R–C(=O) structure with R, R' substituents (thietanone)

8, R = R' = CH₃
9, R = H; R' = (CH₃)₂CH
10, R = R' = C₂H₅
11, R = R' = Ph

rise to thietanone **13**. Elimination of hydrogen chloride from **13** would yield the unsaturated 3-thietanones. The role which pyridine plays in the sequence may be to assist in the enolization process or in the elimination of hydrogen chloride from **12a**, for example. Qualitative studies have thus far indicated merely that its presence enhances the rate of reaction.

established by unambiguous synthesis. Acid-catalyzed condensation of ethylene glycol with 1,3-dibromo-2-propanone, obtained by Jones oxidation of 1,3-dibromo-2-propanol, afforded 1,3-dibromo-2,2-ethylenedioxypropane, **5**. Treatment of **5** with anhydrous sodium sulfide in hot ethylene glycol furnished 3,3-ethylenedioxythietane, **6**, which in turn was hydrolyzed to the known[5] 3-thietanone, **7**. Base-catalyzed condensation of **7** with benzaldehyde yielded the bis adduct, **4**, shown by mixture melting point and by comparison of the ir and nmr spectra to be identical with the bis adduct obtained from **2**.

Both **2** and **4** appear to be single isomers, as judged by sharp melting points and by the nmr spectra, which consist of sharp singlets in the case of **2** and one sharp singlet at τ 2.62 in the case of **4**. A shoulder on the upfield side of the aromatic proton peak of **4** in the 100-MHz spectrum explained the apparent disappearance of the vinyl protons.

Other 3-thietanones have also been synthesized in one step from readily available ketones by the above procedure. 4-Methyl-2-pentanone afforded thietanone **8**, λ_{max}^{neat} 5.75 μm, τ (CCl₄) 5.98 (s, 2 H), 7.86 (s, 3 H), and 8.27 (s, 3 H), in 25% yield, as an oil which polymerized readily at room temperature. 5-Methyl-2-hexanone furnished thietanone **9**, λ_{max}^{neat} 5.68 μm, τ (CCl₄) 3.66 (d, 1 H), 5.80 (s, 2 H), 7.68 (m, 1 H), and 8.87 (d, 6 H) in 16% yield. 4-Ethyl-2-hexanone gave thietanone **10**, λ_{max}^{neat} 5.74 μm, τ (CCl₄) 5.96 (s, 2 H), 7.40 (q, 2 H), 7.93 (q, 2 H), 8.90 (t, 3 H), and 8.94 (t, 3 H) in 12% yield. And 4,4-diphenyl-2-butanone furnished thietanone **11**, mp 130–131°, λ_{max}^{KBr} 5.75 μm, τ (CDCl₃) 2.62 and 2.64 (two overlapping singlets, 10 H) and 5.82 (s, 2 H), in 17.1% yield. Both **9** and **10** are relatively stable oils. The stereochemistry of **9** is assigned as indicated on the basis of the diamagnetic anisotropy effect of the carbonyl group and the chemical shifts of the corresponding aliphatic groups in **8** and **10**.

On the assumption that sulfenyl chloride **12** is formed by an HVZ- and Pummerer-type of sequence, capture of its enol, **12a**, by either (a) addition of the sulfenyl chloride group to the carbon–carbon double bond or (b) nucleophilic attack of the terminal methylene carbon atom upon sulfur, displacing chloride ion, would give

The observation of 3-thietanones from reactions of thionyl chloride with 4-phenyl-2-butanones is in marked contrast to the formation of benzo[b]thiophene derivatives from hydrocinnamic and cinnamic acids.[1a] Apparently the propensity for presumed intermediate sulfenyl chloride **12** to enolize and form a four-membered ring by intramolecular addition to the enolic carbon–carbon double bond is much greater than that for formation of a five-membered ring by intramolecular addition to the aromatic ring.

We are pursuing experiments aimed at further defining the mechanistic and stereochemical consequences of these reactions.

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Calorimetric Study of the Solvation of a Stable Free Radical

Sir:

Recent studies of solvent effects on rate constants for radical termination and chain transfer have suggested that certain free radicals, particularly small relatively unstable ones, may be especially well solvated in aromatic media.[1] We have measured[2] the partial molal heats of solution at substantially infinite dilution of the stable free radical di-*tert*-butyl nitroxide (**1**) and its nonradical

(1) S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969); R. D. Burkhart, *ibid.*, **90**, 273 (1968); *J. Phys. Chem.*, **73**, 2703 (1969).
(2) The calorimeter used is a modification of the design of E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965). Values plotted are averages of three to five heats determined by successive injections of solute. Final solute concentrations were in the range 4–8 × 10⁻³ *M*. No regular trends suggestive of solute–solute interaction were noted with successive solute additions. Maximum standard deviations in measured heats for the radical were 20 cal/mol. Those for the hydroxylamine are shown in Figure 1.
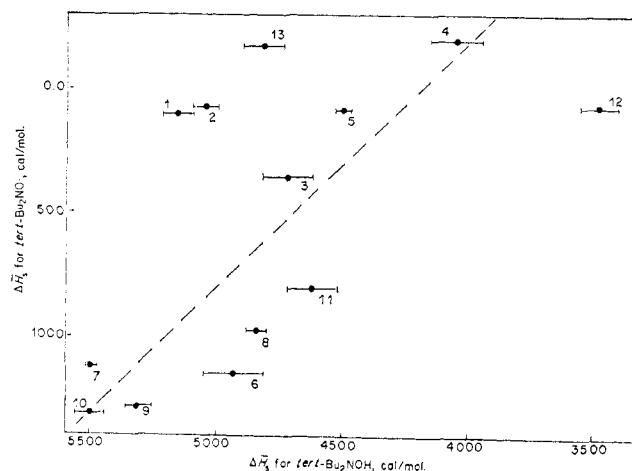
Figure 1. Solution heats at infinite dilution for **1** and **2**. Solvents: 1, benzene; 2, toluene; 3, nitrobenzene; 4, benzonitrile; 5, anisole; 6, *n*-hexane; 7, *n*-heptane; 8, isooctane; 9, decalin; 10, cyclohexane; 11, cyclohexene; 12, *tert*-C$_5$H$_{11}$OH; 13, CCl$_4$.

analog di-*tert*-butylhydroxylamine (**2**) in 13 solvents. The results are interpreted in a way which lends direct thermodynamic support to the idea that aromatics are more effective solvents than alkanes for free radicals.

The heat of solution at infinite dilution for a given solute may be analyzed as a composite of enthalpy terms.[3] These are vaporization of the solute (ΔH_{vap} or ΔH_{sub}, endothermic), formation of solute-sized cavities in the solvent (ΔH_{cav}, endothermic), and interaction of solute with solvent or solvation (ΔH_{solv}, exothermic). The variation in $\Delta \bar{H}_s$ for a single solute in a series of organic solvents is expressed by

$$\delta_M \Delta \bar{H}_s = \delta_M \Delta H_{solv} + \delta_M \Delta H_{cav}$$

since vaporization heat will be a constant. Clearly $\delta_M \Delta \bar{H}_s$ does not show variations in solvating ability alone, but reflects both solvation and cavity heat variations. However, if the size and shape of two solutes are essentially the same, as for **1** and **2**, then differences in $\delta_M \Delta \bar{H}_s$ for the two in the same series of solvents will accurately reflect differences in changes in solvation for the two species.

In Figure 1 are plotted $\Delta \bar{H}_s$ values for the nitroxide *vs.* those for the hydroxylamine. If cyclohexane is taken as a reference solvent, then the dashed 45° line represents the locus of potential points for transfer of **1** and **2** from cyclohexane to another solvent by a process in which $\delta_M \Delta H_{cav}$ and $\delta_M \Delta H_{solv}$ are the same for both solutes. Since $\delta_M \Delta H_{cav}$ is assumed to be essentially the same for **1** and **2**, all points would appear on this line if it were not for differences in solvation enthalpy change (solvation enthalpy of transfer). A deviation of a point from the line in the X or Y direction is thus a direct measure of difference in solvation enthalpy of transfer for the two solutes from cyclohexane to a given solvent.

(3) C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 1572 (1969).

It is clear that in transfer from cyclohexane to all but one of the alkanes and to *tert*-amyl alcohol the hydroxylamine undergoes a more favorable enthalpy of solvation change than does the free radical. For transfer to cyclohexene, *e.g.*, the hydroxylamine is favored by 3–500 cal/mol. In contrast, on transfer to any of the aromatics and CCl$_4$ the radical undergoes at least as favorable a solvation enthalpy change as does the hydroxylamine. For benzene and toluene the solvation enthalpy of transfer favors the radical by close to 900 cal/mol. Electron-withdrawing substituents appear to decrease the solvation advantage of **1** in aromatics.

An interpretation of these results, which is consistent with the kinetic studies,[1] is that the aromatics are able to solvate the nitroxide radical in some specific manner not available to alkanes and cyclohexene. This appears to be strong thermodynamic evidence for the ability of aromatics to solvate radicals. If the effect is smaller here than in some of the kinetic cases, this may be a reflection of the greater stability of the nitroxide.

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The Conformation and Absolute Configuration of (−)-*trans*-Cyclooctene

Sir:

The dissymmetric nature of the molecule *trans*-cyclooctene has been discussed by Cope,[1] who has reported a probable absolute configuration as determined by chemical means, Moscowitz and Mislow,[2] who have discussed the absolute configuration from a theoretical viewpoint, and others. It has been previously noted that there are two nonsuperimposable enantiomorphs for each of the two possible conformations of *trans*-cyclooctene. These four possible spatial arrangements can be roughly described as differing from one another by rotations of the mean place of carbon atoms 8,1,2,3 (containing the double bond) and of the mean plane of carbon atoms 4,5,6,7 about axes approximately passing through atoms (8,3) and (4,7), respectively (Figure 1).

In order to distinguish among these four choices a single-crystal X-ray study of *trans*-dichloro[(−)-*trans*-cyclooctene][(+)-α-methylbenzylamine]platinum(II) (Figure 2), the complex used to effect the resolution of (±)-*trans*-cyclooctene,[3] was undertaken. Crystals of this complex, kindly provided by the late Dr. A. C. Cope, were yellow needles which were first thought to be orthorhombic but later found to be monoclinic with a very strong tendency to twin and to be twisted around the needle axis. With considerable difficulty suitable untwinned crystals were found. The

(1) A. C. Cope and A. S. Mehta, *J. Amer. Chem. Soc.*, **86**, 5626 (1964).
(2) A. Moscowitz and K. Mislow, *ibid.*, **84**, 4606 (1962).
(3) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. van Auken, and H. J. S. Winkler, *ibid.*, **85**, 3276 (1963).