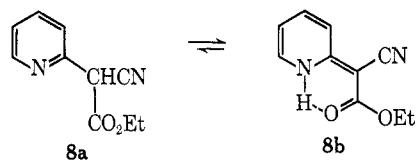
We have recently discovered an anomalous reaction of pyridinium carbethoxycyanomethylide (**1**, X = CN, Y = CO_2Et) with **2**. Instead of the expected indolizine **4** (Y = CO_2Et), the only isolable product proved to be the aconitate ester **7**. Proof of structure rests upon the analytical data given 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, $C_3,_5H$), 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.[5] 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.

(5) M. Hamana and M. Yamazaki, *Chem. Pharm. Bull.*, **11**, 415 (1963); see ref 6 for a review of this and related work.

(6) E. Ochiai, "Aromatic Amine Oxides," Elsevier, New York, N. Y., 1967, Chapter 7.

(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**.

(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.

(2) O. L. Galmarini and V. Deulofeu, *Tetrahedron*, **15**, 76 (1961).

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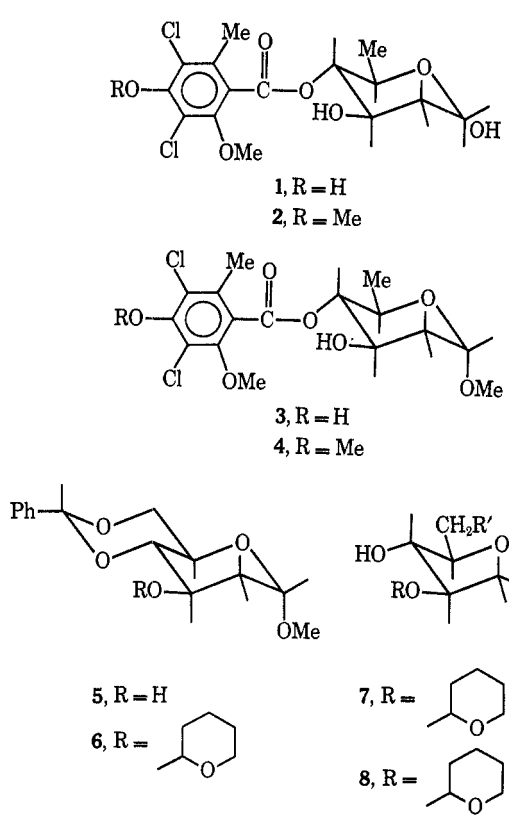
On the other hand, compound **1** was treated with methanol–hydrogen chloride yielding methyl curacinoside (**3**)[6] which was, in turn, methylated with diazomethane to **4**.

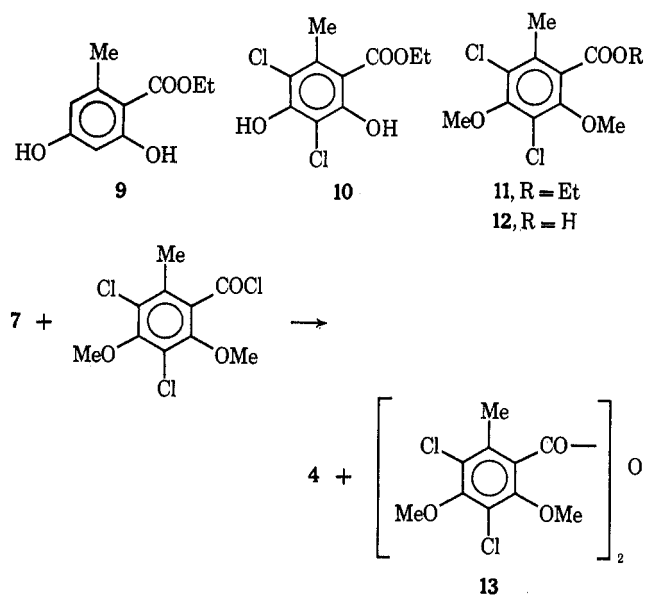
Compound **4** was synthesized starting with methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*arabino*-hexopyranoside (**5**).[8,9] In order to protect the hydroxyl group at C-3 with a substituent stable in alkaline and neutral media but labile under mild conditions of acidic hydrolysis, compound **5** was treated with 2,3-dihydro-4*H*-pyran in *p*-dioxane in the presence of a catalytic amount of *p*-toluenesulfonic acid to give methyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-(tetrahydropyran-2-yl)-α-D-*arabino*-hexopyranoside (**6**).

Recently, Hanessian[10] reported a novel ring opening of benzylidene acetals of sugars by *N*-bromosuccinimide to give, in the case of 4,6-benzylidene derivatives, the corresponding 6-bromo-4-benzoates. Treatment of compound **6** with 1.1 equiv of *N*-bromosuccinimide in boiling carbon tetrachloride, in the presence of an excess of barium carbonate, afforded a product that, without purification, was submitted to lithium aluminum hydride reduction. Removal of the benzoyl group at C-4 and debromination at C-6 occurred simultaneously as the main reaction and gave methyl 2,6-dideoxy-3-*O*-(tetrahydropyran-2-yl)-α-D-*arabino*-hexopyranoside (**7**); this was separated from the benzylic alcohol formed in the reaction by high-vacuum distillation. From the distillation residue, by means of preparative tlc, compounds **5** and **6** were also isolated along with a small amount of a new crystalline product that was shown to be methyl 6-bromo-2,6-dideoxy-3-*O*-(tetrahydropyran-2-yl)-α-D-*arabino*-hexopyranoside (**8**).

On the other hand, dichlorodimethoxy-*o*-orsellinyl chloride was prepared by the following sequence. Ethyl *o*-orsellinate (**9**) was obtained from the reaction of ethyl acetoacetate with ethyl crotonate[11] followed by aromatization with ferric chloride.[12] Chlorination of **9** with sulfuryl chloride in ether yielded ethyl dichloro-*o*-orsellinate (**10**),[13] which on methylation with diazomethane produced ethyl dichlorodimethoxy-*o*-orsellinate (**11**). Saponification of **11** with aqueous potassium hydroxide produced the acid **12**, which had been previously obtained by Nolan and Murphy.[14] Treatment of **12** with thionyl chloride yielded the corresponding acid chloride that was purified by distillation and used immediately thereafter.

Condensation between compound **7** and the chloride from acid **12** was carried out in pyridine using an excess of the acid chloride. After the usual proccess of pouring into ice–water, extraction with chloroform, and washing the chloroform extract with diluted acid and base, two main products were obtained. Crystallization from ethanol afforded dichlorodimethoxy-*o*-orsellinic anhydride (**13**); this finding was not unexpected since aromatic acid anhydrides are readily formed from the corresponding acid chlorides on treatment with pyridine and water.[15] In the ethanolic mother liquors, two products were detected (tlc); these were separated by preparative tlc. The products were identified as the anhydride **13** and the expected product **4** which was identical in all respects (melting point, ir, nmr) with the material obtained from the natural source. This result indicated that the tetrahydropyranyl group had been cleaved during the washing proccess thus confirming its lability to acid media.[16]





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Experimental Section

Melting points are uncorrected. The ir spectra were obtained on a Perkin-Elmer 137 spectrophotometer. Nmr spectra were determined with a Varian A-60 spectrometer. Microanalyses were performed by Alfred Bernhardt Laboratory, W. Germany. Preparative tlc were conducted on aluminium oxide (PF_{254}, Merck).

Methyl 4-*O*-Dichloroisoeverninyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (Methylcuracinoside) (3).—Curacin (1) (562 mg) was dissolved in methanol–hydrogen chloride (10 mg/ml) (28 ml) and the solution was heated under reflux for 6 hr. To the cooled solution, water (60 ml) was slowly added giving crystals that were collected by filtration. Recrystallization from methanol–water (1:1) yielded **3** (426 mg): mp 148–150°; $[\alpha]^{24}D$ 54.5° ($CHCl_3$); nmr ($CDCl_3$) δ 1.32 (d, 3, J = 6 Hz, CH_3CH), 1.70–2.70 (m, 2, CH_2), 2.36 (s, 3, CH_3Ph), 3.34 (s, 3, CH_3O), 3.91 (s, 3, CH_3OPh), 4.80 (q, 1, $J_{1,2a}$ = 3.5, $J_{1,2e}$ = 1.5 Hz, H-1 of α-D form), 4.86 (t, 1, J = 9 Hz, H-4).

Anal. Calcd for $C_{16}H_{20}Cl_2O_7$: C, 48.62; H, 5.10; Cl, 17.94. Found: C, 48.55; H, 5.14; Cl, 18.05.

Methyl 4-*O*-(Dichlorodimethoxy-*o*-orsellinyl)-2,6-dideoxy-α-D-*arabino*-hexopyranoside (4). A. From 3.—Compound **3** (210 mg) was suspended in ether (10 ml) and treated with an excess of diazomethane in ether. After 48 hr at 5°, the solvent was evaporated, and the solid residue was crystallized from petroleum ether (bp 100–120°). Recrystallization from the same solvent gave **4** (170 mg): mp 101–102°; $[\alpha]^{20}D$ 66.8° ($CHCl_3$); nmr ($CDCl_3$) δ 1.33 (d, 3, J = 6 Hz, CH_3CH), 1.75–2.65 (m, 2, CH_2), 2.20 (s, 3, CH_3Ph), 3.33 (s, 3, CH_3O), 3.91 (s, 6, CH_3OPh), 4.79 (q, 1, $J_{1,2a}$ = 3.5, $J_{1,2e}$ = 1.5 Hz, H-1 of α-D form), 4.85 (t, 1, J = 9 Hz, H-4).

Anal. Calcd for $C_{17}H_{22}Cl_2O_8$: C, 51.92; H, 5.64; Cl, 18.03. Found: C, 51.73; H, 5.84; Cl, 17.96.

B. From 2.—Methylated curacin (**2**)[2] (152 mg) was boiled under reflux with methanol–hydrogen chloride (10 mg/ml) (10 ml) for 6 hr. Addition of water (25 ml) produced a gummy residue which was dried and crystallized from petroleum ether (bp 100–120°). After one recrystallization from the same solvent, compound **4** (28 mg) had mp 101–102°, and its ir spectrum which resulted was identical with the one obtained from the previous compound.

Methyl 4,6-*O*-Benzylidene-2-deoxy-3-*O*-(tetrahydropyran-2-yl)-α-D-*arabino*-hexopyranoside (6).—A solution of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*arabino*-hexopyranoside (**5**) (3 g) in *p*-dioxane (15 ml) was treated with freshly distilled 2,3-dihydro-4*H*-pyran (10 ml) and *p*-toluenesulfonic acid (30 mg). The mixture was kept for 24 hr at room temperature with occasional shaking and then for 3 days at 5°. Chloroform (50 ml) was added, and the solution was washed successively with diluted ammonia and water. The residue obtained for evaporation of the dried ($MgSO_4$) solution crystallized after 24 hr in a desiccator. The crystalline product was washed with petroleum ether and then recrystallized from cyclohexane. Compound **6** (1.6 g) had mp 124–125°; $[\alpha]^{20}D$ 132.8° ($CHCl_3$); ir spectrum showing no hydroxy bands; nmr ($CDCl_3$) δ 1.64 (m, 6, tetrahydropyranyl protons), 1.74–2.55 (m, 2, CH_2), 3.36 (s, 3, CH_3O), 4.83 (q, 1, $J_{1,2a}$ = 3.5; $J_{1,2e}$ = 1.5 Hz, H-1 of α-D form), 4.95 (m, 1, hemiacetalic proton of tetrahydropyranyl group), 5.62 (s, 1, benzylic proton), 7.45 (s, 5, aromatic protons).

Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.12; H, 7.48. Found: C, 65.08; H, 7.53.

Methyl 2,6-Dideoxy-3-*O*-(tetrahydropyran-2-yl)-α-D-*arabino*-hexopyranoside (7).—A solution of compound **6** (700 mg) and *N*-bromosuccinimide (390 mg) in dry carbon tetrachloride (70 ml) containing barium carbonate (5 g) was stirred and heated under reflux for 1 hr. The reaction mixture was cooled to 0° and filtered, and the filtrate was evaporated in the presence of a small amount of barium carbonate. The syrupy residue (tlc showed that the starting material had almost all reacted) was dissolved in dry ether (100 ml) and treated with lithium aluminum hydride (3 g), and the mixture was refluxed for 3 hr. The excess of reagent was destroyed by addition of ice, and the mixture was extracted with ether. The ethereal extract was washed with water, dried ($MgSO_4$), and evaporated to dryness. The oily residue was distilled *in vacuo* (10^{-3} Torr) giving, at 25–30°, an oil that was shown to be (ir, nmr) benzyl alcohol, and at 60–65° a glassy product that crystallized on scratching. The crystalline product was purified by repeated sublimation (60°, 10^{-3} Torr) giving 200 mg of **7**: mp 49–50°; $[\alpha]^{22}D$ 160.7° ($CHCl_3$); ir (Nujol) 3320 cm^{-1} (OH), no absorption attributable to benzoate; nmr ($CDCl_3$) δ 1.30 (d, 3, J = 6 Hz, CH_3CH), 1.67 (m, 6, tetrahydropyranyl protons), 1.75–2.50 (m, 2, CH_2), 3.31 (s, 3, CH_3O), 4.74 (m, 2, both hemiacetalic protons).

Anal. Calcd for $C_{12}H_{22}O_5$: C, 58.51; H, 9.00. Found: C, 58.42; H, 8.84.

Methyl 6-Bromo-2,6-dideoxy-3-*O*-(tetrahydropyran-2-yl)-α-D-*arabino*-hexopyranoside (8).—The distillation residue from the previous reaction was submitted to preparative tlc leading to the isolation of three crystalline products; two of them were identified as **5** and **6** (same melting point and ir of those from the previously prepared products). The third product was recrystallized from ethanol, and it was identified as **8**: mp 130–131°; $[\alpha]^{20}D$ 134.1° ($CHCl_3$); ir (Nujol) showed hydroxy but no benzoate bands; nmr ($CDCl_3$) δ 1.65 (m, 6, tetrahydropyranyl protons), 1.80–2.55 (m, 2, CH_2), 3.36 (s, 3, CH_3O), 4.75 (broad signal, 2, both hemiacetalic protons).

Anal. Calcd for $C_{12}H_{21}BrO_5$: C, 44.31; H, 6.50; Br, 24.57. Found: C, 44.19; H, 6.30; Br, 24.59.

Ethyl Dichloro-*o*-orsellinate (10).—To a solution of ethyl *o*-orsellinate (**9**)[12] (700 mg) in dry ether (22 ml) cooled to 0°, sulfuryl chloride (1.10 ml) was added dropwise under continuous stirring, and the solution was then heated under reflux for 10 min. The reaction mixture was washed with water, saturated sodium bicarbonate solution, and water, and it was dried ($MgSO_4$). The crystalline residue obtained for evaporation of the solvent (712 mg) was recrystallized from ethanol giving 610 mg of **10**: mp 158–159° (lit.[13] mp 162°); nmr (acetone-d_6) δ 1.46 (t, 3, J = 7 Hz, CH_3CH_2), 2.63 (s, 3, CH_3Ph), 4.54 (q, 2, J = 7 Hz, CH_3CH_2), no aromatic protons.

Ethyl Dichlorodimethoxy-*o*-orsellinate (11).—A solution of compound **10** (1.4 g) in ether (10 ml) was treated with an excess of diazomethane in ether and kept for 2 days at 0°. Evaporation of the solvent gave a crystalline residue (1.3 g) that was recrystallized from ethanol. Pure **11** (1.1 g) had mp 59–60°; no hydroxy absorption in the ir spectrum; nmr (acetone-d_6) δ 1.40 (t, 3, J = 7 Hz, CH_3CH_2), 2.33 (s, 3, CH_3Ph), 3.95 and 3.97 (s, 3, CH_3O), 4.49 (q, 2, J = 7 Hz, CH_3CH_2).

Anal. Calcd for $C_{12}H_{14}Cl_2O_4$: C, 49.17; H, 4.82; Cl, 24.19. Found: C, 49.36; H, 4.98; Cl, 24.26.

Dichlorodimethoxy-*o*-orsellinic Acid (12).—Compound **11** (1 g) was dissolved in ethanol (30 ml), treated with 1 *N* potassium hydroxide (60 ml), and boiled under reflux for 3 hr. The ethanol was evaporated, and the aqueous solution was acidified with 20% hydrochloric acid to pH 2. The precipitate was filtered off and recrystallized from ethanol–water. Pure **12** (780 mg) had mp 135–136° (lit.[14] mp 135–136°); nmr (acetone-d_6) δ 2.35 (s, 3, CH_3Ph), 3.90 (s, 6, both CH_3O).

Dichlorodimethoxy-*o*-orsellinyl Chloride.—A solution of **12** (500 mg) in thionyl chloride (3 ml) was boiled under reflux for 90 min. The excess of reagent was removed by distillation, and the residue was purified by short-path distillation (150°, 1 Torr) giving 350 mg of a heavy oil. A small portion of this oil was hydrolyzed to a crystalline product that was identified (melting point, ir) as **12**.

Methyl 4-*O*-(Dichlorodimethoxy-*o*-orsellinyl)-2,6-dideoxy-α-D-*arabino*-hexopyranoside (4) and Dichlorodimethoxy-*o*-orsellinic Anhydride (13).—A solution of **7** (230 mg) in dry pyridine (2.5 ml) cooled to 0° was treated with recently prepared dichlorodimethoxy-*o*-orsellinyl chloride (320 mg). The mixture was kept overnight at room temperature, and it was poured into ice–water. The gummy precipitate was extracted with chloroform, which was washed with 2 *N* hydrochloric acid, sodium carbonate solution, and water, and it was dried ($MgSO_4$). Evaporation of the solvent gave an oily residue that crystallized from ethanol. Recrystallization from the same solvent afforded pure **13** (75 mg): mp 99–100°; ir (Nujol) 1775, 1725 (C=O), 1560 (Ph), 1210, 1100 cm^{-1} (COOCO); nmr ($CDCl_3$) δ 2.45 (s, 3, CH_3Ph), 3.92 (d, 6, CH_3OPh), no aromatic protons.

Anal. Calcd for $C_{20}H_{18}Cl_4O_7$: C, 46.90; H, 3.54; Cl, 27.69. Found: C, 46.71; H, 3.62; Cl, 27.76.

The ethanolic mother liquors were evaporated to dryness. The syrupy residue showed two main spots on tlc. These were separated by preparative tlc. Elution of the higher R_f band produced another crop of **13** (10 mg, mp 99–100°), whereas elution of the second band gave a syrup having the same R_f of the natural compound **4**. Crystallization from petroleum ether (bp 100–120°) yielded 40 mg of a product of mp 101–103°, and whose ir and nmr spectra which resulted were identical with those obtained from natural **4**.

Registry No.—**3**, 20585-98-2; **4**, 27808-79-3; **6**, 27808-80-6; **7**, 27808-81-7; **8**, 27808-82-8; **10**, 27808-83-9; **11**, 27808-84-0; **12**, 5859-29-0; **13**, 27808-86-2.

Reaction of Nitrosyl Chloride with Ethylidenecycloalkanes. A Reexamination[1]

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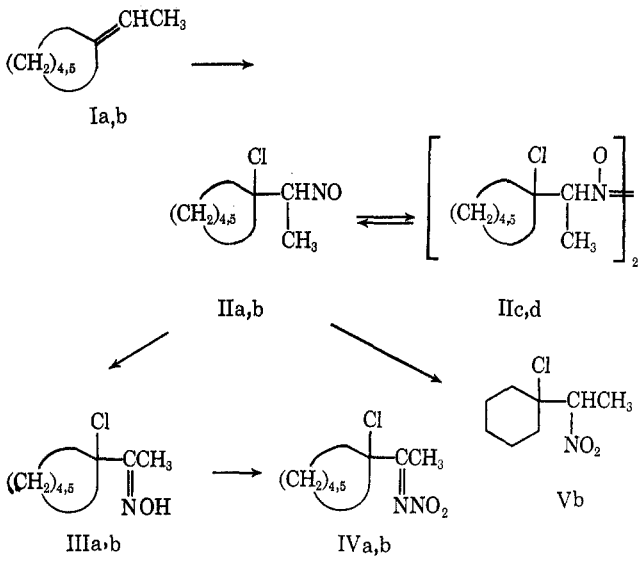
Normal addition of nitrosyl chloride to an olefin gives a chloronitroso product (monomer or dimer) or an α-chlorooxime. Other products have been called anomalous.[2] The normal (primary) products may be oxidized to secondary products. We report additions to two ethylidenecycloalkanes which behave differently in the secondary oxidations. We conclude that the chloronitroso addition is the only primary reaction. After that three pathways may be followed: (1) dimerization of the nitroso group (long known), (2) oxidation of the nitroso group to a nitro gorup, and (3) isomerization to an oxime, followed by oxidation to a nitrimine.

The pathways compete. The second pathway appears to be the only one in a steroid example[3] where dimerization may be inhibited or very slow. Oxidation of an oxime to a nitrimine has been accomplished by nitrous acid,[4] nitrosyl fluoride,[5] and recently by nitrosyl chloride.[6] Isomerization of chloronitroso compound to the oxime is catalyzed by hydrogen chloride and goes very rapidly in polar solvents[7] so that dimerization and oxidation to a nitro group may not compete successfully in such solvents.

In the case of ethylidenecyclohexane, all three reactions compete successfully in ether. Wallach and Evans[8] reported an 83% yield of chloronitroso compound IIb,d in the addition of nitrosyl chloride to ethylidenecyclohexane. Repetition with excess nitrosyl chloride suggests that chloronitroso formation is quantitative (98%) as the primary reaction. Precipitation from ether gives 75% of IIb,d. Oxidation of the remainder in solution gives 16% of chloronitro compound Vb by direct oxidation with nitrosyl chloride and 7% of chloronitrimine IVb through isomerization to IIIb and subsequent oxidation. With ethylidenecyclopentane, only 24% of IIa,c is precipitated. None of the remainder is oxidized to the chloronitro compound, apparently because isomerization to chlorooxime IIIa and subsequent oxidation to chloronitrimine (56%) is so rapid. The isolated chloronitroso compound IIa,c isomerized on standing to IIIa; so only IIIa could be obtained pure in this series.



The molecular mass of 279 by the Rast method[9] in camphor for IIb,d gives a monomer/dimer ratio of 28:72. In the mass spectrometer, only one decomposition pattern was obtained from IIb,d, and IIIb so the dimer must dissociate and/or isomerize in the ion chamber. The maximum m/e observed is that of IIb (= IIIb).

In the presence of nitrosyl chloride, pure IIb,d exhibits the oxime signals of IIIb (nmr) at $-77°$ in a short time. This isomerization for preparative purposes is catalyzed by hydrogen chloride gas or, less effectively, solid sodium carbonate.

Pure IIIb was oxidized only to the nitrimine IVb by nitrosyl chloride but was oxidized to the chloronitro compound Vb by trifluoroperoxyacetic acid. The chloronitroso compound IIb,d was oxidized to chloronitro Vb in 91% yield by trifluoroperoxyacetic acid.

The dimer IId appears to have an anti structure from the interpretation of Gowenlock and Lüttke,[10] exhibiting λ_{max} 265 mμ (ϵ 5400) in ethanol and ir bands at 1185 (s) and 1450 cm^{-1} (m). Compound IIb,d and IIIb gave piperidino[8] and methoxy[11] derivatives as reported. However, IIIa was dehydrohalogenated in methanol to 1-acetylcyclopentenyloxime. Structures of compounds III, IV, and V were corroborated by ir and nmr spectra and IVb was reduced to the corresponding nitramine.

The results reported here bear out Oglobin's suggestion that stable dimer precipitation diminishes opportunity for oxidation to a nitro compound. Oglobin[12] has reported low yields of chloronitro compounds with several olefins of low molecular mass. The present work suggests that rapid isomerization to oxime lowers nitro formation and increases nitrimine formation.

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