

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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(12) A. L. Green and B. Saville, *J. Chem. Soc.*, 3887, (1956).

Novel Synthesis of a 1,2,5,6-Dibenzocycl[3,2,2]-azine¹

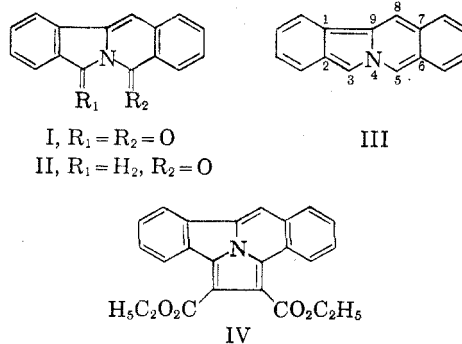
Sir:

The recent synthesis of cycl[3,2,2]azine by Boekelheide and Windgassen² 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 models⁴ 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'-dicarboxydesoxybenzoin³ 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: λ_{\max} 6.05 μ) 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 (CCl₄) has characteristic absorptions at 5.82 μ (shoulder), 5.98 μ , and 8.20 μ , while its ultraviolet spectrum in ethanol has λ_{\max} 232 (log ϵ 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.



(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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(4) J. C. Godfrey, *J. Chem. Educ.*, **36**, 140 (1959).

(5) R. A. Barnes, private communication.

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