Interaction of Carbonyl Compounds with Organometallic Azides. V. Sorboyl Chloride and Its Conversion to an α-Pyridone[1]

John H. MacMillan and Stephen S. Washburne*

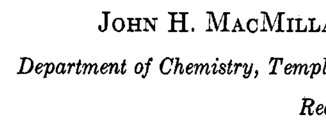
Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

Received April 3, 1973

Electrocyclic ring closure of α,β-*cis*-1,3-pentadienyl isocyanate affords 3-methyl-2(1*H*)-pyridone in fair yield. The isocyanate is formed in good yield by treatment of sorboyl chloride with trimethylsilyl azide in refluxing toluene. In refluxing heptane this reaction affords tetrazolinone **6** rather than isocyanate. The sensitive pentadienyl isocyanate is converted to polymer by either pyrolysis or acid treatment.

Intense current interest in electrocyclic reactions[2] has generated novel synthetic routes to numerous ring systems, particularly those accessible by thermally allowed disrotatory six-electron bond reorganizations. The apparent substituent shift shown by Pirkle to obtain in the α-pyrone series is an example,[3] as is the aza-Cope rearrangement leading to dihydroazepinones uncovered by Ohno.[4]

Since the N=C linkage of the isocyanate has been shown to be a willing participant in electrocyclization reactions, we thought that an α,β-cis-diene isocyanate, *e.g.*, **1**, would cyclize to **2** under thermal conditions. A facile 1 → 5 suprafacial hydrogen shift[2] would then convert **2** to the thermally more stable tautomer **3**.



cis-**1** **2** **3**

However, alkenyl isocyanates are particularly sensitive toward hydrolysis to aldehydes *via* the sequence $>C{=}CN{=}C{=}O \rightarrow >C{=}CNHCO_2H \rightarrow >C{=}CNH_2 \rightarrow >CHCH{=}O$. *o*-Nitrocinnamic acid gives *o*-nitrophenylacetaldehyde in meager yield upon attempted Schmidt reaction.[5] Pure diene isocyanates are unknown.

The recently reported isocyanate synthesis *via* silyl azides[1,6] offers a route to diene isocyanates under nearly neutral conditions. The ready availability of sorbic acid prompted us to investigate the chemistry of 1,3-pentadienyl isocyanate (**1**). Commercial sorbic acid **4** exists as a single, sharp-melting, all-trans isomer,[7a,b] while the α,β-cis isomer of **4** is required for electrocyclization of the corresponding isocyanate, **1**.

$$\underset{\mathbf{4}}{CH_3CH{=}CHCH{=}CHCO_2H} \xrightarrow[2.\ Me_3SiN_3]{1.\ SOCl_2} \underset{\mathbf{1}}{CH_3CH{=}CHCH{=}CHN{=}C{=}O}$$

This acid is a low-melting, readily polymerizing material,[7c] and its transformation to an acid chloride seemed remote. However, the various isomers of sorbaldehyde are equilibrated by vapor phase thermolysis,[8] and we hoped that the various isomers of **1** would equilibrate, affording some α,β-cis material which could cyclize rather than polymerize.

Results

Refluxing trimethylsilyl azide and sorboyl chloride (which appeared from nmr to contain at least two isomers) in toluene resulted in a 90% yield of nitrogen. Infrared analysis showed the presence of isocyanate, together with a strong band at 1770 cm^{-1}. Distillation gave a lachrymatory liquid which readily resinified. The uv spectrum, intense ir absorption at 2300 cm^{-1}, and the nmr spectrum indicated that it was 1,3-pentadienyl isocyanate (**1**). However, the complexity of the nmr olefinic region resisted attempts to decouple resonances, precluding determining if this sensitive material was a mixture of isomers.

If the above product mixture was heated at reflux in *o*-dichlorobenzene, a decrease in intensity of the 2300- and 1770-cm^{-1} peaks and the gradual growth of a new peak at 1660 cm^{-1} occurred. When the intensity of the new peak was maximized (estimated by quantitative ir analysis to correspond to a yield of 30%), work-up gave a 17% yield (from sorboyl chloride) of 3-methyl-2(1*H*)-pyridone (**3**) whose physical and spectral properties were consistent with literature values. This cyclization is subject to either a solvent or a temperature effect, since the yield in refluxing xylene or mesitylene was less than 5%.

In an effort to improve the yield of the cyclization **1** → **3**, the semisolid product mixture, dissolved in chloroform, was pyrolyzed at 400° in a nitrogen flow system. The pyrolysate contained only traces of **3**, together with unreacted **1** and moderate quantities of carbonaceous material. Under the pyrolysis conditions pyridone **3** was completely stable.

Attempted acid-catalyzed cyclization of **1** with trifluoroacetic acid gave only a brown polymer.

The origin of the 1770-cm^{-1} band in the product ir of the toluene reaction mixture is intriguing. Refluxing heptane solutions of azide and sorboyl chloride gave a white power, $C_{12}H_{14}N_4O_2$, assigned structure **6** on the basis of spectral evidence. Tetrazolinone **6** is apparently formed by cycloaddition of sorboyl azide **5** (initial product of trimethylsilyl azide and sorboyl chloride) with **1**. Similar tetrazolinone-yielding reactions of

---

[1] Part IV: W. R. Peterson, Jr., J. Radell, and S. S. Washburne, *J. Fluorine Chem.*, **2**, 437 (1973).

[2] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

[3] W. H. Pirkle, H. Seto, and W. V. Turner, *J. Amer. Chem. Soc.*, **92**, 6984 (1970).

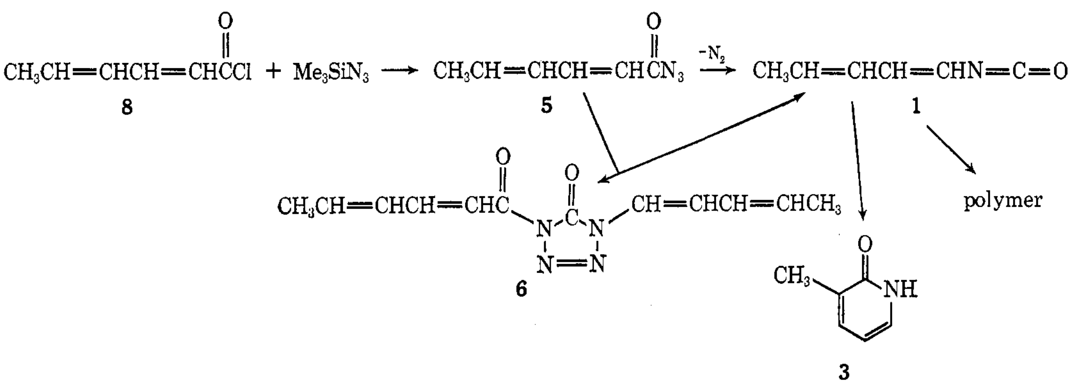
[4] T. Sasaki, S. Eguchi, and M. Ohno, *ibid.*, **92**, 3192 (1970).

[5] D. R. Dalton and S. Miller, private communication.

[6] (a) S. S. Washburne and W. R. Peterson, Jr., *Syn. Commun.*, **2**, 227 (1972). (b) S. S. Washburne, W. R. Peterson, Jr., and D. A. Berman, *J. Org. Chem.*, **37**, 1738 (1972).

[7] (a) Treatment of **4** with diazomethane gave the methyl ester whose nmr olefinic region was simplified with the use of Eu(FOD)$_3$. The spectra confirms an all-trans stereochemistry for commercial **4**. Full details will be published later. (b) U. Eisner, J. A. Elvidge, and R. P. Linstead, *J. Chem. Soc.*, 1372 (1953). (c) J. A. Elvidge and P. D. Ralph, *J. Chem. Soc. B*, 241 (1966).

[8] A. Viola and J. H. MacMillan, *J. Amer. Chem. Soc.*, **92**, 2404 (1970).

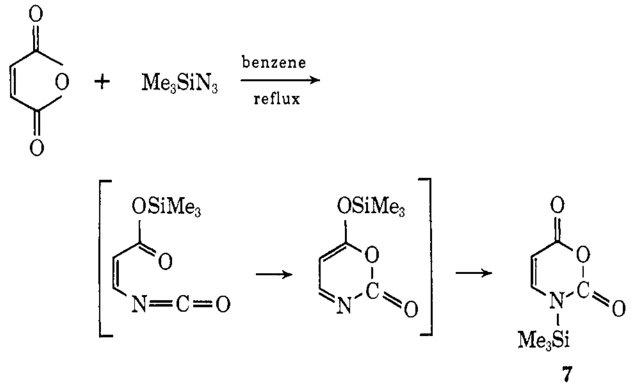


azides with isocyanates bearing electron-withdrawing groups are known.[9]

Heating **6** in refluxing *o*-dichlorobenzene gave only polymeric material, in accord with the known cycloreversion of tetrazolinones.[9a] Cycloreversion of **10** would give two molecules of the readily polymerizing **1**.

Discussion

The **1** → **3** cyclization bears formal analogy to the previously reported synthesis of oxazinedione **7** from maleic anhydride and trimethylsilyl azide,[6b] which is now seen as an electrocyclic ring closure followed by a suprafacial 1,5 shift of trimethylsilyl. **1** → **3** cyclization requires a higher temperature, in accord with the known acceleration of the Cope rearrangement by -OR substituents.[10]



Although sorboyl chloride is converted to 3-methyl-2(1*H*)-pyridone upon silyl azide treatment, the yield is low and subject to two restraints. At low reaction temperatures, unrearranged sorboyl azide **5** accumulates and diverts isocyanate by cycloaddition to **6**. At higher temperatures, isocyanate polymerizes. In addition, only about 30% of **1** appears to be in the cis form capable of cyclization. Optimum conditions are high dilution at a temperature where Curtius rearrangement of **5** is rapid and sufficient activation energy for the **1** → **3** cyclization is available, but where polymerization of **1** is slow. The toluene reaction apparently maximizes the yield of **1**.

Since the spectroscopic yield of **6** was greater than the observed α,β-cis population (11%) of thermolyzed sorbaldehyde,[8] we postulate that an acid-catalyzed equilibrium is present, resulting in the formation of considerable α,β-cis **1**. At lower temperatures, as in the attempted trifluoroacetic acid isomerization of **1**, the high-energy electrocyclic process yielding pyridone cannot compete with acid-catalyzed polymerization. This postulate is also consistent with the observed low yield of pyridone in the vapor phase reaction and with the low yield in mesitylene and xylene.

Experimental Section

General Comments.—All reactions involving azides were carried out under a blanket of purified nitrogen, behind appropriate shielding. Sorbic acid (Fisher) and trimethylsilyl azide (Petrarch Systems) were used as received. Infrared spectra were determined on a Perkin-Elmer Model 700 or 720 spectrophotometer, ultraviolet spectra on a Cary Model 14 spectrophotometer, and nuclear magnetic resonance spectra on a Varian XL-100-15 spectrometer as dilute solutions in deuteriochloroform or carbon tetrachloride with tetramethylsilane as internal standard. Nmr spectra are reported in δ units, parts per million downfield from tetramethylsilane.

Sorboyl Chloride (8).—Thionyl chloride (13 ml) was added over a 1.5-hr period to a warm (60°) solution of 5.6 g (0.05 mol) of sorbic acid in 160 ml of benzene. After the mixture had been heated at reflux for 16 hr, material boiling up to 81° was removed by distillation. Fractionation of the brown residue gave 5.3 g (81%) of **8**: bp 75° (20 mm); ir 1750, 1620 cm^{-1}; nmr δ 7.30 and 7.70 (total 1 H, multiplets, HC=CCOCl), 5.8–6.6 (3 H, multiplet, olefinic), and 1.9 ppm (total 3 H, two doublets, J = 5 Hz, $CH_3CH=$).

1,3-Pentadienyl Isocyanate (1).—Trimethylsilyl azide (5.6 g, 0.05 mol) was added to a refluxing solution of 5.0 g (0.038 mol) of **8** in 70 ml of toluene. After heating for 20 hr at reflux, the mixture had evolved 750 ml of N_2. Ir analysis showed intense N=C=O absorption (2300 cm^{-1}) as well as moderate absorption at 2150 ($RCON_3$) and 1770 cm^{-1}. Removal of the toluene by evaporation at reduced pressure gave highly variable quantities (0.1–1.5 g) of **1**, bp 40° (20 mm), together with a polymeric brown residue. Pure **1** rapidly resinified and was handled in dilute $CHCl_3$ or CCl_4 solution: ir (film) 3050 (m), 3020 (m), 2960 (m), 2930 (m), 2300 (vs), 1620 (s), 1490 (m), 1440 (m), 1380 (m), 1320 (m), 1260 (m), 980 (s), 920 (m), and 600 cm^{-1} (m); nmr δ 5.9 (4 H, m) and 1.7 ppm (3 H, d, J = 5 Hz); uv max (heptane) 247 nm (log ϵ 4.4).

3-Methyl-2(1*H*)-pyridone (3).—The reaction described above for preparation of **1** was carrried out up to removal of the toluene. The semisolid was taken up in 190 ml of *o*-dichlorobenzene and heated at reflux. Ir analysis of periodically removed samples showed a steady decrease in absorption at 2300, 2150, and 1770 cm^{-1} together with the growth of a new peak at 1660 cm^{-1}. After 16 hr at reflux the yield of **3** was maximized at 30% (by ir analysis assuming ϵ 500 at 1660 cm^{-1}). Attempts to increase conversion to **3** by adding hydroquinone to inhibit polymerization failed, giving only hydroquinone-contaminated product. The yield of **3** in reactions using xylene or mesitylene as solvent was less than 5% as estimated by ir.

The mixture was cooled and solvent was removed by evaporation at reduced pressure, resulting in loss of some **3** by codistillation (distillate showed absorption at 1660 cm^{-1}). Sublimation (150°, 0.025 mm) of the residue gave 0.7 g (17%) of **3**, mp 130–

---

[9] (a) J. M. Vandensavel, G. Smets, and G. L'abbé, *J. Org. Chem.*, **38**, 676 (1973); (b) S. S. Washburne and W. R. Peterson, Jr., unpublished results.

[10] J. A. Berson and E. J. Walsh, Jr., *J. Amer. Chem. Soc.*, **90**, 4730 (1968).

140°. Recrystallization from benzene gave white crystals of **3**: mp 140–141° (lit.[11] mp 140–141.5°); picrate mp 158–160° (lit.[11] mp 157.5–159°); ir ($CHCl_3$) 2780, 1660, 1640, 1610, 1570, 1480, 1420, 1380, 1350, 1255, 1230, 1164, 986, 885, 775, 735 cm^{-1} (in complete accord with literature[12] ir); nmr ($CDCl_3$) δ 13.4 (broad s, 1, NH), 7.25 (d, 2, J = 7 Hz), 6.1 ppm (t, 1, J = 7 Hz) (in complete accord with literature[13] nmr).

Anal. Calcd for C_6H_7NO: C, 66.04; H, 6.47; N, 12.84. Found: C, 66.24; H, 6.61; N, 12.88.

Vapor-Phase Pyrolysis of 1,3-Pentadienyl Isocyanate (1).—A 30 × 2.5 cm Pyrex column packed with glass helices and swept with a nitrogen stream was employed. The inlet was a septum cap allowing material to be syringe injected. The semisolid product obtained by the procedure for **1** above was taken up in $CHCl_3$ (20 ml). The oven was heated to 400° in a tube furnace and the material was injected in 1-ml portions with nitrogen sweeping the pyrolysate into a trap at −78°. Considerable carbonization was noticed in the pyrolysis zone. Ir analysis of the pyrolysate showed an intense band at 2300 cm^{-1} (**1**) but only a faint absorption at 1660 cm^{-1} (**3**). Peaks at 1770 (**6**) and 2150 cm^{-1} (**5**) had totally disappeared. Tlc analysis of the pyrolysate showed a faint spot of R_f corresponding to authentic **3** and an intense spot corresponding to **1** (silica gel, 10% *i*-PrOH in $CHCl_3$).

Pyrolysis of 3.—A solution of 50 mg of **3** in 1 ml of $CHCl_3$ was pyrolyzed in an identical fashion. No carbonization in the tube was observed, and the pyrolysate exhibited an unchanged ir spectrum.

Attempted Acid-Catalyzed Isomerization of 1.—A solution of *ca.* 250 mg of **1** in 5 ml of $CHCl_3$ exhibited an unchanged ir spectrum after being stored for 16 hr with 0.15 ml of trifluoroacetic acid. An additional 0.1 ml of CF_3CO_2H was added and the mixture was heated at reflux for 36 hr. The ir of the brown mixture showed no absorption at 2300 or 1660 cm^{-1}. The tlc showed no spot of R_f corresponding to **3**.

Tetrazolinone 6.—A refluxing solution of 4.9 g (0.037 mol) of **8** in 30 ml of heptane was treated over an 0.5-hr period with 5.8 g (0.05 mol) of trimethylsilyl azide. After 16 hr, 600 ml of N_2 had been evolved and a white powder had separated from the solution. Cooling and filtration gave 2.5 g (55%) of **6**: mp 161–162° (colorless crystals from benzene); ir ($CHCl_3$) 3030 (m), 1770 (s), 1730 (s), 1610 (s), 1600 (s), 1580 (s), 1500 (m), 1400 (m), 1380 (m), 1320 (s), 1250 (m), 1200 (s), 1140 (m), 1090 (m), 980 (m), 960 (s), 910 (m), 840 (m), and 640 cm^{-1} (s); nmr ($CDCl_3$) δ 7.6 (m, 1, HC=CC=O), 6.0–6.9 (m, 7, olefinic), 1.8 ppm (d of d, 6, J = 5 Hz, CH_3CH=C); uv max (heptane) 285 nm (log ε 4.4); uv max (heptane, OH^-) 265 nm (log ε 4.5); mass spectrum *m/e* (rel intensity) 247 (4), 246 (27), 152 (7), 137 (6), 109 (22), 95 (100), 81 (20), 80 (19), 67 (34), 54 (22), 41 (42), 39 (35).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 58.53; H, 5.73; N, 22.75. Found: C, 58.01; H, 5.42; N, 22.97.

Thermolysis of 6.—A solution of 50 mg of **6** in 3 ml of *o*-dichlorobenzene was heated at 180° for 16 hr. The solution turned brown and deposited a black polymeric material. Ir analysis showed the absence of absorption at 1770, 1730, and 1660 cm^{-1}, implying that **6** had been consumed but that **3** had not been formed.

Acknowledgments.—This investigation was sponsored under Grant No. CA-13120-01 from the National Cancer Institute. We thank Mr. John Simolike for obtaining the mass spectra.

Registry No.—**1**, 40711-07-7; **3**, 1003-56-1; **4**, 110-44-1; **6**, 40711-50-0; **8**, 2614-88-2.

---

[11] G. F. van Rooyen, C. Brink, and P. de Villiers, *Tydskr. Natuurwetensk.*, **4**, 182 (1964); *Chem. Abstr.*, **63**, 13202*d* (1965).

[12] E. Spinner and J. C. B. White, *J. Chem. Soc. B*, 991 (1966).

[13] C. L. Bell, R. S. Egan, and L. Bauer, *J. Heterocycl. Chem.*, **2**, 420 (1965).

Diaziridines. II. The Addition of Diaziridines to Electrophilic Acetylenes[1]

HAROLD W. HEINE,* THOMAS R. HOYE, PAUL G. WILLIARD, AND REBECCA COWAN HOYE

Department of Chemistry, Bucknell University, Lewisburg, Pa. 17837

Received March 30, 1973

Addition of 3,3-dialkyl-, 1,3-dialkyl-, and 1,3,3-trialkyldiaziridines to dibenzoylacetylene, diethyl acetylenedicarboxylate, and ethyl propiolate gives, generally, adducts in which the diaziridine ring is no longer intact. For example, addition of 1,3-dialkyl- and 1,3,3-trialkyldiaziridines to dibenzoylacetylene forms 2-(alkylidenehydrazino)-1,4-diphenyl-2-butene-1,4-diones (**2**). Evidence is presented that it is the alkylated nitrogen of 1-methyl-3,3-pentamethylenediaziridine which adds to the triple bond of dibenzoylacetylene. Stereochemical studies show that diaziridines add to ethyl propiolate to give trans adducts. Hydrolysis of 2-(alkylidenehydrazino)-1,4-diphenyl-2-butene-1,4-diones is shown to be a useful method for the preparation of 1-alkyl-3-phenyl-5-benzoylpyrazoles.

Only a few studies have been reported on the addition of N-unsubstituted or N-monosubstituted diaziridines to alkenes. Miller has found that 3-ethyl-3-methyldiaziridine adds to acrylonitrile and to butenone to form 1-(β-cyanoethyl)-3-ethyl-3-methyldiaziridine and 1-(β-acetylethyl)-3-ethyl-3-methyldiaziridine, respectively.[2] 1,3,3-Trialkyldiaziridines have been shown to react similarly with esters of ethenesulfonic acid.[3] The reaction of 3,3-pentamethylenediaziridine with diphenylcyclopropenone has also been described.[4] Based on the products of reaction it was presumed that the diaziridine added to the carbonyl group rather than the olefinic linkage

No investigations have yet been reported on the addition of diaziridines to electrophilic acetylenes. We have observed that, in contrast to aziridines which have been shown to add to a number of acetylenes to give *N*-vinylaziridines,[5] diaziridines usually react with activated acetylenes to give products in which the diaziridine ring is no longer intact.

Results

Diaziridines **1a–f** react with dibenzoylacetylene in benzene at ambient temperatures to give the 2-(alkylidenehydrazino)-1,4-diphenyl-2-butene-1,4-diones **2a–f** (Table I) (Scheme I).

The nmr spectra of **2a–f** were consistent with the proposed structures. Thus, a singlet (1 H) corresponding to the vinyl proton appeared in the region of δ 5.6–6.4 for all of these compounds. Furthermore, the

---

[1] For the previous paper in this series, see H. W. Heine, P. G. Williard, and T. R. Hoye, *J. Org. Chem.*, **37**, 2980 (1972).

[2] J. Miller, British Patent 1,081,292 (Aug 30, 1967); *Chem. Abstr.*, **68**, 114071h (1968).

[3] H. Dorn and K. Walter, *Justus Liebigs Ann. Chem.*, **720**, 98 (1968).

[4] J. W. Lown, *J. Chem. Soc. C*, 1338 (1969).

[5] O. C. Dermer and G. E. Ham, "Ethylenimine and Other Aziridines," Academic Press, New York, N. Y., 1969, p 138.