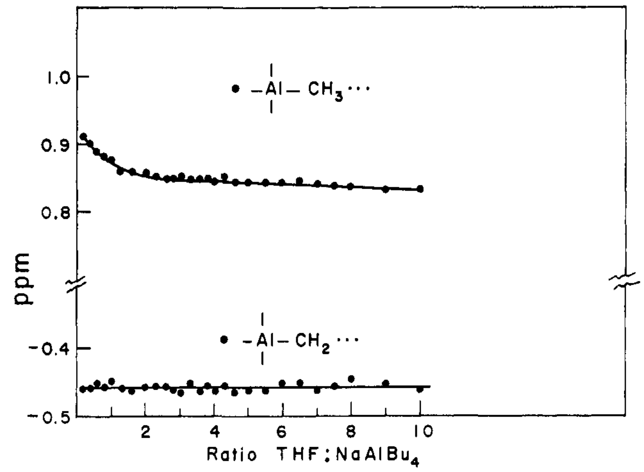

Figure 3. Comparison of the effect of THF on the chemical shifts in proton signals from $\geqslant$AlCH_2··· and $\geqslant$Al···CH_3.

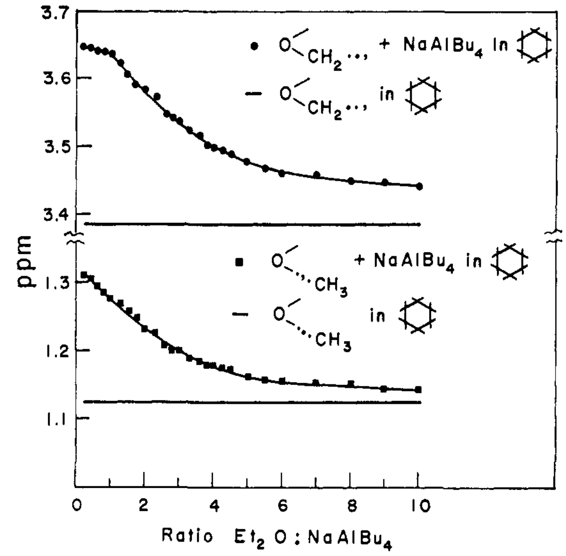

Figure 4. Chemical shifts in Et_2O proton signals as a function of the mole ratio Et_2O:$NaAlBu_4$.

hexane as a solvent. In this study the salt concentration is 0.265 *M*. Measurements were also made at salt concentrations of 0.09, 0.157, 0.96, and 2.00 *M* with substantially the same result. The α- and β-methylene signals of THF in cyclohexane are seen to be constant at respectively 3.64 and 1.75 ppm. With $NaAlBu_4$ present, both signals shift downfield, the chemical shift being an average value of the complexed and uncomplexed ether because of rapid equilibration between the two forms.

Here it can be seen that, up to a ratio of 1:1 THF: $NaAlBu_4$, the shift relative to the unperturbed THF in cyclohexane is very nearly constant. This implies that all of the THF molecules below this ratio see essentially the same environment. We interpret this to be a complex with the sodium ion. Complexation with the sodium ion rather than the aluminum is substantiated in Figure 3. Here the $\geqslant$Al–CH_2··· proton signal is unaffected by the addition of THF whereas that of the $\geqslant$Al···CH_3 shows a marked dependence. Coordination of the THF to the aluminum should cause a significant shift in the $\geqslant$Al–CH_2··· proton signal. The same dependence is noted with diethyl ether. Using triethylamine as a coordinating species, the $\geqslant$Al···CH_3 signal is masked. However, the $\geqslant$Al–CH_2··· signal is unaffected again, indicating complexation with the sodium ion. The shift in the $\geqslant$Al···CH_3 proton signal is most probably due to a change in the nature and extent of ion pairing, that is, the formation of free ions and solvent-separated ion pairs.

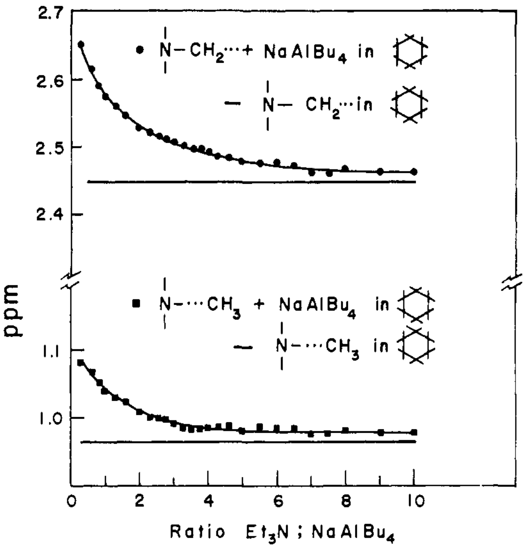

Figure 5. Chemical shifts in Et_3N proton signals as a function of the mole ratio Et_3N:$NaAlBu_4$.

As the ratio of THF to salt is further increased, a distinct break is noted at a ratio of 4:1, showing the existence of a four-coordinated species. This can qualitatively be interpreted in terms of the over-all equilibrium expression

$$[Na\cdot THF]^+ + 3THF = [Na\cdot 4THF]^+$$

in which we have assumed the 1:1 complex to be totally in the complexed form, but the distinct nature of the break at a ratio of 4:1 implies a considerable stability of the 4:1 species. In Figures 4 and 5, analogous plots are shown for diethyl ether and triethylamine. The diethyl ether shows a stable 1:1 complex, but no further well-defined coordinated species is observed as in the case of the THF. The triethylamine is seen to form a much weaker complex toward the sodium ion than either THF or Et_2O.

Acknowledgment. Support of this work by National Science Foundation Grant GP 6421 is gratefully acknowledged.

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Photochemistry of *t*-Butyl Alkyl Ketones in Solution

Sir:

It has been recognized for some time that aliphatic ketones can undergo several distinct types of photochemical reactions. The effects of structure and spin multiplicity of excited states on the competition between these types of reactions, however, are still not completely understood. We have investigated the

Table I. Quantum Yields for the Primary Processes[a]

Compd	ϕ^0	ϕ^S	$\phi_I{}^S$ [b]	$\phi^S{}_{II}$	$\phi^S{}_{cyc}$	ϕ^T	$\phi^T{}_I$	$\phi^T{}_{II}$	$\phi^T{}_{cyc}$
Ia	0.51	0.18	0.18			0.33	0.33		
Ib[c]	0.59	0.24	0.22	0.02	0.00	0.35	0.35	<0.01	0.00
Ic	0.31	0.14	0.07	0.07	0.00	0.17	0.17	<0.01	<0.01
Acetone							<0.02[d]		
2-Pentanone	0.27	0.03[e]		0.02[e]	<0.01[e]	0.24[e]		0.16[e]	0.08[e]
2-Hexanone[f]	0.33	0.11		0.10	<0.01	0.22		0.15	0.07

[a] Values accurate to at least ±10%. [b] Difference of ϕ^S and $\phi^S{}_{II}$. [c] In the vapor phase at 150°, $\phi^0 = 0.65$, $\phi_I = 0.54$, $\phi_{II} = 0.12$ (C. H. Nicol and J. G. Calvert, *J. Am. Chem. Soc.*, **89**, 1790 (1967)). [d] D. H. Yang, unpublished results; the predominant processes involve hydrogen abstraction from the medium. [e] Reference 5a, adjusted for ϕ^0 value given here. [f] Reference 5c.

photochemistry of *t*-butyl alkyl ketones in solution with the intention of further elucidating the correlation of these factors with their photochemical reactivity.

Irradiation of hexane solutions of *t*-butyl alkyl ketones (0.6–0.8 *M*) (Ia–Ic) with light (3130 Å) results in fragmentation of these ketones by both type I (eq 1) and type II (eq 2) processes,[1] and to a lesser extent in photocyclization (eq 3).[2]

$$t\text{-C}_4\text{H}_9\text{COR} \xrightarrow{h\nu} i\text{-C}_4\text{H}_8 + i\text{-C}_4\text{H}_{10} + \text{RCHO} + \text{other products} \quad (1)$$

Ia, $R = CH_3$
b, $R = n\text{-}C_3H_7$
c, $R = n\text{-}C_4H_9$

IIa, $R = CH_3$
b, $R = n\text{-}C_3H_7$
c, $R = n\text{-}C_4H_9$

$$\underset{\text{Ib, c}}{t\text{-C}_4\text{H}_9\text{COR}} \xrightarrow{h\nu} t\text{-C}_4\text{H}_9\text{COCH}_3 + \text{C}_2\text{H}_3\text{R} \quad (2)$$

IIIb, $R = H$
c, $R = CH_3$

$$\underset{\text{Ic}}{t\text{-C}_4\text{H}_9\text{COR}} \xrightarrow{h\nu} \underset{\text{IVc, R = CH}_3}{t\text{-C}_4\text{H}_9(\text{HO})\overline{\text{CCH}_2\text{CH}_2\text{C}}\text{HR}} \quad (3)$$

The total quantum yield for disappearance of starting ketone (ϕ^0, Table I) and the product yields were determined by gas chromatography with the aid of a ferrioxalate actinometer.[3] By quenching the triplet state of the three ketones with added piperylene,[4] we observed a rapid decrease in total quantum yield (ϕ) at lower quencher concentrations, followed by a more gradual decrease at higher quencher concentrations (Figure 1). The quantum yields for ketone decomposition *via* singlet excited state (ϕ^S) were determined from the limiting values of ϕ^0/ϕ from Figure 1. The quantum yields for ketone decomposition *via* the triplet state (ϕ^T) were obtained as the differences between ϕ and ϕ^S (*cf.* Table I). The quantum yield for type II process (ϕ_{II}) from Ic was estimated by determining the yield of propylene formation and by comparison of the yield of propylene to the combined yields of isobutane and isobutylene, and ϕ_{II} from Ib was estimated by comparison of the yield of ethylene to the combined yields of isobutane and isobutylene (Table I). The quantum yield for the type II process *via* the singlet excited state was determined by comparing the yield of ethylene or propylene at zero quencher concentration and at higher quencher concentrations (Table I).

t-Butyl *n*-propyl ketone (Ib) is slightly more reactive than pinacolone (Ia), but not solely because of the intervention of the type II process. *n*-Butyl *t*-butyl ketone (Ic) undergoes a type II process several times more efficiently than does *t*-butyl *n*-propyl ketone (Ib); nevertheless, fragmentation by a type I process is drastically reduced. The secondary γ hydrogen enhanced the efficiency of the type II process but reduced the efficiency of the type I process.

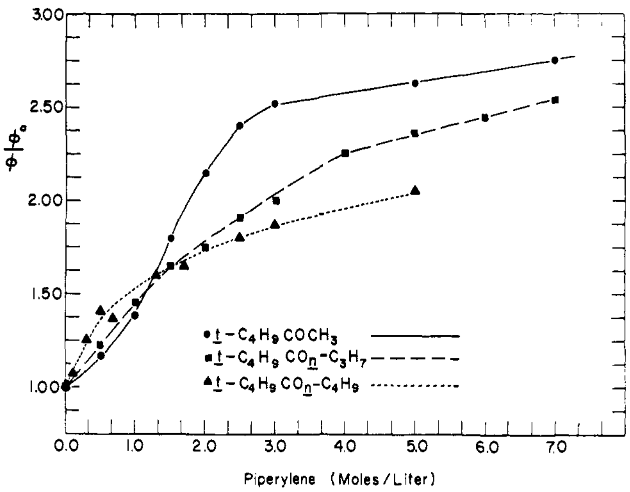

Figure 1.

The present experiments in the condensed phase definitely show that a type I process occurs from both the singlet and the triplet excited states of *t*-butyl alkyl ketones, while a type II process occurs almost exclusively from the singlet excited state of Ib and Ic (Table I). A type II process in the methyl analogs, 2-pentanone and 2-hexanone, however, occurs largely from the triplet state (*cf.* Table I).[5] A very small amount of 1-*t*-butyl-2-methylcyclobutanol (IVc) is detected in the irradiation products of Ic. Coulson and Yang[5c] have shown that cyclobutanol formation from 2-hexanone is predominantly a triplet-state reaction. It is not surprising that little cyclobutanol was formed, since the interaction with the γ hydrogen in the type II process in Ib and Ic is predominantly from the singlet n,π* state.

Straight-chain aliphatic ketones with γ hydrogens such as 2-alkanones undergo a type II process predominantly if not exclusively under the influence of light, while *t*-butyl alkyl ketones with γ hydrogens (Ib and Ic) undergo mainly type I processes in solution, indicating

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(1) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).

(2) N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

(3) C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953); C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956).

(4) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961).

(5) (a) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965); **88**, 1245 (1966); (b) T. J. Dougherty, *ibid.*, **87**, 4011 (1965); (c) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

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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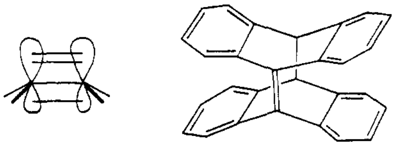
9,9′-Dehydrodianthracene

Sir:

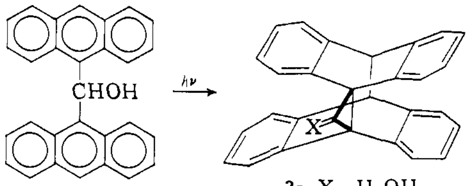
We wish to report the isolation and characterization of 9,9′-dehydrodianthracene[1] (**1**), an unusual olefin in that the probable structure is one in which the double bond atoms lie outside the plane defined by the four atoms attached to the double bond. This type of distortion of the π system is similar 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)].

(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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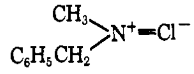
Aziridines. XI. Nitrogen Inversion in N-Haloaziridines

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 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.