

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 Micro-analytical 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,<sup>7</sup> mp 49.0–49.5° (lit.<sup>7</sup> mp 49°).

**2,5-Dimethyl-4-( $\beta,\beta$ -dicyano- $\alpha$ -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 eluent. Unreacted 4-acetyl-2,5-dimethyloxazole (0.15 g) and **2** ( $R = CH_3$ ) (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  $(CN)_2C=C(CH_3)_2$ ].

Anal. Calcd for  $C_{10}H_9N_3O$ : 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-( $\beta,\beta$ -dicyano- $\alpha$ -methylvinyl)oxazole with Malononitrile.**—2,5-Dimethyl-4-( $\beta,\beta$ -dicyano- $\alpha$ -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,<sup>4</sup> bp 68–74° (10–12 mm) [lit.<sup>4</sup> bp 74–75° (15 mm)].

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

Anal. Calcd for  $C_7H_9NO_2$ : 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- $\alpha$ -methylvinyl)oxazole** (**6**,  $R = CH_3$ ).—5-Acetyl-2,4-dimethyloxazole<sup>4</sup> (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 ( $MgSO_4$ ) 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** ( $R = CH_3$ ) (0.2 g) as colorless needles: mp 88–89°; ir 2200  $cm^{-1}$  (CN); nmr  $\delta$  2.55 (s, 6, 2  $CH_3$ ), 2.46 (s, 3,  $CH_3$ ).

Anal. Calcd for  $C_{10}H_9N_3O$ : 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 ( $NH_3$  evolved), cooled to 20°, and neutralized with hydrochloric acid (2 *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.

Anal. Calcd for  $C_{11}H_9N_5O$ : 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°.

Anal. Calcd for  $C_{13}H_{12}N_4O$ : 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

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Received September 2, 1971

The chemistry of triphenylarsonium phenacylide (**1**) has recently been investigated and compared with that of triphenylphosphonium phenacylide (**2**).<sup>1</sup> 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).



*Anal.* Calcd for  $C_{24}H_{19}N_3O_6$ : 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*-nitro- and triphenylphosphonium-*p*-methoxyphenacylides<sup>5</sup> 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 Trimethylcyclopropenyl Azide<sup>1</sup>

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Received September 20, 1971

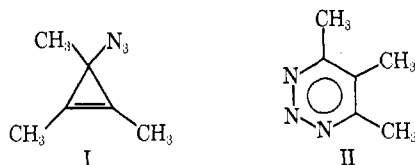
Allylic rearrangements of azides exhibit relatively few of the characteristics associated with ion-pair mechanisms. Alkyl substitution and changes in solvent polarity have minor effects on the reaction rates.<sup>2</sup> Concerted [3,3] sigmatropic shift would appear to be a more appropriate description of the reaction. We wish to report here the allylic rearrangement of trimethylcyclopropenyl 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  $-79^\circ$  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 analysis<sup>3</sup> from spectra recorded between  $-61$  and  $-9^\circ$ . A least-squares analysis of the data gave activation parameters of  $\Delta H^\ddagger = 7.5 \pm 0.6$  kcal/mol and  $\Delta S^\ddagger = -19 \pm 4$  eu. These values should be compared with  $\Delta H^\ddagger = 20$  kcal/mol and  $\Delta S^\ddagger = -10$  eu obtained for  $\alpha,\alpha$ -dimethylallyl azide.<sup>2</sup> The significantly lower enthalpy of activation in the cyclopropenyl system indicated at least partial ionic character of the reaction path.

(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).



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

TABLE I

Solvent	Coalescence temp, °C	$E_a$
$CHCl_3$	-56	7.2
$CH_3OH$	-48	7.4
$CH_2Cl_2$	-33	7.9
$CH_3COCH_3$	-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-trimethyl-*v*-triazine (II), a transformation which had been observed previously for triphenylcyclopropenyl azide.<sup>4</sup> 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 ( $300^\circ$ ) and II (*ca.*  $500^\circ$ ). We were unable to observe any species intermediate between either I or II and the fragmentation products even at photolysis at low temperature ( $-50^\circ$ ). Trimethylcyclopropenylnitrene and trimethylazetetrahedrane are possible intermediates in these reactions.

#### Experimental Section

**Trimethyl-3-azidocyclopropene (I).**—A 1.41-g (8.4 mmol) sample of trimethylcyclopropenyl fluoroborate<sup>5</sup> 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 ( $30$ – $40^\circ$  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 ( $CDCl_3$ )  $\delta$  1.82 (s), ( $CH_2Cl_2$ )  $\delta$  1.80 (s) [ $-79^\circ$ ,  $\delta$  2.09 (s, 2), 1.36 (s, 1)]; ir (neat) 2980, 2960, 2930, and 2860 (m,  $-CH_3$ ), 2490 (w), 2090 (s,  $-N_3$ ), 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 $\mu$  ( $\epsilon$  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

(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).