

PHOTOISOMERIZATION OF AZOALKANES

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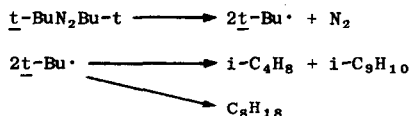
trans-Azoalkanes are commonly employed as photolytic sources of alkyl radicals and the chemistry of such processes has been studied in some detail (1). By analogy with aromatic azo compounds (2) and with olefins (3), one expects that trans - cis isomerization should be an important process competing with dissociation. However, only in the irradiation of solutions of azomethane and azoisopropane have such isomerizations been unequivocally demonstrated (4).

We have irradiated solutions of azoisobutane (AIB), azobis-(isobutyronitrile), azobis(cyanocyclohexane), and azobis(2-methylpropyl acetate) in CFCl_3 , acetone, methanol, or pentane with light $<4000 \text{ \AA}$ in Pyrex vessels at temperatures below -50°C . After several hours, the solutions had turned intensely yellow but only trace amounts of nitrogen were evolved. On warming to 25° the color rapidly disappeared, accompanied by evolution of nitrogen.

The irradiation of AIB was studied in detail. A solution of $116 \mu\text{mole}$ AIB in $\sim 0.3 \text{ ml}$ CH_3OD was irradiated in an nmr tube at -80° using the output of a 200W PEK point-source mercury arc filtered through a Corning 7-84 narrow-pass filter (long wavelength cutoff at 4000 \AA). After 4 hrs irradiation the nmr spectrum of the solution at -70°C showed the presence of two singlets, at $\tau 8.88$ from AIB ($70 \mu\text{mole}$), and at $\tau 8.55$ ($43 \mu\text{mole}$) from a photoisomer. About 2-3 μmole each of isobutane and isobutylene were present. The decay of the $\tau 8.55$ peak and concomitant growth of $\tau 8.31$ triplet, $(\text{CH}_3)_2\text{C}-\text{CH}_2$, and $\tau 9.11-9.13$ doublet, $(\text{CH}_3)_3\text{CH}$, were then measured periodically. At -23°C $10 \mu\text{mole}$ photoisomer disappeared and $11 \mu\text{mole}$ each of isobutylene and isobutane and $1 \mu\text{mole}$ of tetramethylbutane dimer were formed in one hour. At 0° , $19 \mu\text{mole}$ of photoisomer disappeared and $21 \mu\text{mole}$ each of C_4 product and $2 \mu\text{mole}$ of dimer were formed in four minutes.

Plots of the logs of the integrated peak areas for photoisomer versus time at -23° and at 0° gave two first-order rate constants of $8.3 \times 10^{-6} \text{ sec}^{-1}$ and $4.0 \times 10^{-4} \text{ sec}^{-1}$, respectively, corresponding to an activation energy of $23 \pm 2 \text{ kcal/mole}$ with an A-factor of $10^{15.6 \pm 0.5} \text{ sec}^{-1}$ for thermal decomposition of the AIB photoisomer.

In separate experiments the photoisomer was generated below -50° from ~ 0.1 M AIB in deuterioacetone or methanol-OD (trace of N_2). The solutions were then warmed to 25° where the final nitrogen evolution was measured with a Toepler pump and gas buret. Organic products were measured by nmr. Within experimental error the thermal decomposition of the photoisomer is represented by

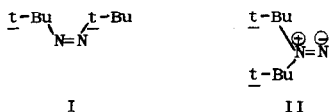


Qualitative experiments showed that the AIB photoisomer decomposed at the same rate in acetone, pentane, or methanol and that the only products were nitrogen and hydrocarbons expected from t-butyl radicals (5). However, decomposition was tenfold more rapid in CFCl_3 or CF_2Cl_2 , some isomerization to AIB occurred, and small amounts of t-butyl chloride were formed along with the hydrocarbon products.

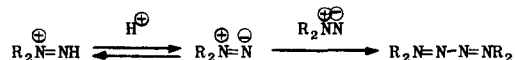
We attribute this change in rate and products to formation of small amounts of HCl from photolysis of the solvents. The acid added to isobutylene to form t-butyl chloride and also rapidly isomerized the photoisomer. This explanation is consistent with the observation that in all cases the sum of t-butyl chloride and isobutylene equaled the isobutane, ruling out the possibility of attack by t-butyl radicals on the solvent (6). That HCl was responsible for the isomerization was confirmed by an experiment wherein ~ 0.05 M photoisomer was rapidly (30 min) and quantitatively isomerized to AIB at -80° (where it is otherwise stable) in the presence of 0.005 M trifluoroacetic acid.

Thermal decomposition of the isomer in oxygen-saturated pentane at -20° led to oxygen uptake and formation of t-butyl peroxide and t-butyl alcohol as well as hydrocarbon products, showing the decomposition produces some free t-butyl radicals. The uv spectrum of the photoisomer at -60° shows an absorption maximum at 4470 Å, about 800 Å longer wavelength than AIB. When irradiated with light of >4000 Å the photoisomer rapidly isomerized to AIB with no detectable decomposition to nitrogen and t-butyl radical products. Neither photochemical isomerization process was affected by oxygen at pressures up to 1000 torr.

Of the two structures isomeric with AIB, cis-AIB (I) and 1,1-di-t-butyldiazene (II),



The latter structure can be excluded for two reasons. First, Lemal and coworkers have shown that the decomposition pathway for dialkyldiazenes is solvent dependent (7,8), and in no case does rearrangement give an azoalkane. Second, McBride and Kruse (9) observed that dialkyldiazenes are stabilized in acidic media as the diazenium ions which, when neutralized to the free diazenes, couple to tetrazenes.

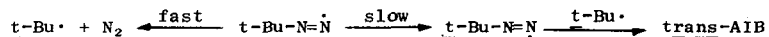


Thus, the very facile acid catalyzed isomerization of the photoisomer to trans-AIB indicates that it must be cis-AIB.

The rapid thermal decomposition of cis-AIB (and of other cis-azoalkanes examined here) below 0° is in striking contrast to the high stability of trans-AIB which has rate parameters (10) of $k_1 = 10^{16.3-42,800/\theta} \text{ sec}^{-1}$ ($\theta = 4.6\text{T}$) and a calculated half-life of $\sim 10^5$ minutes at 200°. Since the transition states for the two reactions must be very similar, the difference in activation energies for thermal decomposition of trans- and cis-AIB of about 20 kcal/mole must arise largely from the steric strain in the cis-isomer. The comparable model pair, cis- and trans-1,2-di-t-butylethylene differ by about 10 kcal/mole in their heats of hydrogenation (11) to the same 1,2-di-t-butylethane. However, 1,2-di-t-butylbenzene has a strain energy of 23 kcal/mole (12) which presumably reflects the greater rigidity of the benzene ring compared to the ethylenic double bond where some twisting may afford partial relief of strain.

We suggest that the two pair of non-bonded electrons in cis-AIB produce an electrostatic repulsive interaction that could account for all or part of the difference in steric strain between cis-AIB and cis-di-t-butylethylene. Since this electrostatic effect should be present in all cis-azoalkanes, measurement of the kinetic parameters for decomposition of cis-azomethane would serve to measure the importance of this effect independently of any steric effects.

Our results do not permit a distinction between a one-bond cleavage mechanism in which t-BuN₂· radical is an intermediate and a two-bond cleavage mechanism in which two t-Bu· radicals and N₂ are formed in a single step. If t-BuN₂· is formed it must decompose rapidly in the solvent cage compared to its rate of isomerization and reunion with a t-Bu· radical to form trans-AIB.



Since only a small fraction of trans- and cis-AIB gave t-butyl radicals on irradiation at low temperatures, the major pathway for formation of t-alkyl radicals at ordinary temperatures

must be via the photoisomerization of the trans-azoalkane, followed by rapid thermolysis of the cis-isomer. This scheme would explain why other investigators (13) have found no differences in the ratios of recombination to disproportionation for t-alkyl radicals generated by photolysis and thermolysis of the corresponding azoalkanes: both processes produce ground-state (singlet) radical pairs. Our results also show that trans-AIB triplet (14) does not readily undergo geometric isomerization, presumably owing to an energy barrier imposed by steric interactions in the cis- form (4).

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