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EFFECT OF HETEROATOMS IN FREE RADICALS. VII. TRANSANNULAR PARTICIPATION OF SULFUR ATOM IN THIACYCLOHEXYL FREE RADICALS

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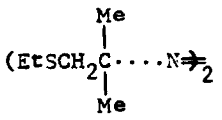
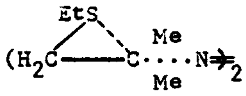
In a previous paper of the series, we have reported that no anchimeric participation of sulfur atom can be observed in decomposition of azobis(ω-ethylthio-tert-butane)(1). This indicates that the structure of transition state of the decomposition is better represented by I than by II, or a sulfur atom positioned β to a radical center does not participate to stabilization of a free radical. Similar result has been obtained from esr spectroscopy(2). However, the possibility of bridging participation of a β-sulfur atom may not be disproved by the above conclusion; the following equilibrium (i) or some other processes may be able to form a bridged radical(3-5).



$$(EtSCH_2\overset{Me}{\underset{Me}{C}}\cdots\cdot N\!=\!)_2$$

I



II

(i)

In this communication, we would like to report that a β- or γ-sulfur atom does indeed participate to stabilization of a free radical, if the location of it is sterically restricted in favor of the participation.

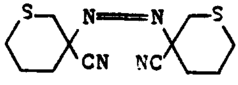
Azobis(1-cyano-3-thiacyclohexane), III (mp 120°C), and azobis(1-cyano-4-

TABLE I

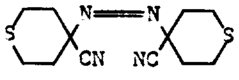
Compd.	k_{rel}[a]	$\Delta H^{\ddagger}$, kcal/mol[a,b]	$\Delta S^{\ddagger}$, eu[a,c]	$\lambda_{max}^{HCCl_3}$, nm
III	26.7[d]	26.9	0.8	359.0
IV	3.3	28.5	1.0	352.9
V[e]	1.0	32.3	9.5	350.6

[a] In tetralin at 80°C. [b] Errors estimated are ±0.5 kcal/mol. [c] Errors estimated are ±2 eu. [d] $k = (3.31 \pm 0.03) \times 10^{-4} sec^{-1}$ at 82.8°C. [e] Cf. C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker, and J. Herbert, *J. Amer. Chem. Soc.*, **75**, 2078 (1953) for activation parameters in toluene.

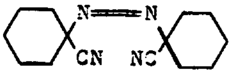
thiacyclohexame), IV (mp 118°C), were prepared respectively from corresponding ketones(6). Azobis(1-cyanocyclohexane), V, was synthesized after Overberger and his co-workers(7). The first-order kinetics were followed by measuring evolved nitrogen at appropriate temperatures with constant-pressure-variable-volume apparatus. In Table I, are summarized relative rates, parameters of activation, and absorption maxima due to n → π* transitions of azo groups. Kinetic data were calculated by least squares method.



III

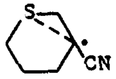


IV

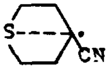


V

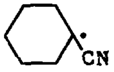
Smaller enthalpies of activation for sulfur-containing compounds than for their methylene analog demonstrate apparently transannular participation of a sulfur atom at β- or γ- position. Since a thiane ring is free from strain(8) as cyclohexane ring is, it is not necessary to take into account this sort of contribution to activation parameters. However, the absorption maximum of III appears at 8.4 nm longer wavelength than that of V, which indicates that the former has about 1.9 kcal/mol higher energy than the latter at the reactant stage due to steric strain(9). The same consideration predicts the correction of 0.5 kcal/mol for IV(10). These energies must be subtracted from enthalpies of activation before the participations of β- and γ-sulfur atoms are discussed. Thus, we might suggest that free radicals VI and VII are about 1.7 and 1.8 kcal/mol more stabilized by resonance with β- and γ-sulfur atom, respectively, than their methylene analog, VIII. Although small, differences in enthalpy of activation obtained here are reasonable for transannular participation of a sulfur atom. Note that about 4 kcal/mol has been assigned for stabilization energy with an α-sulfur atom (11). Entropy of activation also supports the existence of participation: the open-chain compound IX, with which no participation can be detected, has larger entropy of activation ($\Delta S^{\ddagger}$ = 13.6 eu) than corresponding methylene analog X ($\Delta S^{\ddagger}$ = 9.6 eu). In cyclic systems,on the other hand, sulfur-containing compounds have smaller entropies of activation than their methylene analog as have been observed in a series of azo compounds containing an α-sulfur atom, where the participation of sulfur is evident(11).



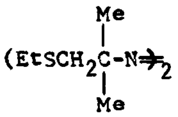
VI



VII

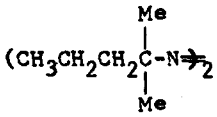


VIII



$$(\mathrm{EtSCH_2}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{-N{=}})_2$$

IX



$$(\mathrm{CH_3CH_2CH_2}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{-N{=}})_2$$

X

A thiirane ring has strain energy of about 20 kcal/mol(8), which is much larger than the transannular stabilization energy (~2 kcal/mol). Thus, in equilibrium (i), the bridged structure has higher energy than the open-chain structure and it is understandable that the transition state of the decomposition of IX is better represented by I than by II.

Consequently, we believe that bridged structure is not essential to a free radical containing a sulfur atom at β- or γ-position. However, when the sulfur atom is forced to take a favorable conformation to bridging, it plays a role to stabilize the free radical. Stronger participations of sulfur atom in cyclic systems than in open-chain systems are also reported for carbonium ions(12) and carbanions(13).

The fact that 3- and 4-thiacyclohexyl radicals have equal amount of stabilization energy seems to suggest that the force of interaction between sulfur and radical center is a function of distance and angle between orbitals on these atoms. However, presently, it is uncertain whether or not vacant 3d-orbitals of sulfur contribute to the interaction.

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