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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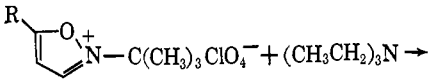
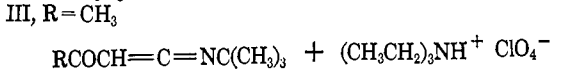
N-*t*-Butylketoketenimines

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



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).

H, 9.41; N, 10.05. Found: C, 68.94; H, 9.42; N, 9.98.

A side reaction was encountered when the method of combining the reagents was reversed in the preparation of IV. Addition of triethylamine to III gave IV along with a contaminant that had a nearly superimposable nmr spectrum, but which could be detected by its infrared absorption at 4.51 μ. Control experiments established that the source of the impurity was a reaction of the ketoketenimine in the presence of the unconsumed isoxazolium salt. In dichloromethane solution containing a small amount of III, compound IV underwent slow isomerization to β-*t*-butoxycrotononitrile (V) which was isolated in 58% yield after distillation and was further purified by recrystallization from a small volume of petroleum ether; mp 36–37°; λ_{max}^{EtOH} 229 mμ (ϵ 14,300)[7]; $\lambda_{max}^{CCl_4}$ 4.51 (conjugated C≡N) and 6.20 μ (conjugated C=O);[9] τ_{CCl_4} 5.58 (1 H, singlet), 7.95 (3 H, singlet), and 8.57 (9 H, singlet). *Anal.* Calcd for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.05. Found: C, 69.17; H, 9.44; N, 10.23.

$$\underset{\text{IV}}{CH_3COCH{=}C{=}NC(CH_3)_3} \xrightarrow{\text{III}} \underset{\text{V}}{CH_3C(OC(CH_3)_3){=}CHCN}$$

The ketoketenimines II and IV are stable below 0°, but both darken on standing at room temperature. The colorless, freshly distilled IV turns pale yellow within a few hours, even under nitrogen in the dark at low temperature. However, the compound shows no further change in its color and shows no change in its infrared and nmr spectra after prolonged storage, with occasional warming to room temperature for removal of samples. The possible use of IV as a reagent for peptide synthesis[10] is under investigation.

(7) Model, β-*n*-butoxycrotononitrile, λ_{max}^{MeOH} 228 mμ (ϵ 14,500).[8]
(8) P. Kurtz, H. Gold, and H. Disselnkötter, *Ann.*, **624**, 1 (1959).
(9) Model,[7] 4.51 and 6.19 μ.
(10) R. B. Woodward, R. A. Olofson, and H. Mayer, *J. Am. Chem. Soc.*, **83**, 1010 (1961).
(11) National Institutes of Health Predoctoral Fellow, 1961–1964. This work was also supported by a grant from the National Institutes of Health.

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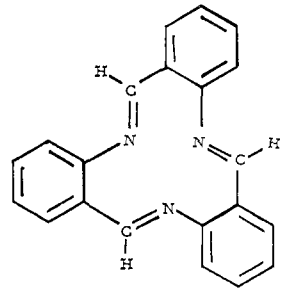
The Coordination Template Effect in *o*-Aminobenzaldehyde–Metal Ion Systems and Formation of a Novel Chelate Sandwich Compound[1]

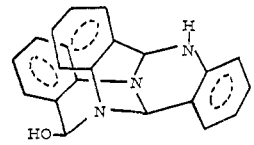
Sir:

In the course of investigations which served to demonstrate the template effects that metal ions exert on the stereochemical course of certain chemical reactions, the self-condensation of *o*-aminobenzaldehyde was reinvestigated.[2] Unlike systems based on the reaction of coordinated mercaptide groups as nucleophiles,[3] the stepwise reaction path and, consequently, the manner of influence of the metal ion have not been clear in the case of *o*-aminobenzaldehyde. It has been shown[2,4] that one of the products of the self-condensation of *o*-aminobenzaldehyde in the presence of nickel(II) ion is a complex containing a closed tridentate macrocyclic ligand tribenzo[*b*,*f*,*j*][1,5,9]triazacycloduodecine, structure I.



I

The principal products from the self-condensation of *o*-aminobenzaldehyde in the absence of metal ions are a bisanhydro trimer and a trisanhydro tetramer.[5] Recently, McGeachin[6] has reexamined this system and assigned structure II to the bisanhydro trimer, 13-hydroxy-6,12-benzo-6H-quinazolino[3,4-*a*]quinazoline.



II

We have found that in a 1:1 mole ratio, 13-hydroxy-6,-12-benzo-6H-quinazolino[3,4-*a*]quinazoline (II) rearranges under the influence of nickel(II) nitrate to give the complex of the tridentate ligand of I. Further, no tetrameric condensate is formed, in contrast to the result when *o*-aminobenzaldehyde undergoes self-condensation in the presence of nickel(II) nitrate.[2] The rearrangement is accomplished by heating a suspension of the quinazoline with an equimolar amount of nickel(II) nitrate hexahydrate in absolute ethanol for 3 hr. During this time, the quinazoline slowly dissolves and the bright orange-yellow dinitratoaquo(tribenzo[*b*,*f*,*j*][1,5,9]triazacycloduodecine)nickel(II) precipitates.

The art of the self-condensation reaction of *o*-aminobenzaldehyde under the influence of metal ions requires that the condensation be initiated several minutes before the metal ion is added. This provides adequate opportunity for the prior formation of the free bisanhydro trimer and trisanhydro tetramer, both of which may then rearrange under the influence of the metal ion. In fact, free trimeric condensate has been isolated from the self-condensation reaction. The formation of the tridentate ligand alone in the case of the reaction of nickel(II) ion with the bisanhydro trimer indicates that the tetradentate macrocyclic ligand is produced by rearrangement of the trisanhydro tetramer.

In the case of copper(II) the self-condensation reaction produces only the complex of the tetrameric Schiff base, $Cu(TAAB)^{2+}$. This result was ascribed to the usual stereochemistry of the copper(II) ion. The fact that the quinazoline reacts with copper(II) ion to form the complex containing the tetrameric Schiff base shows that the rearrangement process involves

(1) This investigation was supported in part by Public Health Service Fellowship 1-F2-GM-28, 091-01 and Public Health Service Grant GM 10040 from the National Institute of General Medical Sciences.
(2) G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 1706 (1965).
(3) M. C. Thompson and D. H. Busch, *ibid.*, **86**, 3651 (1964).
(4) E. B. Fleischer and E. Klem, *Inorg. Chem.*, **4**, 637 (1965).
(5) F. Seidel and W. Dick, *Ber.*, **60**, 2018 (1927).
(6) Private communication.