The Goering–Schewene diagram makes it clear that the factor or factors responsible for the difference in energy between the *exo* and *endo* transition states in norbornyl systems must likewise be responsible for the stereoselectivity leading to the almost exclusive formation of the *exo* products in these systems. It was pointed out that several possibilities exist:[7] (1) the *exo* transition state is stabilized by nonclassical resonance, with the *endo* transition state being normal; (2) the *endo* transition state is destabilized by steric effects, the *exo* transition state being normal; (3) a combination of 1 and 2; or (4) some new factor not now recognized by current theory.[8]

The available evidence indicates that σ participation cannot be a significant factor in the behavior of these stabilized tertiary derivatives. Consequently, we are left only with the possibilities that the *endo* transition state is destabilized by steric strain or that there is some factor not now recognized by current theory.

We wish to caution the reader again that this conclusion that σ participation is not a factor in these stabilized tertiary derivatives should not be extrapolated to the position that σ participation may not contribute to the *exo*:*endo* rate ratios and *exo*:*endo* product ratios observed in secondary norbornyl derivatives.[3b] However, if steric effects make a major contribution to the *exo*:*endo* rate and product ratios in these stabilized tertiary norbornyl derivatives, it is difficult to see why these steric effects will not also make a major contribution to these ratios in the secondary norbornyl derivatives.

(7) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U.S.*, **56**, 1653 (1966).

(8) Torsional effects might be such a factor, but it evidently can make only a minor contribution to the present reactions: P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 699, 701 (1967).

(9) Research assistant on grants (G 19878 and GP 6492 X) from the National Science Foundation.

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Received April 11, 1968

A New Route to Cyclic Azomethine Imides[1]

Sir:

Azomethine imides were first prepared in 1960 through the reaction of diazoalkanes with aromatic azocyanides,[2] and later by utilization of azocarbonyl compounds.[3] More recently, the condensation of 3-pyrazolidones with ketones has been shown to lead to unusually stable azomethine imides.[4]

We report a simple new method for the preparation in good yield of stable cyclic azomethine imides possessing structure II. Thus, treatment of benzophenone chloroacetylhydrazone (Ia) with sodium hydride or potassium *t*-butoxide gave a colorless, crystalline solid, mp 199–200°. Microanalysis and mass spectroscopy (*m/e* 236) confirmed the molecular formula $C_{15}H_{12}N_2O$.

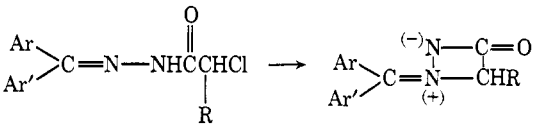
(1) This work was supported by a grant (CA-02551) to Princeton University from the National Cancer Institute, National Institutes of Health, Public Health Service.

(2) R. Huisgen, R. Fleischmann, and A. Eckell, *Tetrahedron Letters*, No. 12, 1 (1960).

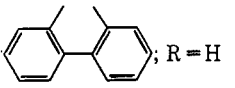
(3) G. F. Bettinetti and L. Capretti, *Gazz. Chim. Ital.*, **95**, 33 (1965).

(4) H. Dorn and A. Otto, *Angew. Chem. Intern. Ed. Engl.*, 7, 214 (1968).

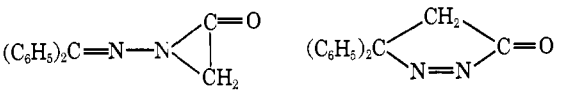
Its uv spectrum ($\lambda_{max}^{C_2H_5OH}$ 245 mμ (ε 17,000), 325 mμ (ε 26,200)) indicated the introduction of a new and potent



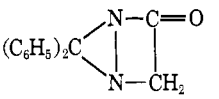
I II

a, Ar = Ar′ = C_6H_5; R = H
b, Ar = C_6H_5; Ar′ = C_6H_4Br-*p*; R = H
c, Ar = Ar′ = R = C_6H_5
d, Ar = C_6H_4Br-*p*; Ar′ = C_6H_5; R = H
e, Ar = Ar′ =  ; R = H

chromophore as compared with the starting hydrazone ($\lambda_{max}^{C_2H_5OH}$ 287 mμ (ε 19,850)). Its ir spectrum revealed the absence of an N–H proton and the presence of two strong bands in the carbonyl region at 1740 and 1775 cm^{-1} (*cf.* the starting hydrazone Ia: 3175 (N–H), 1700 cm^{-1} (C=O)). The high carbonyl absorption suggested the presence of a four-membered cyclic lactam. The nmr spectrum showed a singlet methylene group at δ 5.31, a complex eight-proton aromatic multiplet at 7.41, and a downfield two-proton aromatic multiplet at 7.92. These data are consistent only with formulation of the cyclization product as 1-(diphenylmethylene)-3-oxo-1,2-diazetidinium inner salt (IIa) and exclude other isomeric structures such as i, ii, and iii, all of which may formally be derived from Ia by reasonable



i ii



iii

mechanistic pathways. Structure IIa has been confirmed by X-ray analysis[5] of the mono-*p*-bromophenyl derivative IId (*vide infra*) and by chemical transformations of IIa which are summarized in the accompanying communication.[6]

We suggest that azomethine imide IIa is formed by the route outlined in Scheme I; the following observations support this suggestion.

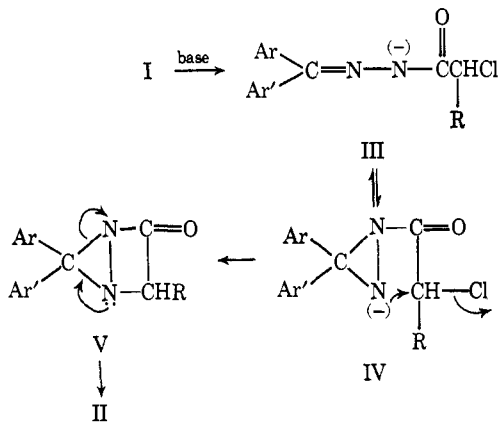
(1) The chloroacetylhydrazone Ia is completely stable in the absence of base. Nucleophilic bases such as pyridine bring about displacement of Cl^- to give quaternary salts. Azomethine imide formation therefore requires preliminary proton abstraction by a strong nonnucleophilic base.

(2) Treatment of the α-chloro-α-phenylacetylhydrazone Ic with sodium hydride gave azomethine imide IIc and diphenyldiazomethane. On the other hand, the α,α-diphenyl-α-chloroacetylhydrazone of benzophenone gave no azomethine imide; instead a viscous red gum was obtained whose ir spectrum indicated the presence of diphenyldiazomethane (2075 cm^{-1}). On standing

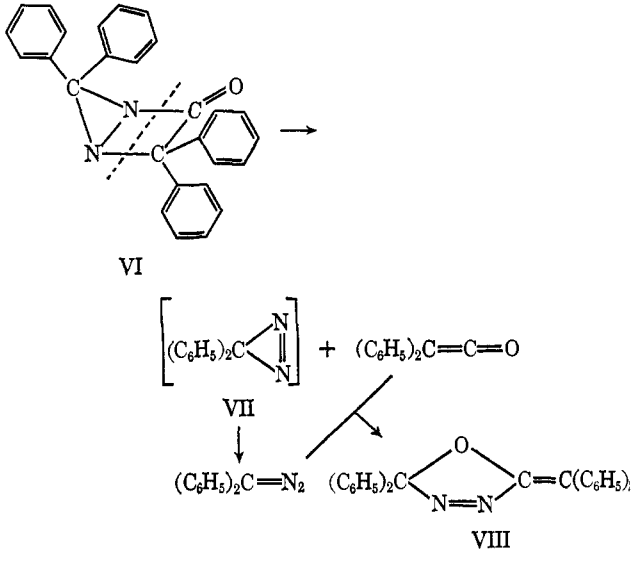
(5) C. J. Fritchie, Jr., and J. L. Wells, *Chem. Commun.*, 917 (1968).

(6) R. B. Greenwald and E. C. Taylor, *J. Am. Chem. Soc.*, **90**, 5273 (1968).

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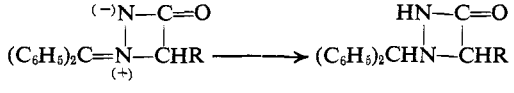
Novel Heterocyclic Syntheses from Azomethine Imides. 2-Unsubstituted Diazetidinones[1]

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.