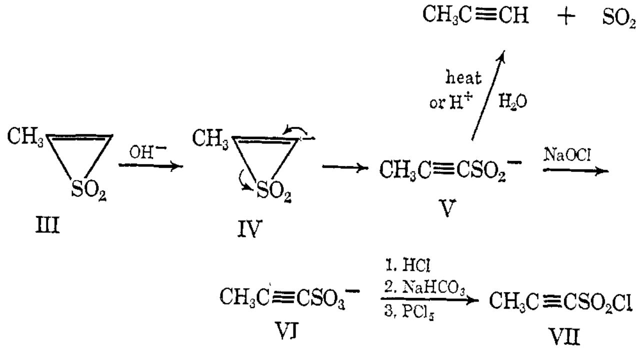
Consistent with its probable intermediacy in the Ramberg–Bäcklund reaction of α,α'-dibromodibenzyl sulfone, 2,3-diphenylvinylene sulfone gives 1,2-diphenylethylenesulfonic acid in 90% yield on treatment with aqueous sodium hydroxide. On the other hand no sulfonic acid was isolated on treatment of III under Ramberg–Bäcklund conditions. When the reaction was carried out at low temperatures (0°) an unstable intermediate was formed which underwent subsequent conversion to methylacetylene.[11] Immediately after addition of 2 *N* sodium hydroxide to an aqueous solution of III, the nmr spectrum shows disappearance of the vinyl absorption and shift of the methyl resonance from δ 2.5 to 2.0. Infrared examination of this solution shows sharp acetylenic absorption at 4.57 μ. Changes in the spectra showed that the species present decomposed rapidly on standing at room temperature. Warming to 50° or acidification caused the evolution of methylacetylene.[12] If the solution is first treated with sodium hypochlorite,[13] a new species is formed which no longer yields methylacetylene on warming or acidification. The oxidized solution contains a stable acetylenic sulfonic acid as shown by infrared absorption at 4.51 ($C\equiv C$) and 8.25, 9.40 μ (SO_2). Neutralizing the acidified hypochlorite-oxidized solution by means of sodium bicarbonate, evaporating, and treating the solid residue with phosphorus pentachloride in carbon tetrachloride gave in an over-all yield of 35% 1-propynesulfonyl chloride[3] [VII, bp 60–62° (6 mm); infrared: $\lambda_{\max}^{\mathrm{CCl_4}}$ 4.50 ($C\equiv C$) and 7.20, 8.47 μ (SO_2); nmr (CCl_4): δ 2.26 (singlet)]. The reactions described are outlined in Chart I. Hydroxide ion is presumably diverted from attack at the sulfone group by the pronounced acidity of the vinyl proton of methylvinylene sulfone.[14,15] Opening follows to give the stable sulfinate V which on oxidation yields the stable sulfonate VI, from which the isolable sulfonyl chloride VII is derived. It is apparent from these results that the recent suggestion[17] that the relative stabilities of substituted vinylene sulfones can be determined by comparison of the ratio of acetylenic to sulfonic acid products formed upon Ramberg–Bäcklund treatment of dihalo sulfones is untenable since the acetylenic products need not arise by thermal elimination of sulfur dioxide from the vinylene sulfone. Whether the stability order of the vinylene sulfones parallels that of the cyclopropenones therefore remains to be determined. Such an investigation of the stability and reactivity under comparable conditions of a varied group of isolable vinylene sulfones is currently in progress. The unusual reactivity of the vinylene sulfones, to be reported in due course, makes these compounds of considerable practical synthetic value.

Chart I



III IV V VI VII

Acknowledgment. This work was generously supported by grants from the U. S. Army Research Office, Durham, and (in its earlier stages) by the Petroleum Research Fund, administered by the American Chemical Society.

---

[11] A careful search for sulfonic acids and other by-products is in progress.

[12] Methylacetylene is not detectably soluble in aqueous sodium hydroxide solution (nmr) and must be derived from some relatively stable soluble precursor. That the anion IV is not stable is shown by the fact that maximum acetylenic absorption is developed immediately after addition of alkali, and just-as-rapid neutralization of this solution with hydrochloric acid regenerates none of the precursor III (nmr analysis).

[13] Sodium hypochlorite has been shown to oxidize sulfinates to sulfonates rapidly in aqueous solution. See L. Ackerman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 243 (1946).

[14] It is interesting in this connection that the α-vinyl proton of 2,3-dihydrothiophene 1,1-dioxide undergoes deuterium exchange in the presence of aqueous alkali. See C. D. Broaddus, *J. Am. Chem. Soc.*, **88**, 3863 (1966).

[15] Confirmed by the large ^{13}C–H coupling constant (J = 230–232 cps) measured for this proton (concentrated water solution). The corresponding values for methylcyclopropenone[7] and methylacetylene[16] are 213 and 248 cps, respectively.

[16] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).

[17] L. A. Paquette and L. S. Wittenbrook, *Chem. Commun.*, 471 (1966).

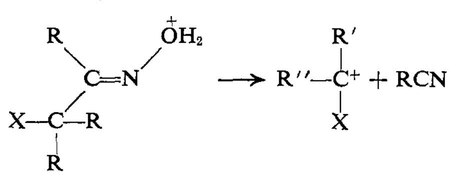
Louis A. Carpino, Ronald H. Rynbrandt
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts

Received September 6, 1966

Evidence for and Synthetic Utility of the Beckmann Fission Intermediate of 2-Methoxycyclohexanone Oxime

Sir:

The feasibility of fragmentation in certain oximes under Beckmann rearrangement conditions has recently been recognized and has attracted considerable attention.[1] In general, the Beckmann fission is well demonstrated by oximes of structural types which furnish carbonium ions $^+CR'R''X$ possesing considerable stability, especially with substituents, X, of alkoxy, alkylamino, and alkylthio groups, and the synthetic application of the reaction has been cited in recent communications.[2–4]



We describe here not only strong evidence for but also a synthetically interesting utility of such carbonium ion intermediates. ω-Cyanoalkyl aldehydes are easily prepared in excellent yields by the treatment of α-alkoxy, α-alkylamino-, and α-ethylthiocycloalkanone oximes with thionyl chloride or phosphorus pentachloride followed by hydrolysis.[2] Among them, 5-cyanopentanal

---

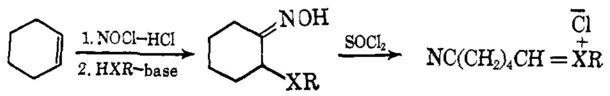
[1] (a) R. K. Hill, *J. Org. Chem.*, **27**, 29 (1962), and references contained therein; (b) C. A. Grob, H. P. Fischer, W. Raudenbusch, and J. Zergenzi, *Helv. Chim. Acta*, **47**, 1003 (1964), and references contained therein; (c) R. K. Hill, R. T. Conley, and O. T. Chortyk, *J. Am. Chem. Soc.*, **87**, 5646 (1965).

[2] M. Ohno, N. Naruse, S. Torimitsu, and I. Terasawa, *ibid.*, **88**, 3168 (1966).

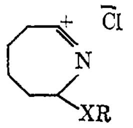
[3] R. L. Autrey and P. W. Scullard, *ibid.*, **87**, 3284 (1965).

[4] Y. L. Chow, *ibid.*, **87**, 4642 (1965).

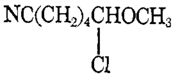
was considered to be formed *via* intermediates I, II, or III rather than cyclic nitrilium ion IV which might be sterically unfavorable. As a representative example, 2-methoxycyclohexanone oxime was chosen in this experiment.



I, X = O
II, X = NR
III, X = S



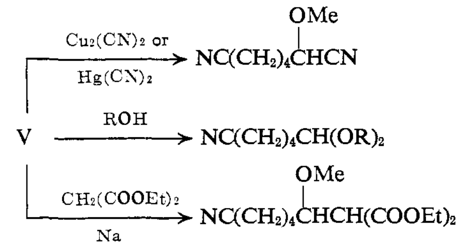
IV



$$\mathrm{NC(CH_2)_4\underset{\displaystyle Cl}{CH}OCH_3}$$

V

A slight excess of thionyl chloride (3 g, 0.0252 mole) in dry carbon tetrachloride (10 ml) well cooled at 0° was added within a few minutes[5] to a carbon tetrachloride solution (10 ml) of 2-methoxycyclohexanone oxime (3 g, 0.0209 mole) also well cooled at 0°. Immediately after the addition, vigorous evolution of hydrogen chloride took place and an aliquot of the solution was quickly subjected to nmr measurement at 0°. The nmr spectrum of 2-methoxycyclohexanone oxime shows absorption peaks at δ 3.05 and 3.73 in a ratio of *ca.* 1:3 for the methine proton, which might be caused by a mixture of *syn* and *anti* configurations of the α-substituted oxime,[6] δ 3.20 for the methoxy group, and δ 10.33 for the hydroxy group. The nmr spectrum of the reaction mixture showed absorption peaks at δ 5.51 (1 H, triplet, J = 5 cps), which reasonably correspond to the α-hydrogen of chloro alkyl ether,[7] and no absorption of the methine proton of the starting material, δ 3.50 (3 H, singlet) for the methoxy group, which shifted to lower field by only 0.2 ppm, and δ 2.41 (2 H, triplet), which was assigned to the α-methylene of the nitrile group; these signals are all consistent with the structure of 1-chloro-5-cyanopentyl methyl ether.[8] This observation has demonstrated that the carbonium ion intermediate in the fragmentation of an α-methoxy oxime can be intercepted by chloride ion to yield α-chloro ethers. Simple addition of methanol and ethanol to the reaction mixture at 5–10° afforded the corresponding acetals[9] in 82 and 91% yields, respectively. This procedure is synthetically important in making a stable acetal of unstable 5-cyanopentanal.[10] The reaction mixture was treated with cuprous cyanide or mercuric cyanide, affording 2-methoxyheptanedinitrile[9] in 50% yield, bp 116° (1.5 mm), infrared at 2210 (CN) and 1118 cm^{-1} (OCH_3), nmr δ 4.08 (1 H, triplet, J = 6.01 cps) for tertiary hydrogen, 3.48 (3 H, singlet) for methoxy, 2.36 (2 H, triplet, J = 6.0 cps) for methylene α to nitrile, and 1.69 (6 H, broad) for other methylene. The treatment of the reaction mixture with the carbanion prepared from ethyl malonate and sodium gave ethyl (5-cyano-1-methoxypentyl)malonate[9] in 64% yield, bp 148° (7 $\times$ 10^{-3} mm), infrared 2220 (CN), 1732–1750 (ester), and 1030 cm^{-1} (OCH_3), nmr δ 4.15 and 1.25 for ester hydrogens, 3.70 and 3.50 for tertiary hydrogens, 3.32 for methoxy, 2.33 for methylene α to nitrile, and 1.58 for other methylene. These observations strongly confirm that the intermediate of the Beckmann fission of 2-methoxycyclohexanone oxime is acyclic 1-chloro-5-cyanopentyl methyl ether, and the chloro ether produced in this way undergoes the usual reactions[11] with cyanide and malonate ions to afford useful synthetic sequences, especially when coupled with our method of preparing the starting oximes.[2]



Masaji Ohno, Isao Terasawa
Basic Research Laboratories, Toyo Rayon Company Ltd.
Kamakura, Japan

Received September 9, 1966

---

[5] When the same reaction was carried out at room temperature, the solution became brown in 10 min and a tarry material was obtained, which was difficult to identify.

[6] Various α-substituted oximes were prepared from displacement reactions of 2-chlorocycloalkanone oxime; see (a) M. Ohno, N. Naruse, S. Torimitsu, and M. Okamoto, *Bull. Chem. Soc. Japan*, **39**, 1119 (1966); (b) M. Ohno and N. Naruse, *ibid.*, **39**, 1125 (1966); (c) M. Ohno, S. Torimitsu, N. Naruse, M. Okamoto, and I. Sakai, *ibid.*, **39**, 1129 (1966); a detailed investigation of the stereochemistry of them is in progress and the results will be published soon.

[7] For instance, see K. Nukada, O. Yamamoto, and T. Suzuki, *Anal. Chem.*, **35**, 1892 (1963).

[8] If the trapped intermediate were (5-cyanopentylidene)methyloxonium chloride (I) expected from the electromerically assisted Beckmann fission, the nmr spectrum of the reaction mixture should contain signals for $HC{=}^{+}OCH_3$ at much lower field. For instance see, B. G. Ramsey and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 3058 (1966).

[9] Satisfactory elemental analyses have been obtained for all new compounds reported herein.

[10] The ethylene acetal was obtained only in 10–15% yields when 5-cyanopentanal was treated with ethylene glycol in the presence of *p*-toluenesulfonic acid in boiling benzene.

[11] L. Summers, *Chem. Rev.*, **55**, 301 (1955).

The Synthesis of a 4′,5′-Unsaturated Nucleoside

Sir:

The recent characterization of several nucleoside antibiotics containing unsaturated sugars[1,2] has stimulated considerable activity toward the synthesis of such compounds. Toward this end elegant methods for the synthesis of 2′,3′-unsaturated pyrimidine nucleosides have been developed by Horwitz, *et al.*,[3] and extended to the purine series by Robins[4] *via* a variety of elimination reactions. Some progress has also been made in the introduction of 2′,3′ unsaturation *via* desulfurization of 2′,3′-O-thionocarbonates.[5] In this paper we describe the first synthesis of a nucleoside containing a 4′,5′ double bond, a structural feature that is present in the nucleoside antibiotic angustmycin A (decoyinine, I).

The synthesis of 6-deoxy 5,6-unsaturated hexopyranosides through reaction of suitably protected 6-deoxy-6-iodopyranosides with silver fluoride in pyridine has

---

[1] H. Hoeksema, G. Slomp, and E. E. Van Tamelen, *Tetrahedron Letters*, 1787 (1964).

[2] N. Otake, S. Takeuchi, T. Endo, and H. Yonehara, *ibid.*, 1411 (1965).

[3] J. P. Horwitz, J. Chua, M. A. DaRooge, M. Noel, and I. L. Klundt, *J. Org. Chem.*, **31**, 205 (1966).

[4] J. R. McCarthy, M. J. Robins, L. B. Townsend, and R. K. Robins, *J. Am. Chem. Soc.*, **88**, 1549 (1966).

[5] W. V. Ruyle, T. Y. Shen, and A. A. Patchett, *J. Org. Chem.*, 30, 4353 (1965).