Attack of water or hydroxide ion on singly protonated II, followed by ring opening, a proton shift and hydrolysis of the resulting amino alcohol, could give the aldehyde IV.

Further work is being carried out on the mechanism of formation of II, on its reactions and on the possibility of reactions of I with other nucleophilic reagents.

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## $\alpha$-Oximino Ketones. I. The "Normal" and "Abnormal" Beckmann Rearrangements

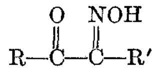
*Sir:*

The Beckmann rearrangement of $\alpha$-oximino ketones possessing the *anti* or $\alpha$-configuration is commonly described[1,2,3] as proceeding "normally," to a secondary amide and/or the hydrolysis products thereof, when brought about by an acid or an acid chloride, but "abnormally," to a nitrile and a carboxylic acid, when brought about by an acylating agent and base[1,4] (rearrangement of the "second order"[5]). It was reported originally that rearrangement of $\alpha$-oximino ketones in polyphosphoric acid was "normal",[6] but more recent work[7,8] has shown that actually the "abnormal" route is followed.

In this laboratory both types of rearrangement have been studied by submitting several unsymmetrical $\alpha$-oximino ketones to the action of 85% sulfuric acid ("normal") and benzenesulfonyl chloride and aqueous base ("abnormal"). All products obtained are reported in Table I, except that no attempt was made to isolate two-carbon materials. Of particular interest are the first two pairs of $\alpha$-oximino ketones, since if a secondary amide intermediate were formed in the "normal" reaction, both 2-oximino-1-phenyl-1-propanone and 1-oximino-1-phenyl-2-propanone should give $N$-acetylbenzamide or the same hydrolysis products therefrom, and 1,3-diphenyl-2-oximino-1-propanone and 1,3-diphenyl-1-oximino-2-propanone should give $N$-benzoylphenylacetamide or the same hydrolysis products.

TABLE I

BECKMANN REARRANGEMENTS OF $\alpha$-OXIMINO KETONES



$$R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}R'$$

| $\alpha$-Oximino Ketone R | R' | Products and Yields from 85% $H_2SO_4$ | $PhSO_2Cl + NaOH$ |
|---|---|---|---|
| Ph | Me[a] | $PhCO_2H$ (84%) | $PhCO_2H$ (91%) |
| Me | Ph[b] | $PhCONH_2$ (92%) | PhCN (87%) |
| Ph | $CH_2Ph$[c] | $PhCH_2CONH_2$ (47%) | $PhCH_2CN$ (68%) |
| | | $PhCO_2H$ (86%) | $PhCO_2H$ (74%) |
| $PhCH_2$ | Ph[d] | $PhCONH_2$ (61%)[e] | PhCN (77%) |
| | | $PhCH_2CO_2H$ (68%) | $PhCH_2CO_2H$ (74%) |
| Me | Bu[f] | $BuCONH_2$ (59%) | BuCN (70%) |
| Me | $CH_2Ph$[g] | $PhCH_2CONH_2$ (83%)[h] | $PhCH_2CN$ (87%) |
| Pr | Et[i] | $EtCONH_2$ (19%) | EtCN (45%) |
| | | $PrCO_2H$ (78%) | $PrCO_2H$ (84%) |

[a] Purchased from Distillation Products Industries, Rochester, N. Y. [b] M.p. 162–163°. H. Rheinboldt and O. Schmitz-Dumont, *Ann.* **444,** 113 (1925) report 164–165°. [c] M.p. 126–127.5°. W. Schneidewind, *Ber.,* **21,** 1323 (1888) reports 125–126°. [d] M.p. 114–114.5°. *Anal.* Calcd. for $C_{15}H_{13}O_2N$: C, 75.29; H, 5.48; N, 5.85. Found: C, 75.46; H, 5.43; N, 5.81. [e] An 8% yield of $PhCO_2H$ was obtained also. [f] M.p. 59–60°. *Anal.* Calcd. for $C_7H_{13}O_2N$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.85; H, 9.25; N, 9.77. [g] M.p. 80–81°. G. Ponzio, *Gazz. chim. ital.,* **35,** 394 (1905) reports 80–81°. [h] A 12% yield of $PhCH_2CO_2H$ was obtained also. [i] B.p. 62–63° (0.45 mm.), $n_D^{25}$ 1.4548. *Anal.* Calcd. for $C_7H_{13}O_2N$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.97; H, 9.30; N, 9.51.

The results obtained show that in both so-called types of rearrangement the nitrogen in the products was attached to the radical which originally bore the oxime carbon, and the conclusion seems inescapable that both reactions proceeded by the same path, except that hydrolysis of the nitrile took place in sulfuric acid. Additional confirmation for this view was obtained when other typical catalysts for the "normal" reaction were examined: Phosphorus pentachloride gave valeronitrile (70%) from 3-oximino-2-heptanone, and phenylacetonitrile (86%) from 2-oximino-1-phenyl-3-butanone; thionyl chloride gave benzonitrile (88%) from 1-oximino-1-phenyl-2-propanone. Trifluoroacetic acid, which has been shown[9–11] to give normal amide products from simple ketoximes, gave

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(6) E. C. Horning, V. L. Stromberg, and H. A. Lloyd, *J. Am. Chem. Soc.,* **74,** 5153 (1952).

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(8) R. T. Conley and F. A. Mikulski, *J. Org. Chem.,* **24,** 97 (1959).

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(10) M. Hudlicky, *Chem. listy,* **51,** 490 (1957); *Collection Czechoslov. Chem. Communs.,* **23,** 462 (1958).

(11) W. D. Emmons, *J. Am. Chem. Soc.,* **79,** 6522 (1957).

valeronitrile (58%) from 3-oximino-2-heptanone, and benzonitrile (94%) and benzoic acid (88%) from α-benzil monoxime.

It seems reasonable to conclude that all Beckmann rearrangements of α-oximino ketones possessing the *anti* configuration proceed by the same route, and therefore that the terms "normal" and "abnormal" as applied to this reaction are superfluous. The term "second order" might well be retained to refer to the rearrangement of all α-oximino ketones, which, since it appears to involve shift of a pair of electrons only,[12] is mechanistically quite distinct from the rearrangement of simple ketoximes, which involves shift of an electron pair and the accompanying organic group.

Full details of this study will be reported later.

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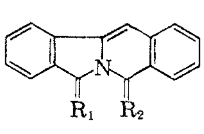
## Novel Synthesis of a 1,2,5,6-Dibenzocycl[3,2,2]azine[1]

*Sir:*

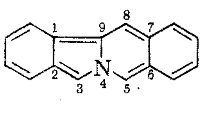
The recent synthesis of cycl[3,2,2]azine by Boekelheide and Windgassen[2] suggested that the readily available 1,2,6,7-dibenzo-3,5-dihydro-3,5-diketopyrrocoline,[3] I, might lend itself to synthesis of additional examples of this interesting class of heterocycles. Inspection of accurate molecular models[4] of pyrrocoline and of possible Diels-Alder adducts of pyrrocoline clearly indicated that the steric requirements alone of 3,9- or 5,8-adducts should effectively preclude their formation, while a 3,5-adduct (the product of 1,8- rather than 1,4-Diels-Alder addition) should be quite free of strain. Formation of a 3,5-adduct should be favored by the resonance energy of such a product, which would be expected to be greater than that of 3,9- or 5,8-adducts. Finally molecular orbital calculations indicate that the localization energy for simultaneous attack at the 3- and 5-positions is comparable to that of normal Diels-Alder additions.[5] In the case of III, formation of a 3,5-adduct carries the additional advantage of the recovery of the full resonance energy of two benzenoid rings.

The starting material I was prepared in 91% yield by heating the dry diammonium salt of 2,2′-dicarboxydesoxybenzoin[3] to 240° in the presence of a heat-transfer agent such as diphenylamine. Reduction of I with tin and hydrochloric acid in refluxing acetic acid produced II, which was recrystallized from benzene-hexane, m.p. 193–194°, (Found: C, 82.15; H, 4.77; N, 6.04: $\lambda_{max}$ 6.05 $\mu$) in 62% yield. Reduction of II to III proceeded in 71% yield when carried out with excess lithium aluminum hydride in refluxing ether for 3 days. The product, 1,2,6,7-dibenzopyrrocoline, III, was purified by solution in dilute acid, treatment with charcoal, and reprecipitation with sodium bicarbonate. Although all operations were carried out under nitrogen, the yellow-green product which melted at 200–202° under vacuum was so sensitive to oxygen that satisfactory analyses could not be obtained.

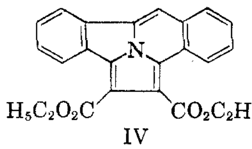
1,2,5,6 - Dibenzo - 3,4 - dicarbethoxycycl[3,2,2]-azine, IV (Found: C, 74.77; H, 5.17; N, 3.87), yellow crystals, m.p. 125–126°, was obtained in 54% yield when toluene solutions of diethyl acetylenedicarboxylate and III containing a catalytic amount of 10% palladium-on-charcoal and a trace of hydroquinone were mixed and refluxed for 14 hr. under nitrogen. The product possesses no basic properties and has a strong yellow-green fluorescence in ether or benzene solution. Its infrared spectrum ($CCl_4$) has characteristic absorptions at 5.82 $\mu$ (shoulder), 5.98 $\mu$, and 8.20 $\mu$, while its ultraviolet spectrum in ethanol has $\lambda_{max}$ 232 (log $\epsilon$ 5.59), 255 (5.28), 293 (5.42), 317 (5.36), 343 (shoulder), and 420 (4.11). The picrate, m.p. 134–135° (Found: C, 58.53; H, 3.77; N, 9.19), and *sym*-trinitrobenzene adduct, m.p. 161–163° (Found, C, 60.38; H, 3.87; N, 9.56) were prepared in absolute ethanol.



I, $R_1 = R_2 = O$
II, $R_1 = H_2$, $R_2 = O$



III



IV

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(1) Work done at the School of Chemistry, Rutgers, The State University, New Brunswick, N. J.

(2) V. Boekelheide and R. J. Windgassen, Jr., *J. Am. Chem. Soc.*, **80**, 2020 (1958); R. J. Windgassen, Jr., W. H. Saunders, and V. Boekelheide, *J. Am. Chem. Soc.*, **81**, 1459 (1959).

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