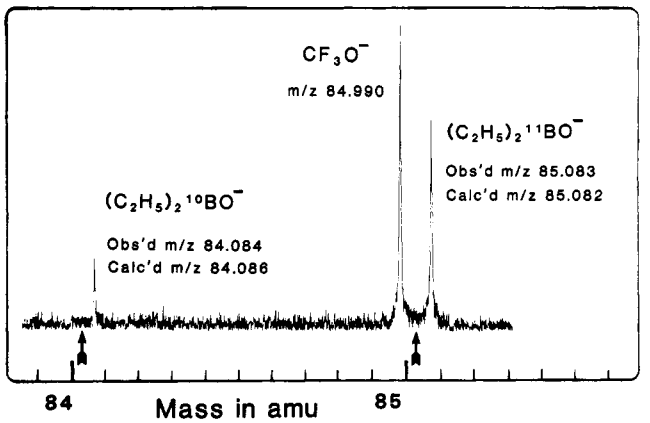


Figure 1. Fourier transform mass spectrum at 3 T of products from reaction of anion 1 with carbon dioxide and molecular oxygen at a total pressure of 10^{-7} torr. Boldface arrows indicate where ions with molecular formula $C_3H_6BO_2^-$ would have been observed, had they been present. Resolution=14 500.

dioxide by the carbanionic center to form carboxylate **2** can be estimated to be on the order of 10 kcal/mol exothermic. Subsequent expulsion of two ethylene molecules or of a butene molecule would yield $H_2BCH(CH_3)CO_2^-$, which has the same nominal mass as diethylborinate.

High-resolution mass measurements can distinguish between the alternative pathways of reaction 6. The isobaric products actually differ in exact mass by 0.036 amu, and base-line resolution of this difference is well within the capability of FTMS.[4] Figure 1 shows a high-resolution FTMS spectrum of the products from reacting **1** with carbon dioxide. The mass scale is calibrated with the CF_3O^- ion from perfluorokerosene. Molecular oxygen was also present in the reaction mixture. Reaction of **1** with oxygen unquestionably yields diethylborinate, and the reaction products of **1** with carbon dioxide are observed at exactly the same masses. No ion is seen above the base line at the masses corresponding to $H_2BCH(CH_3)CO_2^-$, and we conclude that reaction 5 is indeed taking place. We interpret this to mean that the intermediate adduct ion **2** (which is not observed) decomposes via path b shown in reaction 6. Of course, the neutral product is not directly identified, but we note that methylketene is the most stable C_3H_4O isomer.[5]

Wittig reaction of carbon dioxide to yield a ketene has not, to our knowledge, been previously reported. We observe it as a reaction of free boron-stabilized carbanions in the absence of counterions. But there is no apparent reason why this same reaction should not also proceed in solution. We foresee that FTMS may provide useful approaches for exploring reaction pathways of potential synthetic utility.

Acknowledgment. This work was supported by grants from the Research Corp. (T.H.M.) and by NSF Grant CHE 80-18245 (C.L.W. Co-P.I. with M. L. Gross, University of Nebraska). The UCR departmental FTMS facility was purchased with the help of NSF departmental research instrumentation Grant No. CHE 82-17610 and of Grant No. BRSG SO7 RR07010-18 awarded by the Biomedical Research Grant Program, Division of Research Resources, National Institutes of Health.

Registry No. 1, 86120-54-9; CO_2, 124-38-9; $(C_2H_5)_3B$, 97-94-9; $(C_2H_5)_3BH^-$, 75338-98-6; $(C_2H_5)_2BO^-$, 86120-55-0; $CH_3CH{=}C{=}O$, 6004-44-0.

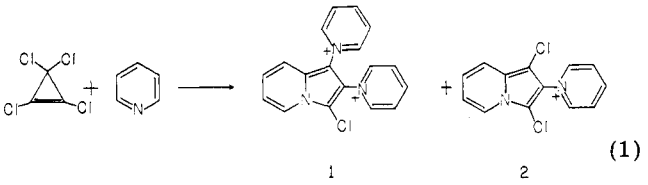
(5) Schiess, P.; Radimerski, P. *Helv. Chim. Acta* **1974**, *57*, 2583–2597.

C. L. Johlman, C. F. Ijames
C. L. Wilkins, Thomas Hellman Morton*
Department of Chemistry
University of California
Riverside, California 92521
Received May 3, 1983

An Offbeat Reaction of Pyridine with Tetrachlorocyclopropene: A New Synthesis of Indolizines

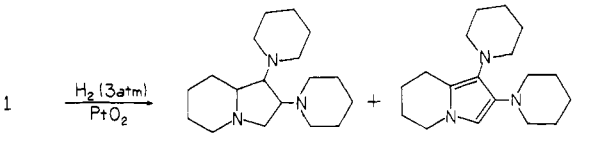
Summary: Pyridine reacts with tetrachlorocyclopropene to give indolizine derivatives.

Sir: During investigations of cyclopropenium systems derived from tetrachlorocyclopropene (TCC),[1] we observed an unexpected reaction with pyridine. When pyridine was added to a methylene chloride solution of TCC at 0 °C, a purple color occurred instantly. With time the color faded and a green-brown precipitate formed. This solid, **1**, was washed with CH_2Cl_2 and recrystallized from aqueous acetonitrile to yield yellow sheets, soluble in water and insoluble in nonpolar organic solvents. Two additional compounds were isolated from washes and supernatant. One was pyridinium hydrochloride; the other, isolated as its tetraphenylborate salt, was a bright orange, multifaceted solid, **2**. The proposed structures of **1** and **2** are indicated in eq 1.[2]



1 2 (1)

The structures were deduced primarily from UV–vis (H_2O; λ, nm [log ε]: 219 [4.36], 264 [3.96], 390 [3.42])[3] and ^1H NMR (Table I). In addition, **1** was hydrogenated to a complex mixture from which column chromatography ($CHCl_3$–CH_3OH) provided a 60% yield of material indicated by NMR and mass spectroscopy to be a 72:28 mixture of **3** and **4**.



3 4

Assignment of protons of **1** was facilitated by carrying out the reaction with 4-picoline, which gave the corresponding methyl-substituted products and the expected changes in intensity/coupling patterns [H_6 (δ 7.01, d of d);

(1) (a) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2481. (b) Tobey, S. W.; West, R. *Tetrahedron Lett.* **1963**, 1179. This preliminary report of TCC synthesis is especially interesting in that pyridine was investigated as a base to convert pentachlorocyclopropene to TCC.

(2) **1** (as monohydrate): Anal. Calcd for $C_{18}H_{14}N_3Cl_3{\cdot}H_2O$: C, 54.50; H, 4.06; N, 10.59; Cl, 26.81. Found: C, 54.35; H, 4.07; N, 10.55; Cl, 26.58. **2**: Anal. Calcd for $C_{37}H_{29}N_2Cl_3B$: C, 76.18; H, 5.01; N, 4.80; Cl, 12.15. Found: C, 76.11, H, 5.08; N, 4.82; Cl, 12.03.

(3) Compare: Katriztsky, A. R. "Physical Methods in Heterocyclic Chemistry"; Academic Press: New York, 1963; Vol. II.

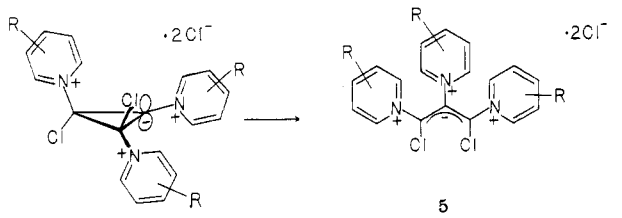
0022-3263/83/1948-2629$01.50/0 © 1983 American Chemical Society

Table I. NMR Comparisons of 1 and 2 with Indolizine

	chemical shift, ppm				coupling constants, Hz					
	H_5	H_6	H_4	H_8	5,6	5,7	5,8	6,7	6,8	7,8
indolizine[a]	7.76	6.31	6.50	7.25	6.8	1.0	1.2	6.4	1.0	8.9
2	8.21	7.05	7.18	7.63	7.0	0.9		6.5	1.1	9.2
1	8.33	7.15	7.32	7.51	7.1	0.9		6.9	0.9	9.1

[a] Black, P. J.; Heffernon, M. L.; Jackman, L. M.; Porter, Q. N.; Underwood, G. R. *Aust. J. Chem.* **1964**, *17*, 1128.

Scheme I



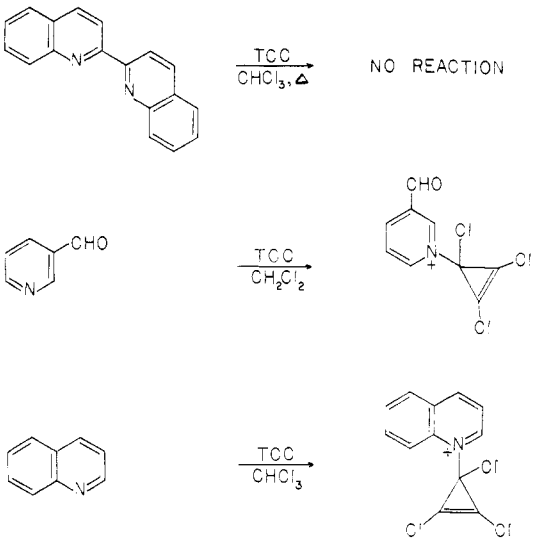
5

H_8 (δ 7.22, br s); H_5 (δ 8.20, d of d); $J_{5,6}$ = 7.7, $J_{6,8}$ = 1.1, $J_{5,8}$ = 1.0].

The pattern of substitution about the pyrrole part of the indolizine nucleus was ascertained indirectly by comparing the relative chemical shifts of indolizine protons as one proceeds from the parent unsubstituted indolizine to the monopyridinium system, **2**, and the bis(pyridinium) structure, **1** (Table I). The relatively symmetric Δ shifts of proton pairs, H_5, H_8, and H_6, H_7, in **2** suggest that the pyridinium is at the most nearly symmetric or 2-position. The anomalous (somewhat upfield) Δ shift of H_8 in **1** argues for the second pyridinium to be in the 1-position and interacting so as to deshield the peri proton. Single-crystal X-ray analysis of **2** confirms the assigned structure.[4]

In addition to producing indolizines possessing substituents that are either unknown (pyridinium) or rare (Cl on the pyrrole ring),[5] the reaction is interesting mechanistically. The limiting reagent is pyridine, and the combined yield of **1** and **2** based on TCC is essentially quantitative. The major product under all conditions is **1**; the ratio, **1**/**2**, varies only slightly, 3.5–5.0,[6] over a wide range of reactant ratios. Pyridines having electron-donating substituents produce indolizines unless both positions 2 and 6 of the pyridine are blocked, as in 2,6-lutidine and 2,4,6-collidine. A reaction occurs between these substrates and TCC but it is qualitatively much slower and indolizines are not isolated. The dark solids that are produced are insoluble in organic solvents and appear to react with water. We propose that these products are the corresponding allylic systems, **5**, and that **5** is an intermediate (R = H) in the reaction with pyridine itself. These suggestions are now being investigated as part of a general study of reaction mechanism including reaction kinetics.[7] Compound **5** is a novel allyl nitrogen ylid that is assumed to arise from the sequential addition of pyridine to TCC followed by electrocyclic ring-opening of the tris(pyridinium) cyclopropyl anion (Scheme I). Such substitution reactions of TCC are well-known with nucleophilic species.[8] The electrocyclic ring closure of pyridinium *N*-allylides to the indolizine ring structure has been documented.[9]

Pyridines with electron-withdrawing groups or heterocycles with electron-deficient nitrogens either do not react or yield the corresponding monosubstituted products, (trichlorocyclopropenyl)pyridinium chlorides. These salts apparently do not rearrange to trichloroindolizine derivatives. Typical examples are shown in the following reactions.



Acknowledgment. This research was supported in part by NSF Grant No. CHE 82-05696.

Registry No. **1**·2Cl⁻, 86289-23-8; **2**·BPh_4^-, 86289-25-0; **3**, 86289-26-1; **4**, 86289-27-2; **5**·2Cl⁻ (R = H), 86289-28-3; TCC, 6262-42-6; pyridine, 110-86-1; 3-pyridinecarboxaldehyde, 500-22-1; quinoline, 91-22-5; 1-(3-trichlorocyclopropenyl)pyridinium-3-carboxaldehyde chloride, 86289-29-4; 1-(3-trichlorocyclopropenyl)quinolinium chloride, 86289-30-7.

Kennith A. Smith, Andrew Streitwieser, Jr.*
Department of Chemistry
Univeristy of California
Berkeley, California 94720
Received March 28, 1983

(4) Smith, K. A.; Hollander, F.; Streitwieser, A., Jr., manuscript in preparation.
(5) Berg-Nielsen, K. *Acta Chem. Scand., Ser. B.* **1977**, *31*, 224. Ohsawa, A.; Abe, Y.; Igeta, H. *Chem. Lett.* **1979**, 241–4.
(6) Determined by NMR of chlorides. Isolated yields of **2** as the tetraphenylborate were lower because of repeated recrystallization to remove pyridinium tetraphenylborate.
(7) Waterman, K. C., unpublished results.
(8) Yoshida, Z. *Top. Curr. Chem.* **1973**, *40*, 47.
(9) Sasaki, t.; Kanematsu, K.; Kakehi, A.; Ito, G. *Tetrahedron* **1972**, *28*, 4947. Pohjala, E. *Tetrahedron Lett.* **1972**, 2585.

An Efficient Synthetic Route to (±)-Nanaomycin A

Summary: An efficient synthetic route to (±)-nanaomycin A (**1**) involving a new type of Claisen rearrangement is described.

Sir: Nanaomycin A (**1**), a member of the family of pyrananaphthoquinone antibiotics, exhibits significant antimicrobial activity[1] and also bears potential antineoplastic activity.[2] The total synthesis of **1** has recently been a

(1) (a) Omura, S.; Tanaka, H.; Koyama, Y.; Oiwa, R.; Katagiri, M.; Awaya, J.; Nagai, T.; Hata, T. *J. Antibiot.* **1974**, *27*, 363. (b) Tanaka, H.; Koyama, Y.; Awaya, J.; Marumo, H.; Oiwa, R.; Katagiri, M.; Nagai, T.; Omura, S. *Ibid.* **1975**, *28*, 860. (c) Tanaka, H.; Koyama, Y.; Nagai, T.; Marumo, H.; Omura, S. *Ibid.* **1975**, *28*, 868.

0022-3263/83/1948-2630$01.50/0 © 1983 American Chemical Society