7.0–7.5 (m, 10); mass spectrum (70 eV) *m/e* (rel intensity) 292 (14), 183 (72), 165 (18), 105 (100), and 77 (66).

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.36; H, 7.21. Found: C, 82.48; H, 6.68.

Methyl 2-Benzhydrylidenecyclohexanecarboxylate (7).—A solution of 5.84 g of lactone **6** in anhydrous methanol saturated with hydrogen chloride gas was stirred at ambient temperature for 48 hr. The solvent was removed and the residue taken up in ether and washed with water, 5% sodium bicarbonate solution, and saturated salt solution. The ether solution was dried ($MgSO_4$) and evaporated leaving 6.0 g (98%) of crude ester **7**. A distilled sample of **7**, bp 162–164° (0.4 mm), crystallized slowly from hexane and showed mp 51–52°; ir 5.75 μ; nmr ($CDCl_3$) 1.3–2.0 (m, 6), 2.0–2.65 (m, 3), 3.60 (s, 3, OCH_3), and 7.1 ppm (broad s, 10); mass spectrum (70 eV) *m/e* (rel intensity) 306 (90), 275 (12), 247 (70), 246 (90), 167 (95), and 91 (100).

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.36; H, 7.21. Found: C, 82.44; H, 7.28.

1-(Hydroxydiphenylmethyl)-2-benzhydrylidenecyclohexane (2).—To a solution of phenyllithium, prepared from 7.8 g of bromobenzene and 0.7 g of lithium, in ether was added an ether solution of 5 g of unsaturated ester **7**. After stirring for 2.5 hr the reaction was worked up in the usual manner to give, after crystallization from hexane, 6.8 g of pale yellow solid. A pure sample of unsaturated alcohol **2** was obtained by recrystallization from hexane (Norit) and showed: mp 154.5–156.5° (lit.[3] mp 112–113°); ir ($CHCl_3$) 2.8 μ (OH); nmr 1.4–2.0 (m, 8), 2.3 (s, 1), 2.3–2.9 (m, 2), 3.85 (broad s, 1), 6.5–6.9 (m, 5) and 7.0–7.3 ppm (m, 15); uv $\lambda_{\max}^{\mathrm{EtOH}}$ 249 nm (ϵ 10,900); mass spectrum (70 eV) *m/e* (rel intensity) no molecular ion, 412 (4), 249 (12), 248 (56), 247 (17), 205 (5), 184 (16), 183 (100), 169 (7), 117 (14), 105 (56), 91 (24), and 77 (32).

Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.03. Found: C, 88.96, H, 7.11.

1,2-Dibenzhydrylidenecyclohexane (1).—A solution of alcohol **2** in benzene containing several crystals of iodine was refluxed for 24 hr. The solution was washed with sodium bisulfite solution and evaporated to leave 1.26 g of solid. Recrystallization from hexane afforded 333 mg of white solid, mp 174–175° (lit.[8] mp 247–248°). An analytical sample was prepared by sublimation *in vacuo:* nmr ($CDCl_3$) 1.4–2.0 (m, 4), 2.0–2.3 (m, 4), 6.5–6.9 (m, 4), and 7.0–7.3 ppm (m, 16); uv $\lambda_{\max}^{\mathrm{EtOH}}$ inflection at 240 nm (ϵ 15,400), 286 (7500); mass spectrum (70 eV) *m/e* (rel intensity) 413 (37), 412 (100), 335 (40), 297 (14), 291 (14), 215 (19), 167 (19), and 165 (24).

Anal. Calcd for $C_{32}H_{28}$: C, 93.21; H, 6.79. Found: C, 93.09; H, 6.82.

A solution of 300 mg of **1** diene in methylene chloride was ozonized at −78° for 8 min at which time the solution turned blue. The solution was flushed with nitrogen to remove excess ozone and was then added to a stirred solution of 8 ml of 30% hydrogen peroxide in 8 ml of 10% sodium hydroxide solution. The mixture was extracted with ether affording 206 mg of solid which was converted into a 2,4-dinitrophenylhydrazone derivative, mp 239–241°, which did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone derivative of benzophenone.

2-Benzhydrylidene-1(hydroxydi-*p*-tolylmethyl)cyclohexane (2a).—The reaction of *p*-methylphenyllithium, prepared from 10.26 g (0.06 mol) of *p*-bromotoluene and 0.833 g (0.12 g-atom) of lithium, with 6.40 g (0.02 mol) of methyl-2-benzhydrylidenecyclohexanecarboxylate gave after the usual work-up and recrystallization from hexane 6.3 g (69%) of **2a**: mp 167–169°; $\lambda_{\max}^{\mathrm{EtOH}}$ 251 nm (ϵ 13,700); nmr ($CDCl_3$) 1.2–2.0 (m, 7), 2.21 (s, 6, CH_3Ar), 2.3–2.8 (m, 2), 3.80 (broad s, 1), 6.35–6.80 (m, 4), 6.82 (s, 4), and 6.90–7.12 ppm (m, 10); mass spectrum (70 eV) *m/e* (rel intensity) no molecular ion, 440 (16) 248 (21), 212 (19), 211 (100), 119 (48), and 91 (30).

Anal. Calcd for $C_{34}H_{34}O$: C, 89.04; H, 7.47. Found: C, 88.98; H, 7.69.

1-Benzhydrylidene-2-*p*-tolylidenecyclohexane (1a).—A solution of 0.458 g of **2a** in benzene containing a trace of iodine was heated at reflux for 1 day. The solvent was removed and the residue recrystallized from hexane to yield 392 mg (89%) of a white solid: mp 185–186°; $\lambda_{\max}^{\mathrm{EtOH}}$ 286 nm (ϵ 11,000); nmr ($CDCl_3$) 1.2–2.0 (m, 4), 2.0–2.98 (m, 2), 2.22 (s, 3, CH_3Ar), and 6.30–7.35 ppm (m, 18); mass spectrum (70 eV) *m/e* (rel intensity) 440 (100), 363 (31), and 349 (14).

Anal. Calcd for $C_{34}H_{32}$: C, 92.68; H, 7.32. Found: C, 92.68; H, 7.42.

Registry No.—**1**, 27621-80-3; **1a**, 27621-81-4; **2**, 27621-82-5; **2a**, 27621-83-6; **6**, 27621-84-7; **7**, 27621-85-8.

A Novel 1,3-Dipolar Addition Reaction of Pyridinium Carbethoxycyanomethylide

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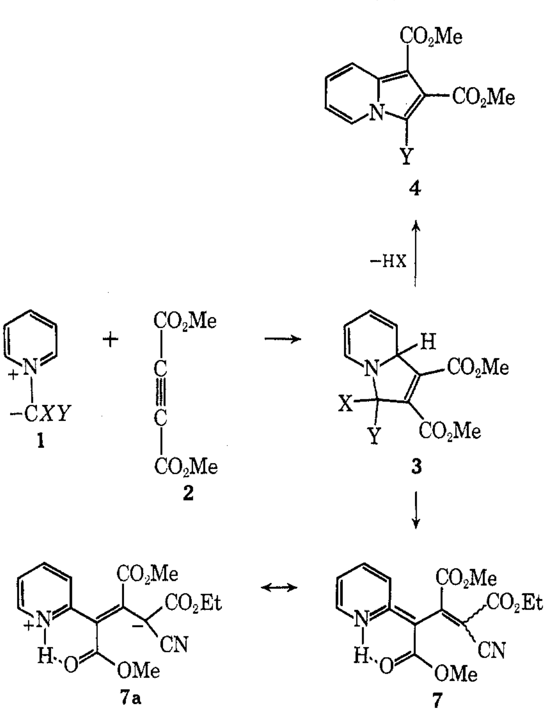
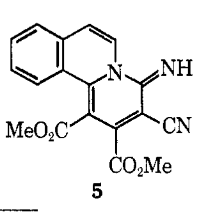
Numerous pyridinium, and related heteroaromatic, ylides (**1**) have been reported to react with dimethyl acetylenedicarboxylate (**2**) to yield indolizines (**4**) *via* the intermediate dihydroindolizines (**3**).[1-3]



In a few cases, however, these 1,3-dipolar additions give other products as well. For example, Linn and coworkers[2] found that isoquinolinium dicyanomethylide reacts with **2** to yield the iminoquinolizine **5** in addition to the expected benzindolizine. At about the same time Boekelheide and Fedoruk[4] reported the isolation of compound **6** from the reaction of 3-methyl-1-imidazolium dicyanomethylide with **2**, rather than the anticipated diazapentalene.



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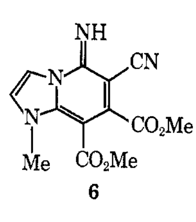

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[2] W. J. Linn, O. W. Webster, and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3652 (1965).

[3] V. Boekelheide and K. Fahrenholtz, *ibid.*, **83**, 458 (1961).

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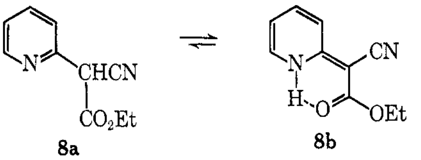
We have recently discovered an anomalous reaction of pyridinium carbethoxycyanomethylide (**1**, X = CN, Y = CO_2Et) with **2**. Instead of the expected indolizine **4** (Y = CO_2Et), the only isolable product proved to be the aconitate ester **7**. Proof of structure rests upon the analytical data given in the Experimental Section. A noteworthy feature of **7** is its intramolecularly hydrogen-bonded anhydro base grouping, proof of which is most strikingly demonstrated by the broad singlet observed in its nmr spectrum at δ 14.6. Such marked deshielding is, of course, characteristic of intramolecularly hydrogen-bonded protons. The downfield displacement of the aromatic protons with respect to their positions in **8b** (*vide infra*) suggests that charge-separated structures such as **7a** may be important contributors to the resonance hybrid.

In order to test the generality of occurrence of the anhydro base grouping observed in **7**, the closely related compound, ethyl α-(2-pyridyl)cyanoacetate (**8**), was synthesized.[5] Although Hamana and Yamazaki gave the structure as **8a**, the nmr evidence obtained in our laboratory (a broad singlet at δ 14.1) clearly calls for the tautomeric form **8b**. If any **8a** is present in equilibrium with **8b**, its concentration is below the limits of detection by nmr spectrometry.



8a **8b**

The formation of **7** can be rationalized in terms of a base-catalyzed ring opening of the intermediate dihydroindolizine (**3**), a scheme similar to that suggested by Boekelheide and Fedoruk[4] for the formation of **6**.

Experimental Section[7]

Pyridinium Carbethoxycyanomethylide (1).—A solution of 19.0 g (0.10 mol) of ethyl bromocyanoacetate (Aldrich Chemical Co.), 15.8 g (2.20 mol) of pyridine, and 100 ml of chloroform was allowed to stand at room temperature under nitrogen for 2 days. The deep red mixture was then extracted with two 50-ml portions of 5% aqueous K_2CO_3. The chloroform layer was dried (K_2CO_3), reduced to *ca.* one-fourth its original volume, and chromatographed on neutral alumina eluting with a mixture of chloroform and benzene (1:1 v/v). Evaporation of the eluate gave 9.7 g (51% based upon ester) of the bright yellow ylide, mp 113.5–114° (lit.[8] 112–113°).

***α,β*-Dimethyl *α*-Ethyl *α*-(2-Pyridyl)-*α*-cyanoaconitate** (7).—A solution of 2.96 g (21.0 mmol) of freshly distilled dimethyl acetylenedicarboxylate in 10 ml of methanol was added dropwise to a stirred solution of 4.00 g (21.0 mmol) of pyridinium carbethoxycyanomethylide dissolved in 50 ml of methanol at room temperature under nitrogen. After the addition was complete (*ca.* 15 min), the mixture was stirred for an additional hr. The orange precipitate was filtered off, washed with cold methanol, and dried. Recrystallization from acetonitrile gave 4.8 g (68%) of **7** as orange flakes: mp 232–233°; ir (KBr) 2190 (CN), 1740, 1705 (CO), 1635 cm^{-1} (C=C); nmr (DMSO-d_6, TMS) δ 1.14 (t, 3, CH_2CH_3), 3.60 and 3.88 (2 × s, 2 × 3, CO_2CH_3), 4.08 (q, 2, CH_2CH_3), 8.19 (m, 2, $C_{3,5}H$), 8.64 (m, 1, C_4H), 9.05 (m, 1, C_6H), 14.6 ppm (broad s, 1, NH); uv max (95% EtOH) 345 nm (log ϵ 4.51), 258 (3.71), 222 (3.84); mass spectrum *m/e* 332 (35, M^+), 301 (31, $M^+ - OCH_3$), 287 (6, $M^+ - OC_2H_5$), 273 (11, $M^+ - CO_2CH_3$), 259 (20, $M^+ - CO_2C_2H_5$), 253 (17, $M^+ - C_5H_5N$), 227 (100, $M^+ - C_5H_4NHCN$), 225 (85, $M^+ - C_5H_4NC_2H_5$), 80 (40, $C_5H_5NH^+$), 79 (29, $C_5H_5N^+$), 78 (28, $C_5H_4N^+$).

Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: C, 57.59; H, 5.02; N, 8.53.

Ethyl *α*-(2-Pyridyl)cyanoacetate (8).—Ethyl cyanoacetate (22.6 g, 0.20 mol) was added dropwise to a stirred ice-cold solution of 19.0 g (0.20 mol) of pyridine *N*-oxide dissolved in 30.6 g (0.30 mol) of acetic anhydride. After the addition was complete (*ca.* 30 min), the mixture was allowed to warm to room temperature and stand overnight under dry N_2. Water (100 ml) was added and the resulting mixture was steam-distilled under reduced pressure on a rotary evaporator until the distillate was no longer acidic. The residue was taken up in 100 ml of chloroform, washed with water (two 50-ml portions), and then dried over basic alumina. After removing the solvent under reduced pressure, the remaining dark red oil was chromatographed on neutral alumina using ethyl acetate as the eluting solvent. Evaporation of the solvent from the yellow fraction which was obtained yielded a yellowish brown oil which slowly solidified upon standing for several days. Two recrystallizations from benzene afforded 7.3 g (19%) of **8** as yellow powder: mp 104–105° (lit.[6] 107–108°); ir (KBr) 2210 (CN), 1710 cm^{-1} (CO); nmr ($CDCl_3$, TMS) δ 1.30 (t, 3, CH_3), 4.22 (q, 2, CH_2), 6.76 (broad t, 1, C_5H), 7.32 (broad d, 1, C_3H), 7.67 (m, 1, C_4H), 7.92 (broad d, 1, C_6H), 14.0 ppm (broad s, 1, NH).

Registry No.—**1**, 17281-70-8; **7**, 27808-63-5; **8**, 27808-64-6.

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[7] Melting points were determined on a calibrated Mel-Temp apparatus. Infrared Spectra were recorded on a Perkin-Elmer 237 spectrophotometer, nmr spectra on a Varian A-60A spectrometer, and uv spectra on a Beckman DB spectrophotometer. The mass spectrum was kindly provided by the Union Carbide Technical Center, South Charleston, W. Va., and was determined with a Bendix time-of-flight spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

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Synthesis of Methyl 4-*O*-(Dichlorodimethoxy-*o*-orsellinyl)-2,6-dideoxy-*α*-D-*arabino*-hexopyranoside (Methyl Glycoside of Methylcuracin)[1]

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Curacin, the carbohydrate ester end group isolated from several antibiotics, *e.g.*, Curamycin,[2] Avilamycin,[3] and Everninomicins B and D,[4,5] has been proved to be 4-*O*-dichloroisoeverninyl-2,6-dideoxy-D-*arabino*-hexose (**1**) by physical and chemical methods.[3,6,7]

The present research was undertaken to confirm the structure of curacin by synthesis, but to simplify the problem, curacin (**1**) was first converted to **4** by two alternative methods. Thus, methylation of **1** with diazomethane produced methylcuracin (**2**)[2] which on treatment with methanol–hydrogen chloride afforded **4**.

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[1] Support of this work by the Consejo Nacional de Investigaciones Científicas y Técnicas is gratefully acknowledged. One of us (E. M. G.) thanks the Universidad de Buenos Aires for a research fellowship.

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