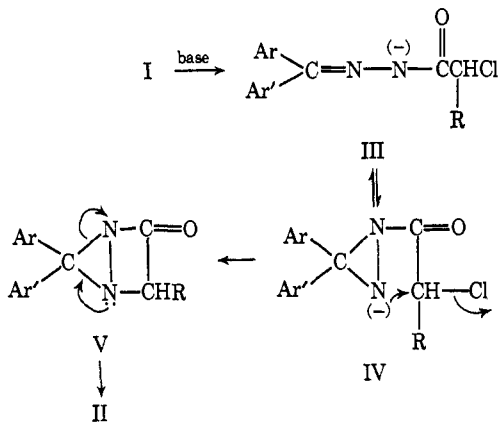
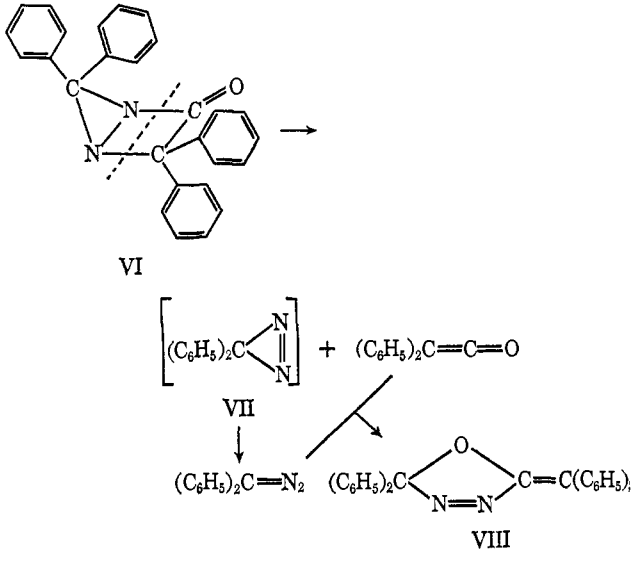
Scheme I



overnight, however, the reaction mixture yielded bright yellow crystals of 2,2-diphenyl-5-diphenylmethylene-1,3,4-oxadiazoline (VIII), which had been prepared previously by condensation of diphenyldiazomethane with diphenylketene.[7] All of these results are readily interpretable in terms of the proposed mechanism (Scheme I). Molecular models show that the bicyclodiaziridine intermediate VI is highly crowded because of unavoidable compression of the two *endo*-oriented phenyl rings; it apparently fissions to diphenylketene



and diphenyldiazirene (VII), which has been shown by Overberger[8] to rearrange rapidly to diphenyldiazomethane. It follows that cyclization of the α-monophenylchloroacetylhydrazone Ic must give *two* intermediate isomeric fused bicyclic diaziridines, one with an *endo*- and the other with an *exo*-oriented phenyl group in the four-membered ring. The former, to relieve ring strain, breaks down to phenylketene and diphenyldiazomethane; the latter yields azomethine imide IIc by the route depicted in Scheme I.

(3) The above mechanism (Scheme I) requires initial attack of a nitrogen anion at the sp^2-hybridized hydrazone carbon (*cf.* III, Scheme I). That this should be a stereospecific process has been confirmed by our observation that the *syn*- and *anti*-chloroacetylhydrazones of *p*-bromobenzophenone (Ib,d)[9] gave two *isomeric* azomethine imides (IIb,d). The fact that these two compounds are stable and noninterconvertible indicates conclusively that there is no delocalization of positive charge into the aromatic rings, *i.e.*, that there is no single-bond character to the exocyclic C=N bond. This is substantiated not only by the X-ray determination of the structure of the isomer derived from the hydrazone Id[5] but also by the fact that the chloroacetylhydrazone of fluorenone (Ie) readily yielded azomethine imide IIe, in which positive charge delocalization into the five-membered ring is clearly unfavorable energetically.

(7) W. Kirmse, *Chem. Ber.*, **93**, 2357 (1960).

(8) C. G. Overberger and J. P. Anselme, *Tetrahedron Letters*, 1405 (1963).

(9) Prepared by the action of chloroacetyl chloride on the *syn* and *anti* isomers of *p*-bromobenzophenone hydrazone, which had previously been characterized: D. E. Pearson, K. N. Carter, and C. M. Greer, *J. Am. Chem. Soc.*, **75**, 5905 (1953).

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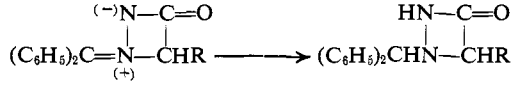
Novel Heterocyclic Syntheses from Azomethine Imides. 2-Unsubstituted Diazetidinones[1]

Sir:

We have described in a preceding communication[2] the preparation of a series of azomethine imides possessing structure I from the treatment of α-chloroacylhydrazones of benzophenones with base. We describe here some chemical transformations of these and a homologous azomethine imide (VI) which represent effective synthetic routes to previously inaccessible small-ring heterocyclic systems.

Reduction of 1-(diphenylmethylene)-3-oxo-1,2-diazetidinium inner salt (Ia)[2] with sodium borohydride in methanol gave a dihydro compound, mp 174–175° (76%). Its ir spectrum showed bands at 3100 (NH), 1680 (sh), 1720 and 1750 cm^{-1} (carbonyl); its nmr spectrum exhibited a ten-proton aromatic multiplet at δ 7.35, a single methine proton at 4.57, and a two-proton



a, R = H
b, R = CH_3
c, R = C_6H_5

quartet centered at 3.88 (J = 14.5 Hz). These data indicate that the reduction product is the 2-unsubstituted diazetidinone IIa; this represents the first synthesis of a diazetidinone not involving an azo compound as a starting material.[3] Analogous reductions with borohydride of the azomethine imides Ib and Ic gave the diazetidinones IIb and IIc [IIb: mp 163–165° (55%); ir, 3175, 1750, 1730 (sh) cm^{-1}; nmr, δ 1.17 (J = 7 Hz) (CH_3 group), 3.92 (J = 7 Hz) (1 H, quartet), 4.6 (1 H, singlet), 7.36 (10 H, aromatic multiplet); IIc: mp

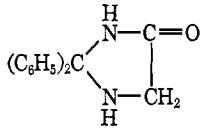
(1) This investigation was supported by a grant (CA-02551) to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service.

(2) R. B. Greenwald and E. C. Taylor, *J. Am. Chem. Soc.*, **90**, 5272 (1968).

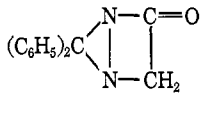
(3) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions; The Formation of Three- and Four-Membered Heterocycles," Interscience Publishers, Inc., New York, N. Y., 1967, pp 246–257.

158–159° (83%); ir, 3175, 1760 cm^{-1}; nmr, δ 4.62 (1 H, singlet), 4.92 (1 H, singlet), 6.9–7.7 (15 H, aromatic multiplet)]. The rate of inversion of the benzhydryl grouping of N_1 of compound Ia was measured utilizing the method of Mannschreck.[4,5] In dimethyl-d_6 sulfoxide compound Ia had k_c = 102.8 sec^{-1} and $\Delta G^{\ddagger}$ = 18.4 kcal/mol with a coalescence temperature (T_c) of 97°.

Reduction of azomethine imide Ia with Raney nickel in ethanol gave α-diphenylmethylaminoacetamide (mp 109–110.5°), which was prepared independently from ethyl α-diphenylmethylaminoacetate[6] and ammonia; its formation from Ia follows a well-established precedent for N–N bond cleavage of both acyclic[7,8] and cyclic[9,10] acylhydrazides. However, catalytic reduction of azomethine imide Ia with deactivated Raney nickel[11] gave 2,2-diphenyl-4-imidazolidinone (III) [mp 165–166.5° (67%); ir, 3410, 3100, 1680 cm^{-1}; nmr, δ 3.96 (2 H, singlet), 6.34 (1 H, broad N–H), 7.43 (10 H, complex



III

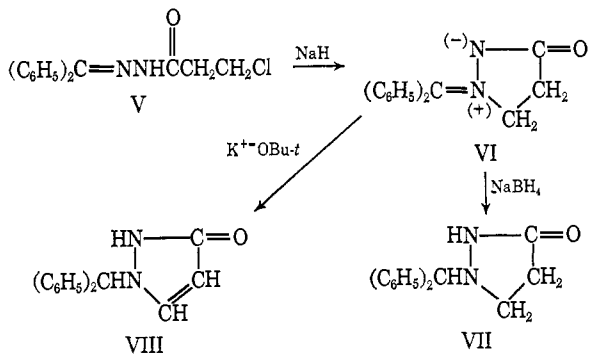


IV

aromatic multiplet); *m/e* 238]. The structure of III was confirmed by dilute acid hydrolysis to benzophenone and glycinamide hydrochloride.

The formation of III from the azomethine imide Ia suggests the possible intermediacy of the bicyclodiaziridine valence bond tautomer IV, which was previously implicated as an intermediate in the pathway to Ia from the chloroacetylhydrazone of benzophenone.[2]

Our new route to cyclic azomethine imides[2] has been extended to the use of the homologous β-chloropropionylhydrazone of benzophenone (V), which yielded VI with sodium hydride in benzene. The structure of VI was confirmed by its spectroscopic and chemical properties. Mass spectroscopy and microanalysis confirmed its molecular formula as $C_{16}H_{14}N_2O$ (*m/e* 250), mp 228–230° dec (77%). Its uv spectrum (ethanol) showed maxima at 240 mμ (ε 13,400) and 335 mμ (ε 23,600); its ir spectrum, in contrast with that of Ia, revealed a carbonyl band at 1685 cm^{-1}, consistent with a five-membered cyclic lactam. Finally, its nmr spectrum showed two triplets at δ 2.59 and 4.12 (J = 7 Hz, with further fine splitting) and a complex eight-proton aromatic multiplet centered at 7.40, with an additional two-proton multiplet at 7.95. Acid hydrolysis of VI in aqueous ethanol gave benzophenone and 3-pyrazolidinone hydrochloride (mp 195° dec, 74%), identical with an authentic sample.[12] Sodium borohydride reduction of VI gave 1-diphenylmethyl-3-pyrazolidinone (VII) [mp 158–160° (66%); ir, 3150, 1680 (split) cm^{-1}; nmr, δ 2.38 (2 H, triplet; J = 8 Hz, with finer splitting), 3.18 (2 H, triplet; J = 8 Hz, with finer splitting), 4.57 (1 H, singlet), 7.0 (broad N–H singlet), 7.34 (10 H, aromatic multiplet)]. Reduction of VI with Raney nickel in ethanol gave β-diphenylmethylaminopropionamide (mp 99–100°).



V

VI

VIII

VII

Treatment of the azomethine imide VI with potassium *t*-butoxide in refluxing benzene resulted in its conversion in 75% yield into an isomer, mp 179–180°. Spectral data [nmr, δ 7.12 (10 H, aromatic multiplet), 6.5 (1 H, singlet), 5.6 and 7.0 (2 H, doublet; J = 3.5 Hz); ir, 2625 (broad), 1675 cm^{-1} (weak); uv, $\lambda_{max}^{ethanol}$ 230 mμ (sh)] showed that this isomeric compound must possess structure VIII. It formed a monobromo derivative and both a hydrochloride and a sodium salt. The mechanism of the conversion of VI to VIII, as well as cycloaddition reactions and further chemical transformations of the cyclic azomethine imides I and VI, will be described in the full paper.

(4) E. Fahr, W. Fischer, A. Jung, L. Sauer, and A. Mannschreck, *Tetrahedron Letters*, 161 (1967).
(5) A. Mannschreck, G. Rissmann, F. Vögtle, and D. Wild, *Chem. Ber.*, 100, 335 (1967).
(6) H. H. Fox and W. Wenner, *J. Org. Chem.*, 16, 225 (1951).
(7) C. Ainsworth, *J. Am. Chem. Soc.*, 76, 5774 (1954).
(8) C. Ainsworth, *ibid.*, 78, 1636 (1956).
(9) E. C. Taylor, J. W. Barton, and T. S. Osdene, *ibid.*, 80, 421 (1958).
(10) E. C. Taylor and J. W. Barton, *ibid.*, 81, 2448 (1959).
(11) This deactivation was carried out by boiling commercial Raney nickel catalyst in water for 30 min.
(12) J. C. Howard, G. Gever, and P. H. L. Wei, *J. Org. Chem.*, 28, 868 (1963).

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The Reaction of Vitamin B_{12a} and of Cobaloximes with Carbon Monoxide. Evidence for Self-Reduction of Vitamin B_{12a} in Neutral Solution[1]

Sir:

Bayston and Winfield[2] recently reported the reduction of vitamin B_{12a} with carbon monoxide in aqueous solution (eq 1). This reaction suggests a unique reactivity

$$2B_{12a} + CO + H_2O \longrightarrow 2B_{12r} + CO_2 + 2H^+ \qquad (1)$$

of the Co(III) ion in vitamin B_{12a}, since conventional Co(III) chelates are known to be unreactive with CO. Cobaloximes(III), *e.g.*, hydroxy(aquo)- or hydroxy(pyridine)bis(dimethylglyoximato)cobalt(III), are likewise not reduced by CO, but if a trace of a cobaloxime(II) is added, reduction to the Co(I) derivatives is observed. The reduction of cobaloximes(III) with carbon monoxide yields the Co(I) nucleophiles under extremely mild conditions and is recommended for the synthesis of sensitive organocobaloximes. The reaction with CO proceeds in a manner typical of autocatalyzed reactions (Figure 1) and appears to be similar to that

(1) Supported by National Science Foundation Grant GB 6174.
(2) J. N. Bayston and M. E. Winfield, *J. Catalysis*, 9, 217 (1967).