vigorously shaken in a stoppered flask at 20° for 16 hr. The red solution was filtered, the volume of the filtrate reduced in vacuo by two-thirds, and the red precipitate collected and washed with aqueous alcohol (2:1). The dimethylamino derivative of 10 crystallized from aqueous acetone (1:8) as red needles (0.1 g, 88%), mp 194-195°.

acetone (1:8) as red needles (0.1 g, 88%), mp 194-195°. Anal. Calcd for $C_{18}H_{12}N_4O$: C, 65.05, H, 5.04; N, 23.35. Found: C, 65.18; H, 5.29; N, 23.21.

Registry No.—1, 23000-12-6; 2 (R = Me), 33303-94-5; 4, 33223-92-6; 5 (R = H), 23012-19-3; 5 (R = Me), 23012-25-1; 6 (R = Me), 33223-95-9; 10, 33223-96-0; 10 dimethylamino derivative, 33223-97-1; malononitrile, 109-77-3.

Reactions of Triphenylarsonium and Triphenylphosphonium Phenacylides with 1-p-Nitrobenzoylaziridine

HAROLD W. HEINE* AND GEORGE D. WACHOB

Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837

Received September 2, 1971

The chemistry of triphenylarsonium phenacylide (1) has recently been investigated and compared with that of triphenylphosphonium phenacylide (2). It was observed that 1 and 2 showed the same sensitivity to hydrolysis and oxidation, and both gave O-alkylated

(1) A. W. Johnson and H. Schubert, J. Org. Chem., 35, 2678 (1970).

products exclusively when treated with ethyl iodide. 1-3 However, on heating in toluene, 1 gave a high yield of trans-1,2,3-tribenzoylcyclopropane, while 2 was recovered unchanged when it was subjected to the same experimental conditions. We now report the reactions of 1 and 2 and some of their analogs with 1-p-nitrobenzoylaziridine (3). Seemingly, the carbanionic centers of both 1 and 2 attack the aziridinyl carbon of 3 to form similar ring-opened intermediates. These intermediates, however, decompose to give different reaction products.

We have found that the reaction of equimolar amounts of 1 and 3 in refluxing toluene gives $N-(\gamma$ benzoyl- γ -triphenylarsenanylpropyl)-p-nitrobenzamide (4) in 41% yield.

$$(C_{\theta}H_{\delta})_{3}AsCHCC_{\theta}H_{\delta} \quad + \quad ArCN \underset{(C_{\theta}H_{\delta})_{3}}{\overset{O}{\longrightarrow}} \\ 1 \qquad \qquad 3 \qquad \underset{(C_{\theta}H_{\delta})_{3}AsCCC_{\theta}H_{\delta}}{\overset{O}{\longrightarrow}} \\ \qquad \qquad CH_{2}CH_{2}NHCAr \\ \qquad \qquad 4$$

 $Ar = p \cdot O_2 N C_6 H_4 -$

The structure of the new ylide is indicated by its infrared spectrum and by its chemical reactions. The infrared spectrum of 4 shows a carbonyl stretching frequency at 1550 cm⁻¹ (as expected for a phenacyl group participating in extensive charge delocalization) and stretching frequencies at 1670 and 3130 cm⁻¹ for the amido carbonyl and amido hydrogen groups, respec-

Compound 4 is easily hydrolyzed in warm aqueous methanol to N- $(\gamma$ -benzoylpropyl)-p-nitrobenzamide (5). The mass spectrum of 5 shows the molecular ion at m/e312 and important mass fragments at m/e 207, 193, 162, and 150, indicative of successive cleavages α and β to the carbonyl group and at the amidocarbonyl linkage. Compound 4 also undergoes the Wittig reaction with p-nitrobenzaldehyde in refluxing toluene to give a 65% yield of N-(γ -benzoyl- γ -p-nitrobenzylidenepropyl)-p-nitrobenzamide (6).

In contrast to the reaction of 1 with 3, triphenylphosphonium phenacylide (2) catalyzes the isomerization of 3 to 2-p-nitrophenyl-2-oxazoline (7). As little as 0.1 equiv of 2 (relative to 3) causes complete isomerization of 3 within a few hours in refluxing toluene. Control runs of 3 in refluxing toluene resulted in complete recovery of 3.

Triphenylphosphonium-p-nitrophenacylide and triphenylphosphonium-p-methoxyphenacylide also catalyze the isomerization of 3 to 7.

Both the reactions of 1 and 2 with 3 can be explained by a mechanism involving an initial nucleophilic attack of the carbanionic centers of 1 and 2 on the aziridinyl carbon of 3 to give intermediates 8a and 8b, respectively.

In the case of the arsonium intermediate 8a, proton transfer takes place to form the arsenic ylide 4, whereas in the case of the phosphonium intermediate 8b, displacement of the ylide 2 by the negatively charged benzamido moiety forms the oxazoline 7. Although the rearrangement of 1-aroylaziridines into 2-aryl-2oxazolines by various nucleophiles such as iodide ion or trialkylamines is a well-known reaction, it is not clear why the triphenylphosphonium phenacylides catalyze the rearrangement of 3 to 7, while the corresponding triphenylarsonium phenacylide reacts with 3 to give 4. Furthermore, reaction of 3 with carbethoxymethylenetriphenylphosphorane (9) gives the ylide 10,4 a result analogous to the reaction of 1 with 3. However, it is interesting to note that reaction of 3 with carbethoxyethylidinetriphenylphosphorane does form a small quantity of the oxazoline 7 (8%) along with the major product 1-(p-nitrobenzoyl)-2-ethoxy-3-methyl-2-pyrroline.4

Experimental Section

Reaction of 1 with 3.—To a solution of 430 mg (2.24 mmol) of 3 in 30 ml of dry toluene was added 1.00 g (2.35 mmol) of 1. The reaction mixture was refluxed for 2 hr and then allowed to stand overnight. Filtration gave 592 mg (43%) of crude 4. Recrystallization from chloroform-benzene gave 4 melting at 195-

Anal. Calcd for C₃₅H₂₉AsN₂O₄: C, 68.15; H, 4.74; N, 4.54. Found: C, 68.10, 4.88; N, 4.36.

Hydrolysis of 4.—A mixture of 300 mg (0.49 mmol) of 4, 6 ml of methanol, and 2 ml of water was refluxed for 1 hr. The reaction mixture was cooled and filtered to give 103 mg (67%) of 5. Recrystallization from methanol gave 5 melting at 161-163°. Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.38; H, 5.16; N, 8.97. Found: C, 65.28; H, 5.31; N, 9.03.

Conversion of 4 to 6.—A mixture of 300 mg (0.49 mmol) of 4 and 75 mg (0.49 mmol) of p-nitrobenzaldehyde in 13 ml of dry toluene was refluxed for 1 hr. The solvent was evaporated and the residual oil was slurried in a small quantity of absolute ethanol. The crude 6 that precipitated was filtered (140 mg, 64%) and recrystallized from absolute ethanol, mp 179-181°.

⁽²⁾ F. Ramirez and S. Dershowitz, J. Org. Chem., 22, 41 (1957). (3) F. Ramirez, R. B. Mitra, and N. B. Desai, J. Amer. Chem. Soc., 82, 5763 (1960).

⁽⁴⁾ H. W. Heine, G. B. Lowrie, and K. C. Irving, J. Org. Chem., 35, 444 (1970).

Anal. Calcd for $C_{24}H_{19}N_8O_6$: C, 64.70; H, 4.29; N, 9.43. Found: C, 64.90; H, 4.66; N, 9.26.

Isomerization of 3 to 7.—A mixture of 190 mg (0.49 mmol) of 2 and 96 mg (0.50 mmol) of 3 in 10 ml of dry toluene was refluxed for 4 hr. The solvent was evaporated and the residue was extracted twice with 15-ml portions of hot petroleum ether (bp 65-75°). Evaporation of the pooled extracts gave 89 mg (92%) of 7. The petroleum ether insoluble residue was shown to be 2. The isomerization of 3 also occurred in high yield using 20 mg of 2 and 96 mg of 3. Essentially the same results were obtained when triphenylphosphonium-p-mitro- and triphenylphosphonium-p-methoxyphenacylides were substituted for 2.

Registry No.—1 (charged form), 24904-06-1; 1 (uncharged form), 20691-73-0; 2, 859-65-4; 3, 19614-29-0; 4 (charged form), 33406-31-4; 4 (uncharged form), 33406-30-3; 5, 33406-32-5; 6, 33406-33-6.

Acknowledgment.—We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also thank Professor Charles C. Sweeley for the mass spectrum of N- $(\gamma$ -benzoylpropyl)-p-nitrobenzamide.

(5) S. Fliszar, R. F. Hudson, and G. Salvadori, Helv. Chim. Acta, 46, 1580 (1963).

Rearrangements, Pyrolysis, and Photolysis of Trimethylevelopropenyl Azide¹

GERHARD L. CLOSS* AND ARNOLD M. HARRISON

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

Received September 20, 1971

Allylic rearrangements of azides exhibit relatively few of the characteristics associated with ion-pair mechanisms. Alkyl substitution and changes in solvent polarity have minor effects on the reaction rates.² Concerted [3,3] sigmatropic shift would appear to be a more appropriate description of the reaction. We wish to report here the allylic rearrangement of trimethyl-cyclopropenyl azide (I), a system which might be expected to favor the ion-pair mechanism.

The azide I was readily prepared from the known trimethylcyclopropenyl fluoroborate and sodium azide. The nmr spectrum of I in methylene chloride showed only one transition at 1.80 ppm (TMS) at room temperature. At lower temperature the line broadened. and at -79° two sharp transitions were observed at 1.36 and 2.09 ppm with relative intensities of 1:2, respectively. The activation parameters of the apparent allylic rearrangement were extracted from a complete nmr line shape analysis³ from spectra recorded between -61 and -9° . A least-squares analysis of the data gave activation parameters of $\Delta H^{\pm} = 7.5 \pm 0.6 \text{ kcal/}$ mol and $\Delta S^{\pm} = -19 \pm 4$ eu. These values should be compared with $\Delta H^{\,\pm}$ = 20 kcal/mol and $\Delta S^{\,\pm}$ = -10eu obtained for α, α -dimethylallyl azide.² The significantly lower enthalpy of activation in the cyclopropenyl system indicated at least partial ionic character of the reaction path.

$$CH_3$$
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

The solvent dependence of the reaction rate lends support for this hypothesis. Table I shows the activa-

	TABLE I	
Solvent	Coalescence temp, °C	$E_{\mathbf{a}}$
CHCl_3	-56	7.2
$\mathrm{CH}_3\mathrm{OH}$	-48	7.4
$\mathrm{CH_{2}Cl_{2}}$	-33	7.9
$\mathrm{CH_{\$}COCH_{\$}}$	-20	8.4
CCl ₄	+35	10.2

tion energies estimated from the coalescence point of the methyl resonances in I in various solvents. Since no line shape analyses were made in those cases, the numbers were obtained by assuming identical preexponential factors in all solvents. This factor was determined from the data for methylene chloride. With the exception of chloroform, which shows an unusually fast rate, the general trend is as expected for an ionic pathway.

Competing with the allylic shift, although with much slower rate, is the rearrangement of I to 4.5.6-trimethylv-triazine (II), a transformation which had been observed previously for triphenyleyelopropenyl azide.⁴ Photolysis of either the azide I or the triazine II gave 2-butyne and acetonitrile in almost quantitative yield. The same products were formed on pyrolysis of I (300°) and II (ca.500°). We were unable to observe any species intermediate between either I or II and the fragmentation products even at photolysis at low temperature (-50°). Trimethyleyelopropenylnitrene and trimethylazatetrahedrane are possible intermediates in these reactions.

Experimental Section

Trimethyl-3-azidocyclopropene (I).—A 1.41-g (8.4 mmol) sample of trimethylcyclopropenyl fluoroborate⁵ and 0.59 g (9.2 mmol) of sodium azide were dissolved in 100 ml of water. The aqueous solution was stirred in an ice bath for 3 min and was then extracted with three 50-ml portions of methylene chloride. Vacuum fractionation (30-40° at 0.7-0.2 Torr) gave 1.10 g of material. On the basis of an nmr integral, this material was 67% I (0.74 g, 6.0 mmol, 71% yield) and 33% methylene chloride. This purity was sufficient for most of our studies.

Further purification by vacuum fractionation $(-78^\circ, 8~\mu)$ removed most of the methylene chloride, allowing I to be prepared with greater than 99% purity (by nmr): nmr (CDCl₃) δ 1.82 (s), (CH₂Cl₂) δ 1.80 (s) $\{-79^\circ, \delta$ 2.09 (s, 2), 1.36 (s, 1)]; in (neat) 2980, 2960, 2930, and 2860 (m, -CH₃), 2490 (w), 2090 (s, -N₃), 1859 and 1849 (w), 1438 (s), 1379 (m), 1279 (m), 1248 (s), 1083 (s), and 862 cm⁻¹ (m); uv max (95% EtOH) 308 m μ (ϵ 71), end absorption.

4,5,6-Trimethyl-v-triazine (II).—A 0.50-g (3.0 mmol) sample of trimethylcyclopropenyl fluoroborate and 0.19 g (3.0 mmol) of sodium azide were treated as above. The methylene chloride extracts however, were dried over sodium sulfate and allowed to stand in the dark at room temperature for 2 days. The solvent was stripped off, and the residue was crystallized from 50:50

⁽¹⁾ Supported by NSF Grant GP-18719X.

⁽²⁾ A. Gagneux, S. Winstein, and W. G. Young, J. Amer. Chem. Soc., 82, 5956 (1960).

⁽³⁾ G. Binsch, Top. Stereochem., 3, 97 (1968).

⁽⁴⁾ E. A. Chandross and G. Smolinsky, Tetrahedron Lett., No. 13, 19 (1960).

⁽⁵⁾ G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, J. Amer. Chem. Soc., 90, 173 (1968).