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.

N. C. Yang,[7] Eugene D. Feit[7,8]
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

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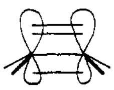
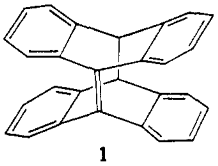
9,9′-Dehydrodianthracene

Sir:

We wish to report the isolation and characterization of 9,9′-dehydrodianthracene[1] (**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 arynes[2] 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]

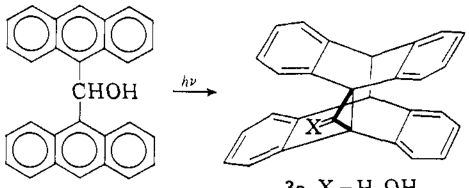




1

Irradiation of 9,9′-dianthrylcarbinol (**2**) in dioxane effected ring closure to the cyclopropanol **3a**.[4] Oxidation of the alcohol with diisopropylcarbodiimide in dimethyl sulfoxide[5] afforded the cyclopropanone **3b**:[6] mp 240–260° dec (mp of dianthryl ketone 266–267°); ir (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 $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 94.68; H, 5.24); nmr (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 metaperiodate[8] in dioxane to 10,10′-bianthrone, and in the conversion of **1** to the corresponding epoxide by *m*-chloroperbenzoic acid.



2

3a, X = H, OH
3b, X = O

(1) 3,4:7,8:9,10:11,12-Tetrabenzotricyclo[4.2.2.2^{2,5}]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. Steinhardt, 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)].

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(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.

Ned M. Weinshenker,[9] Frederick D. Greene
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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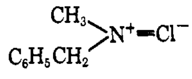
Aziridines. XI. Nitrogen Inversion in N-Haloaziridines

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 workers[1] concluded that N-chloroaziridine undergoes rapid nitrogen inversion (Ia ⇄ 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 Roberts[3] 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


$$\begin{matrix} CH_3 \\ C_6H_5CH_2 \end{matrix}\!\!>\!N^+\!=\!Cl^-$$

i

by d-orbital resonance.