two cyclopropane carbon–carbon bonds necessary to liberate dichlorocarbene. While the plethora of possible mechanisms, ranging from extrusion of dichlorocarbene to transfer of dichlorocarbon from excited I, makes us reluctant to insist upon dichlorocarbene at this time, both the available data and Occam's razor make it the most attractive candidate.

We have not yet been able to determine if the dichlorocarbene produced in this reaction undergoes the carbon–hydrogen insertion reaction. Further, we do not know if I may be fragmenting in more than one direction. Minor products, combining at least fragments of I and solvent molecules, are produced, however. The elucidation of their structures is being actively pursued.

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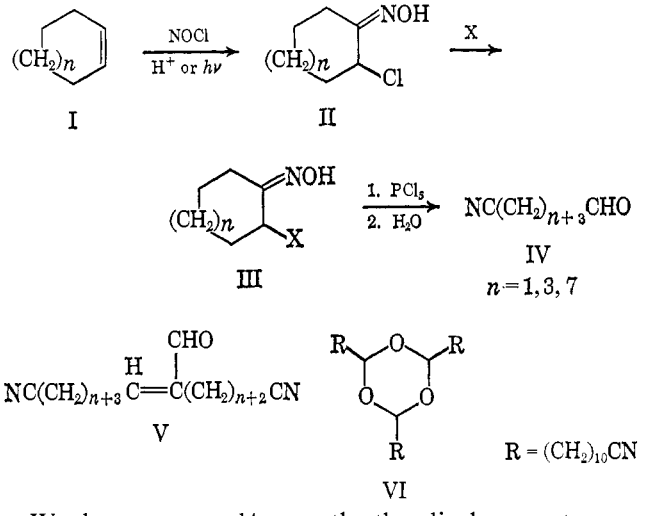
Synthesis of ω-Cyanoaldehydes through Carbon–Carbon Double Bond Cleavage of Cycloolefins

Sir:

We describe here a synthesis of ω-cyanoaldehydes by a novel sequence of apparent general applicability for carbon–carbon double bond cleavage of cycloolefins. ω-Cyanoaldehydes are not easily accessible, but are interesting synthetic intermediates, since the *termini* of the compounds are left in different oxidation states and may readily be separately modified. Only β-cyanoaldehyde has been prepared, by the oxo reaction of acrylonitrile[1] and the Michael reaction of acrolein,[2,3] but such methods cannot be applied generally.



We have reported[4] recently the displacement reactions of α-chlorocycloalkanone oximes, prepared by the addition of nitrosyl chloride to cycloolefins, with various nucleophilic reagents to give, *via* intermediates of α,β-unsaturated nitroso derivatives, α-substituted cycloalkanone oximes. Thus, oximes of 2-alkoxy-, 2-ethylthio-, and 2-alkylaminocycloalkanone have been prepared in excellent yields and were subjected to second-order[5] Beckmann rearrangement under different conditions. The results are summarized in Table I.

Table I. Yields of α-Substituted Oximes (III) and ω-Cyanoaldehydes (IV)

X	III, %[a] *n* = 1, 3, 7	IV, %[b] *n* = 1, 3, 7
$-OCH_3$	72, 92, 80	64, 90, 82
–OEt	76, 91, 81	60, 82, 75
–SEt	45, 72, 85	32, 50, 52
	81, 85, 71	30, 69, 84
	72, 88, 77	31, 65, 51
	82, 84, 87	24, 11, 21

[a] Over-all yields from cycloolefins. [b] Based on α-substituted oximes, using PCl_5 as Beckmann reagent.

2-Methoxycyclooctanone oxime (30 g) was treated with phosphorus pentachloride (50 g) in absolute ether (200 ml) at 0° for 5 hr and the product was carefully hydrolyzed with ice–water at 0–5°. The ethereal extract afforded a pale yellow liquid (21.1 g), infrared 2800 and 1725 (–CHO) and 2250 cm^{-1} (–CN). It was converted to an acetal derivative by treatment with ethylene glycol in the presence of a catalytic amount of *p*-toluenesulfonic acid, infrared 2250 (–CN) and 1000–1100 cm^{-1} (–C–O–C), bp 105–108° (0.25–0.3 mm). *Anal.* Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.27; H, 9.47; N, 7.60. The 2,4-DNP showed mp 76–77°, yellow needles. *Anal.* Calcd for $C_{14}H_{17}N_5O_4$: C, 52.66; H, 5.37; N, 21.93. Found: C, 52.80; H, 5.32; N, 21.83. Oxidation of the cyanoaldehyde with potassium permanganate afforded suberic acid in quantitative yield. These results confirm the assignment of the structure to 7-cyanoheptanal (IV, *n* = 3). When 2-alkylaminocyclooctanone oximes were treated with either phosphorus pentachloride or acetic anhydride–acetic acid they afforded IV (*n* = 3) along with an aldol condensation product, 2-(5-cyanopentyl)-9-cyano-2-nonenal (V, *n* = 3), in 5–14% yields, infrared 2700 and 1680 (–C=CCHO) and 2250 cm^{-1} (–CN); 2,4-DNP mp 112–113°, orange-red crystals. *Anal.* Calcd for $C_{22}H_{28}N_6O_4$: C, 59.98; H, 6.41; N, 19.08. Found: C, 60.04; H, 6.40; N, 18.94. 11-Cyanoundecanal (IV, *n* = 7) was obtained from α-alkoxy, α-ethylthio, and α-alkylamino oximes of 12-membered rings[6] in fairly good yields. Its infrared spectrum displayed the usual bands for aldehyde and nitrile groups at 2700 and 1720 cm^{-1}, respectively. The ethylene acetal showed mp 48–49°. *Anal.* Calcd for $C_{14}H_{25}NO_2$: C, 70.25; H, 10.53; N, 5.85. Found: C, 70.10; H, 10.63; N, 5.79. The 2,4-DNP showed mp 90–92°, yellow

(1) J. Kato, H. Watanabe, T. Komatsu, R. Iwanaga, and T. Yoshida, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, 64, 2142 (1961).
(2) J. Tanaka, *J. Pharm. Soc. Japan*, 60, 219 (1940).
(3) D. T. Warner and O. A. Moe, U. S. Patent 2,565,537; *Chem. Abst.*, 46, 2565*d* (1952).
(4) M. Ohno, N. Naruse, M. Okamoto, S. Torimitsu, and I. Sakai, *Bull. Chem. Soc. Japan*, in press.
(5) Other types of electromerically assisted Beckmann reactions have been reviewed recently (H. P. Fischer and C. A. Grob, *Helv. Chim. Acta*, 45, 2528 (1962); 46, 936 (1963); H. P. Fischer, C. A. Grob, and E. Renk, *ibid.*, 45, 2539 (1962)) and are also described in recent communications (R. L. Autrey and P. W. Scullard, *J. Am. Chem. Soc.*, 87, 3284 (1965); Y. L. Chow, *ibid.*, 87, 4642 (1965)).
(6) The most convenient method of the preparation of α-substituted cyclododecanone oximes is to use *cis,trans,trans*-1,5,9-cyclododecatriene as a starting material, *i.e.*, addition of nitrosyl chloride in the presence of hydrochloric acid, displacement with nucleophilic reagents, and catalytic hydrogenation with palladium–charcoal [M. Ohno, M. Okamoto, and K. Nukada, *Tetrahedron Letters*, 4047 (1965), and ref 4].

crystals. *Anal.* Calcd, for $C_{18}H_{25}N_5O_4$: C, 57.59; H, 6.71; N, 18.65. Found: C, 57.64; H, 6.73; N, 18.47. No aldol condensation product was obtained from a 12-membered ring system, but a colorless solid, mp 46–48°, was obtained in quantitative yield by allowing IV (n = 7) to stand at room temperature for 48 hr. Its infrared spectrum showed no absorption for aldehyde, but 2240 cm^{-1} (–CN) and new bands at 1170, 1130, 1120, 1105, and 1060 cm^{-1} (–C–O–C–). The elemental analysis and molecular weight determination are in agreement with structure VI. *Anal.* Calcd for $C_{36}H_{63}O_3N_3$: C, 73.80; H, 10.84; N, 7.17; mol wt, 588. Found: C, 73.67; H, 10.81; N, 7.01; mol wt, 573. The similar treatment of α-alkoxy, α-ethylthio, and α-alkylamino oximes of the six-membered ring afforded 5-cyanopentanal IV (n = 1) in good yields, 2,4-DNP mp 97–98°. *Anal.* Calcd for $C_{12}H_{13}N_5O_4$: C, 49.48; H, 4.50; N, 24.04. Found: C, 49.54; H, 4.57; N, 23.70. However, in the case of α-alkylamino oximes, an aldol condensation product, 2-(3-cyanopropyl)-7-cyano-2-heptenal[7] (V, n = 1), was obtained in 10–30% yields. The 2,4-DNP showed mp 167–168°, orange-red crystals. *Anal.* Calcd for $C_{18}H_{20}N_6O_4$: C, 56.24; H, 5.24; N, 21.87. Found: C, 56.28; H, 5.26; N, 21.91.

From these results, ω-cyanoaldehydes are most readily available from the cleavage of α-alkoxy and α-morpholino oximes, and as they are unstable to heat and base, it is recommended that they be kept in acetal form for further reactions.

The combination of nitrosyl chloride addition to cycloolefins and displacement reactions with nucleophilic reagents such as alcohols, thioalcohols, and alkylamines having unshared electron pairs provide one of the most convenient methods to the frameworks[8] for the second-order Beckmann rearrangement. Investigations of the scope and the limitation of this cleavage reaction and the chemistry of ω-cyanoaldehydes are in progress in this laboratory and the results will be published soon.

Acknowledgment. The authors wish to thank Dr. T. Hoshino, manager of this laboratory, for his helpful advice and encouragement.

(7) α-Dimethylaminocyclohexanone oxime tosylate, prepared from α-bromocyclohexanone oxime, was cleaved in alkaline medium to afford only V (n = 1) (C. A. Grob, H. P. Fischer, H. Link, and E. Renk, *Helv. Chim. Acta*, **46**, 1190 (1963)). Therefore, our results show the first isolation of 5-cyanopentanal.

(8) R. K. Hill, *J. Org. Chem.*, **27**, 29 (1962).

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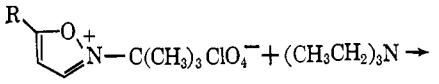
N-*t*-Butylketoketenimines

Sir:

We wish to report the first isolation of ketoketenimines. Spectral evidence (infrared absorption in the cumulene region) was previously presented in support of the postulated intermediacy of ketoketenimines in the ring-opening reaction of 3-unsubstituted isoxazolium salts with bases.[1] During a subsequent study of isoxazolium salts bearing an N-*t*-butyl substituent,[2,3] a spectral test of the reaction of triethylamine with N-*t*-butyl-5-phenylisoxazolium perchlorate (I) in dichloromethane also revealed cumulene absorption at 4.84 μ. However, in contrast to the N-ethylketoketenimine detected in the earlier study, the product N-*t*-butylbenzoylketenimine (II) appeared to be relatively stable. The reaction mixture showed strong absorption at 4.84 μ even after 80 hr at room temperature.



I, R = C_6H_5
III, R = CH_3

$$RCOCH{=}C{=}NC(CH_3)_3 + (CH_3CH_2)_3NH^+ ClO_4^-$$

II, R = C_6H_5
IV, R = CH_3

For the purpose of isolating II, a fresh solution was prepared by slow addition of I to an excess of triethylamine in dichloromethane. The reaction mixture was stirred vigorously during the addition, and stirring was continued until all of the isoxazolium salt had dissolved. The by-product triethylammonium perchlorate was removed as a gum by pouring the solution into a large volume of carbon tetrachloride. Removal of the solvents under reduced pressure left the crude ketoketenimine as an orange oil. Molecular still distillation[4] (0.01 mm) gave 60% of pure, yellow-green II: $n^{20}D$ 1.5155; $\lambda_{max}^{cyclohexane}$ 242 (ϵ 9900) and 284–294 mμ (ϵ 12,900–13,400); $\lambda_{max}^{CCl_4}$ 4.84 (C=C=N) and 6.12 μ (conjugated C=O); τ_{CCl_4} 2.05–2.76 (5 H, multiplet), 4.74 (1 H, singlet), and 8.62 (9 H, singlet). *Anal.* Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.58; H, 7.69; N, 6.84.

We have also prepared N-*t*-butylacetylketenimine (IV) from N-*t*-butyl-5-methylisoxazolium perchlorate (III). The isoxazolium salt III was obtained from a mixture of 5- and 3-methylisoxazole,[5] using 35 mole % excess of *t*-butyl alcohol and perchloric acid in our previously reported[2] *t*-butylation procedure. A mixture, mp 80–110°, of the 3- and 5-methylisoxazolium salts precipitated on dilution of the reaction mixture with acetone and ether. Repeated fractional precipitation from acetone with ether gave pure III in 50% yield, mp 119–121°, $\lambda_{max}^{0.1\ N\ HCl}$ 234 mμ (ϵ 8900). *Anal.* Calcd for $C_8H_{14}ClNO_5$: C, 40.09; H, 5.89; Cl, 14.79; N, 5.85. Found: C, 40.14; H, 5.85; Cl, 15.04; N, 5.74. The ketoketenimine IV was prepared by slowly adding a solution of III in dichloromethane to an ice-cold solution of excess triethylamine in the same solvent. Isolation as before and distillation gave pure IV (70–80%); bp 33–35° (0.2 mm); $n^{20}D$ 1.4895; $\lambda_{max}^{cyclohexane}$ 214 (ϵ 10,500) and 253 mμ (ϵ 15,400); $\lambda_{max}^{CCl_4}$ 4.87 (C=C=N) and 5.97 μ (conjugated C=O); τ_{CCl_4} 5.58 (1 H, singlet), 7.96 (3 H, singlet), and 8.57 (9 H, singlet). *Anal.* Calcd for $C_8H_{13}NO$: C, 69.03;

(1) R. B. Woodward and R. A. Olofson, *J. Am. Chem. Soc.*, **83**, 1007 (1961).

(2) R. B. Woodward and D. J. Woodman, *J. Org. Chem.*, **31**, 2039 (1966).

(3) D. J. Woodman, Ph.D. Thesis, Harvard University, 1965.

(4) Because of the possibility of residual perchlorate salts, the distillation was conducted behind an explosion shield, the temperature was kept below 100°, and the oil was not distilled to dryness.

(5) Prepared by the method of Eugster, *et al.*[6] Shown by nmr assay to contain 74% of the 5-methyl isomer.

(6) C. H. Eugster, L. Leichner, and E. Jenny, *Helv. Chim. Acta*, **46**, 543 (1963).