

that the incipient stability of *t*-butyl and acyl radicals dominates the course of the photolysis of *t*-butyl ketones. This situation is not clear in vapor phase photochemistry.⁶ The difference between the photochemical behavior of carbonyl compounds in vapor phase and in solution may be attributed to the fact that the excited molecules lose their vibrational energy more rapidly in solution.

We also found that at relatively low piperylene concentrations (0.05 *M*) the quantum yield for photolysis of *t*-butyl alkyl ketones was reduced by only about 10% while the formation of isobutylene was more than 90% suppressed. This observation suggests that isobutylene is formed mainly from free-radical processes.

In summary, we have shown (1) that the type I process in the photolysis of *t*-butyl alkyl ketones is the major reaction mode in solution and arises from both the singlet and the triplet excited states and (2) that the type II process arises predominantly from a singlet excited state.

(6) See Table I, footnote *c*.

(7) The authors wish to acknowledge the National Science Foundation and the U. S. Atomic Energy Commission for their support of this work, and Mr. David L. Williams for some preliminary investigation on the photochemistry of pinacolone.

(8) NASA Trainee, University of Chicago, 1965-1967.

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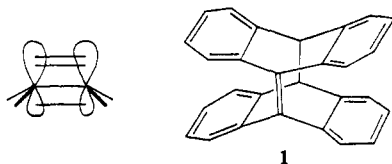
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Received August 24, 1967

9,9'-Dehydrodianthracene

Sir:

We wish to report the isolation and characterization of 9,9'-dehydrodianthracene¹ (**1**), an unusual olefin in that the probable structure is one in which the double bond atoms lie outside the plane defined by the four atoms attached to the double bond. This type of distortion of the π system is similar to that of the triple bond in species such as arynes² and medium-ring cycloalkynes.² The transient existence of **1** was first suggested by Applequist, *et al.*, in studies of the reaction of 9-bromodianthracene with strong bases.³



Irradiation of 9,9'-dianthrylcarbinol (**2**) in dioxane effected ring closure to the cyclopropanol **3a**.⁴ Oxidation of the alcohol with diisopropylcarbodiimide in dimethyl sulfoxide⁵ afforded the cyclopropanone **3b**:⁶ mp 240-260° dec (mp of dianthryl ketone 266-267°); ir

(1) 3,4:7,8:9,10:11,12-Tetrabenzotricyclo[4.2.2.2^{2,2}.^{2,2}]dodeca-1,3,7,9,11-pentaene.

(2) For recent references and reviews, see L. K. Montgomery and L. E. Applegate, *J. Am. Chem. Soc.*, **89**, 5305 (1967).

(3) D. E. Applequist, R. L. Litle, E. C. Friedrich, and R. E. Wall, *ibid.*, **81**, 452 (1959). See also D. E. Applequist, R. Searle, M. Steinhart, E. C. Friedrich, and R. L. Litle, *J. Org. Chem.*, **30**, 2126 (1965).

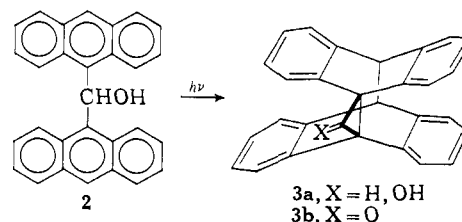
(4) F. D. Greene, *Bull. Soc. Chim. France*, 1356 (1960); F. D. Greene, J. G. Jewett, L. A. Kaminski, and S. C. Cherkofsky, in preparation.

(5) K. E. Pfitzner and J. C. Moffatt, *J. Am. Chem. Soc.*, **87**, 5661, 5670 (1965).

(6) A full investigation of this compound is in progress [see also J. F. Pazos and F. D. Greene, *ibid.*, **89**, 1030 (1967)].

(KBr) 1836, 1796 (carbonyl), 1467, 1451 (characteristic of anthracene dimers), and 775 cm^{-1} (*o*-xylene units); nmr (CDCl_3) δ 4.6 (singlet, 2 H), 6.9 (multiplet, 16 H); mass spectrum (70 ev) identical with that of 9,9'-dianthryl ketone. Irradiation (3500 Å) of the cyclopropanone in benzene solution yielded a mixture of products. Chromatography on silicic acid and recrystallization from acetonitrile afforded a colorless crystalline material, assigned structure **1** (*Anal.* Calcd for $\text{C}_{28}\text{H}_{18}$: C, 94.88; H, 5.12. Found: C, 94.68; H, 5.24); nmr ($\text{DMSO}-d_6$) δ 4.71 (singlet, 2 H), 7.01 (seven-line multiplet, 16 H, width at half-height 15 Hz); uv (hexane) similar to that of dianthracene;⁷ mass spectrum (70 ev) identical with that of 9,9'-bianthryl; ir (KBr) 1463, 1452, 1442, 1219, 1140, 1027, 940, 778, 761, 752, 689, and 678 cm^{-1} .

Compound **1** turns yellow on heating, mp and mmp 309-311°, identical with that of 9,9'-bianthryl. Isomerization to 9,9'-bianthryl also occurs on heating in solution (at 80° in hexane, $t_{1/2} \cong 30$ min, followed by uv). Further evidence in support of structure **1** is found in its reduction by hydrogen, Pd-C to dianthracene, in its oxidation by osmium tetroxide-sodium metaperiodate⁸ in dioxane to 10,10'-bianthrone, and



in the conversion of **1** to the corresponding epoxide by *m*-chloroperbenzoic acid.

(7) C. A. Coulson, L. E. Orgel, W. Taylor, and J. Weiss, *J. Chem. Soc.*, 2961 (1955). Neither the structure nor the ultraviolet of **1** is suggestive of conjugation between the 9,9'-double bond and the aryl rings.

(8) R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

(9) National Institutes of Health Predoctoral Fellow, 1965-1968.

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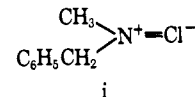
Aziridines. XI. Nitrogen Inversion in N-Haloaziridines

Sir:

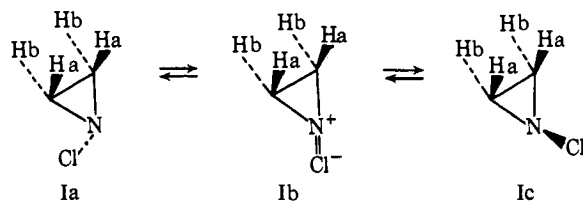
Recently the proton spectrum of N-chloroaziridine (**I**) was described by Bystrov and coworkers.¹ Since the ring-proton spectrum consisted of a singlet at 25° and lower temperatures, the Russian workers¹ concluded that N-chloroaziridine undergoes rapid nitrogen inversion (**Ia** \rightleftharpoons **Ic**) even at -100°. These authors reasoned that a substantial contribution from **Ib** stabilized the planar transition state for nitrogen inversion, by d-orbital resonance.² As a result of such

(1) V. F. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. V. Stepanyants, and O. A. Iuzhakova, *Opt. Spectry. (USSR)*, **19**, 122 (1965).

(2) By analogy, Griffith and Roberts³ ascribed the rapid inversion in N-benzyl-N-methylchloramine above -70° to a significant contribution from **i** toward stabilization of the transition state for inversion



by d-orbital resonance.

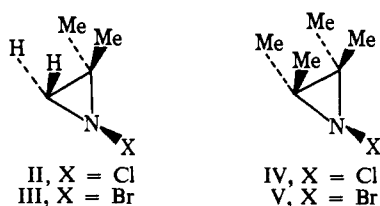


stabilization, a decrease in the potential barrier to inversion occurs. They¹ propose that this decrease in ΔE leads to an appreciable increase in the nitrogen inversion frequency.

In a later paper, Anet, *et al.*,⁴ also conclude that the rate of nitrogen inversion in N-chloroaziridine is probably high. However, these authors suggest that I would be predicted to have a low rate of inversion because of high electronegativity and electrostatic effects. Significantly, N-chloroimines have been found⁵ to have lower rates of inversion than N-alkylimines.

In this communication we present spectral data which clearly define the remarkable role that halogens play in governing the rate of nitrogen inversion in N-haloaziridines.

The N-haloaziridines II-V selected for study were prepared *via* halogenation of 2,2-dimethylaziridine and 2,2,3,3-tetramethylaziridine with either N-chloro or N-bromosuccinimide in ether at room temperature.



The 60-MHz spectra of the purified⁶ N-haloaziridines were recorded as 25% (w/v) CCl_4 solutions at room temperature. The spectra are depicted in Figure 1.

The conspicuous nonequivalence of the geminal nuclei in II-V reveals that nitrogen inversion in these molecules is slow on the nmr time scale at $\sim 25^\circ$. *More significantly, the spectra of the N-chloroaziridines as dilute solutions in o-xylene remained unchanged even at 120° .* The thermal lability of the N-haloaziridines has so far precluded attempts to determine their coalescence temperatures. However, further variable-temperature studies on the more stable N-chloroaziridines are in progress. A full account of our nmr spectral studies will be forthcoming.

In sharp contrast to earlier claims,^{1,4} the rate of pyramidal inversion of nitrogen in N-chloroaziridines is remarkably low. The failure to detect a low rate of inversion for N-chloroaziridine in an earlier study¹ may imply that the relative chemical shift, ν_{AB} , is quite small in I. Nevertheless the dramatic retardation of nitrogen inversion due to halogen substitution not only negates the concept of d-orbital resonance stabilization in N-chloroaziridines¹ but clearly accents the remarkable con-

(3) D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965).

(4) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967).

(5) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *ibid.*, **88**, 2775 (1966).

(6) Vacuum distillation of II and III and sublimation of IV and V afforded analytically pure products.

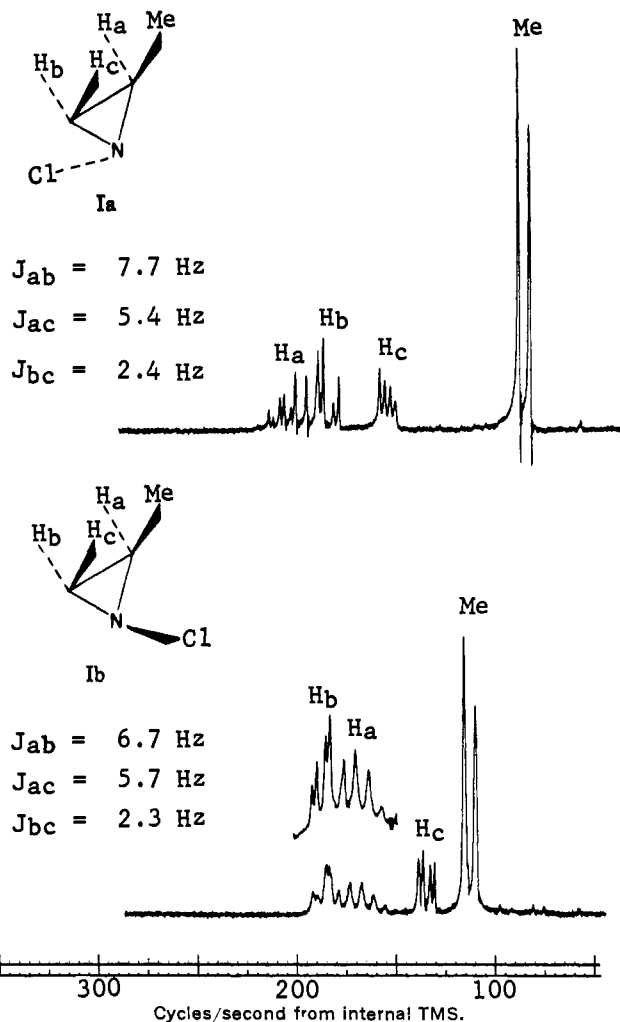


Figure 1. Nmr spectra (100 MHz) of *trans*- and *cis*-1-chloro-2-methylaziridine (Ia and Ib, respectively) as 25% (w/v) benzene solutions. The decoupled spectrum (insert) of Ib was obtained by irradiation of the methyl protons.

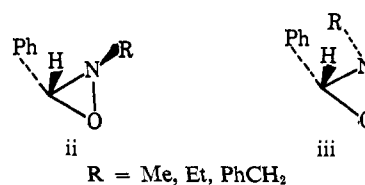
figurational stability of pyramidal nitrogen in these molecules.

Assuming a coalescence temperature (T_c) of 120° , a lower limit of 21 kcal/mole was calculated⁷ for the free-energy barrier to pyramidal inversion in II. Significantly, the appreciable value of ΔF^* represents the highest barrier to nitrogen inversion yet observed in aziridines⁸ and strongly suggests that II may be re-

(7) For relevant equations see: (a) L. W. Reeves, *Advan. Phys. Org. Chem.*, **3**, 18 (1965); (b) C. S. Johnson, Jr., *Advan. Magnetic Chem.*, **1**, 35 (1965); (c) A. Mannschreck, R. Radeglia, E. Gründemann, and R. Ohme, *Chem. Ber.*, **100**, 1778 (1967).

(8) Very recently, a similar high energy barrier to nitrogen inversion in diaziridines and oxaziridines⁹ was reported by Mannschreck and co-workers.^{7c}

(9) In a recent study¹⁰ we detected the existence of discrete *trans* (ii) and *cis* (iii) invertomers (diastereomeric conformers) of 2-alkyl-3-phenyloxaziridines by nmr spectroscopy. Remarkably, the invertomers ii and iii exhibited configurational stability even at temperatures



of $\sim 120^\circ$.

(10) S. J. Brois and R. G. Pews, manuscript submitted for publication.

solvable into stable optical antipodes at room temperature. We are actively investigating this possibility.

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Aziridines. XII. Isolation of a Stable Nitrogen Pyramid

Sir:

So far, all attempts to resolve substituted aziridines have been unsuccessful.¹ Moreover, Bottini and

We wish to describe here the successful synthesis of *cis* (Ib) and *trans* (Ia) isomers of 1-chloro-2-methylaziridine (I). Ia and Ib represent the first isolable invertomers of trivalent nitrogen, and their isolation provides clinching evidence for the existence of a stable nitrogen pyramid in N-chloroaziridines.

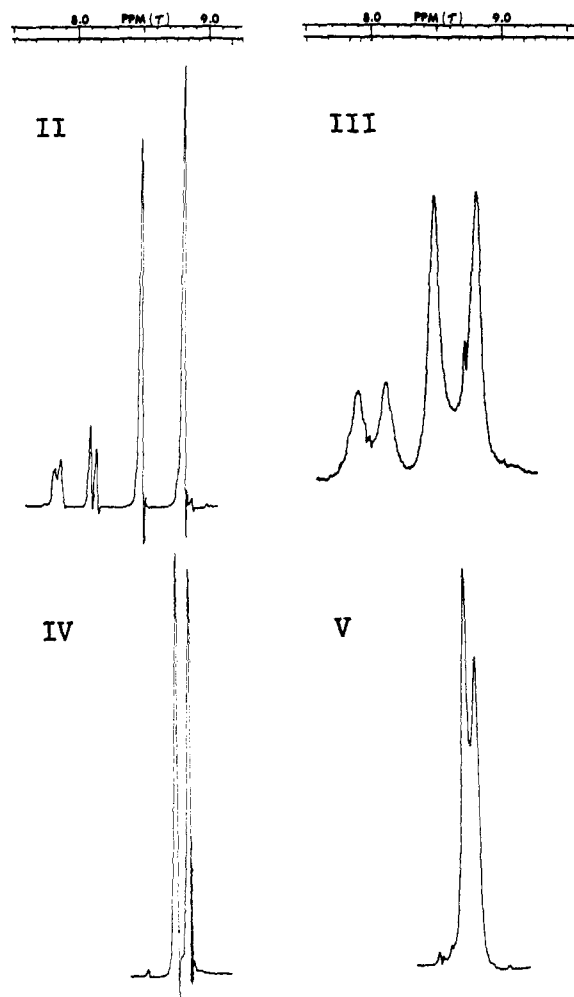
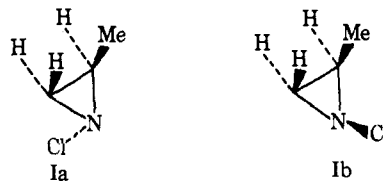


Figure 1. Proton spectra of N-haloaziridines as 25% (w/v) CCl_4 solutions at 25°.

Roberts¹⁸ have concluded that "substituted aziridines with molecular asymmetry due to trivalent nitrogen are likely only to be resolvable into reasonably stable optical antipodes at temperatures below -50°."

However, we have recently uncovered nmr spectral evidence² which suggests that N-haloaziridines may indeed be resolvable at room temperature. The present study lends further substance to this proposal.

(1) (a) R. Adams and T. L. Cairns, *J. Am. Chem. Soc.*, **61**, 2464 (1939); (b) P. Maitland, *Ann. Rept. Chem. Soc. London*, **36**, 239 (1939); (c) J. Meisenheimer and L.-H. Chou, *Ann.*, **539**, 70 (1939); (d) J. D. C. Mole and E. E. Turner, *Chem. Ind. (London)*, **17**, 582 (1939); (e) T. L. Cairns, *J. Am. Chem. Soc.*, **63**, 871 (1941); (f) H. M. Kissman and D. S. Tarbell, *ibid.*, **74**, 4317 (1952); (g) A. T. Bottini and J. D. Roberts, *ibid.*, **80**, 5203 (1958).

(2) S. J. Brois, *J. Am. Chem. Soc.*, **90**, 506 (1968).

The diastereogenic³ aziridine I selected for study was prepared *via* the addition of 0.1 mole of propylenimine to 1 equiv of N-chlorosuccinimide in refluxing ether. Gas chromatographic analysis of the filtered reaction mixture on a 3-ft 10% silicone oil (mol wt 200) column at 25° showed two product peaks (Ia and Ib) in ~2:1 intensity ratio, respectively. Elemental analysis of the gc purified products revealed that Ia and Ib were identical in composition.⁴ The alleged isomers gave positive halogen tests and liberated propylenimine on treatment with a secondary amine.

The 100-MHz nmr spectra of the *cis* and *trans* invertomers are shown in Figure 1 along with the first-order coupling constants obtained from the normal and decoupled (insert) spectra. The assignment of peaks is based on recent nmr data⁵ for configurationally pure N-chlorostyrenimines. The magnitudes of the vicinal and geminal coupling constants for Ia and Ib are in consonance with our previously reported⁵ J_{vic} and J_{gem} value for N-haloaziridines.

The rather weak *cis* coupling in Ib may be ascribed to a stereospecific electronegativity effect⁶ by chlorine on H_a and H_b in the *cis* invertomer. Owing to steric compression between the chlorine and the methyl group, the dihedral angle between the *trans* protons (H_a and H_b) and chlorine approaches 180°, the angle of maximum electronegativity effect and minimum J_{ab} .

Steric compression between the ring substituents in Ib is also reflected in the low-field shift of the methyl protons and the upfield shift of H_a relative to the corresponding protons in the *trans* invertomer. Apparently nonbonded interactions between chlorine and the methyl group in Ib shift the electron cloud away from the methyl hydrogens toward the region of H_a , thus accounting for the deshielding of the methyl protons and higher shielding of H_a .⁹ The upfield shift of H_c in the *cis* isomer compared to H_c in Ia is attributable to the magnetic anisotropy of chlorine.¹⁰ Details of the nmr

(3) Capable of diastereoisomerism owing to the presence of asymmetric carbon and nitrogen atoms.

(4) *Anal.* Calcd for $\text{C}_2\text{H}_5\text{NCl}$: C, 39.36; H, 6.61. Found (Ia): C, 39.34; H, 6.89; (Ib): C, 39.37; H, 6.85.

(5) (a) S. J. Brois and G. P. Beardsley, *Tetrahedron Letters*, 5113 (1966); (b) S. J. Brois, manuscript in preparation.

(6) By analogy, variations in vicinal coupling constants due to the orientation of electronegative substituents in six- and five-membered rings have recently been reported.

(7) H. Booth, *Tetrahedron Letters*, 411 (1965).

(8) L. H. Zalkow and M. Ghosal, *Chem. Commun.*, 922 (1967).

(9) For a relevant discussion of dispersion-induced shielding and deshielding effects in aziridines, see S. J. Brois, *Tetrahedron*, in press.

(10) A similar chemical shift trend has also been observed¹¹ in chlorooxiranes. Assuming *cis* coupling is stronger than *trans* couplings we find that the proton *cis* to chlorine in 2-chlorooxirane resonates at higher field relative to the *trans* proton.¹²

(11) S. J. Brois and E. L. Stogryn, unpublished results.

(12) The chemical shift values previously assigned¹³ to the protons