Combination Reaction of Caged Germinate Radical Pairs Formed from the Photolysis of trans-Azo-Adamantane

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Decomposition of free radical initiators in solution produces a pair of radicals in solvent cage. Alkoxy[1] and tert-butyl[2-5] radicals may be produced from wide variety of precursors and are subject to a variation in cage effect with change in solvent viscosity[2,6,7]. Engel[8] et al. have shown that irradiation of trans-azo-1-adamantane produces the cis isomer which undergoes loss of nitrogen generating adamantyl radicals and reversion to trans. In this communication, the effect of solvent viscosity on cage collapse of adamantyl radicals and their reactivities are briefly discussed.

Solution of trans-azo-1-adamantane in solvents of viscosities ranging from 0.16 to 1.66 CP were photolyzed using medium pressure Hg-Arc lamp and decomposed at 65°C. Products listed in Table 1 were identified by comparison of GC retention times and mass spectra with those of authentic samples. Irradiation of trans-azo-1-adamantane is a clean
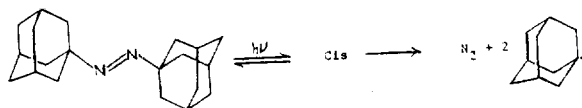
Trans-Azo-1-Adamantane

method for generating adamantyl radicals. Since these radicals are bridgehead, they are presumed either to recombine or to react with solvent. It was recognized that biadamantane may be formed in solvent cage and after escape from the cage. The latter mode of reaction was easily ruled out in the case of recombination by the demonstration that the yield of biadamantane was directly controlled by the solvent fluidity (Figure 1). If biadamantane were formed outside of solvent cage in toluene, the yield should be lower in cumene, which is a better hydrogen donor[9]. Table 1 and Figure 1 show that this is not to be the case. The decreasing yield of biadamantane with increasing temperature in toluene is also consistent with temperature change.

The low yield (4.0%) of adamantyl toluene suggest that all adamantane comes from the side chain attack but not phenyl
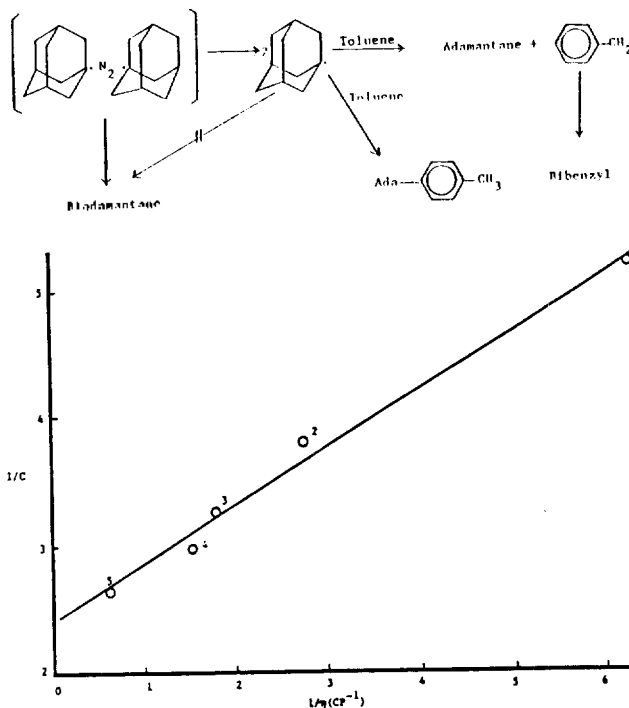

Figure 1. Plots of reciprocal of the fraction cage products[13] as a function of the fluidity $(1/\eta)$ of the solvents for the decomposition of cis-azo-adamantane. Numbers correspond to the solvents listed in Table 1.

ring attack. Moreover, the adamantane formed in PhCD₃ is deuterated despite the large isotope effect of side chain hydrogen abstraction $(\frac{k_H}{k_D} = 11.7)$. In methyl deuterated tolune, of course, the biadamantane yield increased (54.1%) with decrease of adamantane (19.7%).

On theoretical grounds, the maximum calculated isotope effect raises to 9.5 for methyl radical hydrogen abstraction[10].

Table 1. Decomposition Products of Cis-Azo-1-Adamantane in Various Solvents (65°C).

Entry	Solvent	η[a](CP)	Cis-Azo-Ada. mmol × 10[1]	Products, mmol × 10[2]				Total[e]	Fraction[f] of Cage Collapse(C)
				Ada-H	biada(%)[b]	Ada-Ar	other		
1	n-Pentane	0.16	14.36	18.15	2.78 (19.3)	—	2.8[c]	83	0.193
2	Toluene	0.37	25.37	22.86	6.63 (26.1)	2.03	8.4[d]	75	0.261
3	Cumene	0.57	11.91	13.20	3.62 (30.4)	—	2.0[r]	86	0.304
4	Cyclohexane	0.66	12.85	14.83	4.92 (33.4)	—	—	91	0.334
5	n-Hexadecane	1.66	13.91	7.66	5.00 (37.9)	—	—	65	0.379

[a]Taken from "Handbook of Chemistry and Physics", 50ᵗʰ ed., CRC, 1970. Some of the values were calculated by the equation, $\eta = Ae^{\Delta E vis/RT}$ (log η = A + $\frac{B}{T}$). A and B were taken from Tans. Faraday Soc., 39, 48 (1943). [b]Yields of biadamantane. [c]n-Decane [d]Bibenzyl [r]Bicumyl [f]Fraction of biadamantane Yields. [e]product balance

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which is insufficient for the present value ($\frac{k_H}{k_D}$ = 11.7). Since isotope effects come from the change of stretching and vibrational energy in transition state and a tunnel effect, one or both of these factors must be large for bridgehead free radicals. So long as the energy barrier in hydrogen transfer is not infinitely high nor infinitely wide[11] there is always certain probability that hydrogen atom will leak through. Hence, tunnel[12] effect is the most probable explanation for unusually large isotope effect.

Unlike tert-butyl, adamantyl radical shows no disproportionation and mostly side chain attack on toluene, this radical would be suitable for rho determination in Hammett correlation. Hammett studies with substituted toluene are under investigation.

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Characterization of 2-Aminodihydropyrimidines

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The chemistry of dihydropyrimidines which has been virtually unknown due to the instability of these compounds and the difficulty for purification, has been quite well studied and discussed recently[1]. But the available literature data on 2-aminodihydropyrimidines which are biologically interesting are speculated due to the difficulty to obtain pure compounds. 2-Amino-4,4,6-trimethyl-3,4-dihydropyrimidine has been demonstrated to show a selectivity for the sodium channel in muscle membrane[2] qualitatively similar to that possessed by tetrodotoxin[3] and saxitoxin[4] which contain guanidine ring moieties. Dihydropyrimidines have been known to be important intermediate in the catabolism and anabolism of pyrimidines[5-7]. However the structure of 2-aminodihydropyrimidines is still uncertain due to their instability and impurity. Ealier work[8] demonstrated that 2-aminodihydropyrimidine obtained by the cyclization of guanidine with mesityl oxide is the structure 1.
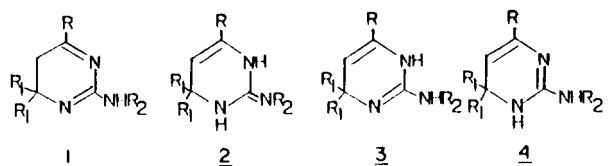
Later work[9] revealed that the reaction of guanidine with mesityl oxide gave a mixture of dihydropyrimidines 2, 3, or

4 and its dimer. Recently, Wendelin and Harler[10] reported that a possible structure of 2-alkylaminodihydropyrimidine may be 2 without using suitable model compounds. Previously, we described facile syntheses of pure 2-aminodihydropyrimidines by the reactions of substituted guanidines with α,β-unsaturated ketones[11]. In this paper, we report a plausible structure of 4 by comparing ultra violet spectral data of various good model compounds for 2-aminodihydropyrimidines and unusual instability of 2-aminodihydropyrimidines in protic solvents such as water, methanol, and ethanol. In order to compare uv spectrum of nonconjugative system in 3 with that from 4, 3,4-dihydro-1-ethyl-2-methylthio-4,4,6-trimethylpyrimidine (5, ^{1}H nmr (DMSO-d_6) δ 1.25t, 1.35s, 2.05s, 2.85s, 3.90q, 5.30m; $\lambda_{max}^{MeOH}(\varepsilon)$ 212(6.298 × 10^{3})) was prepared by S-methylation of 3,4-dihydro-1-ethyl-2-thio-4,4,6-trimethylpyrimidine[12] with methyl iodide. 3,4-Dihydro-1-ethyl-2-thio-4,4,6-trimethylpyrimidine was prepared by the cyclization of ethylamine and 2-methyl-2-thiocyano-4-pentanone[13].

As a nonconjugative system in 2, compound 7 is a good model compound because N,N-disubstituted amine by two methyl groups cannot form its imine between C_2 and N in 2. The hydroiodide(5) was easily freed to 6 by treating with aqueous ammonia. The freed dihydropyrimidine(6) can neither have a double bond between N_1 and C_2 nor between C_2 and S: namely two nonconjugative double bonds of $C_2=N_3$ and $C_5=C_6$ can exist. The λ_{max} values of various 2-aminodihydro-