Alternatively, when methanol is excluded and the methylation carried out in THF solution using diazomethane, everheptose (**11**) is cleaved to **4** and **2**. It is not unlikely that diazomethane besides methylating the phenolic hydroxyl group causes (a) the opening of the ester linkage (which is probably enhanced by the hydrogen bonding with the β-hydroxyl group in the intermediate) and (b) cyclization to the δ-lactone **4** through anion formation.[9]

Acknowledgment. We wish to express our thanks to Sir Derek Barton and Professor J. Meinwald for many stimulating discussions.

(9) Satisfactory elementary analyses were obtained for all new compounds; ir spectra were recorded in chloroform solution; optical rotations were measured in chloroform solution; nmr spectra were taken at 100 MHz in $CDCl_3$ with internal TMS standard. All the coupling constant values were obtained using spin–spin decoupling experiments. The mass spectral assignments were based on high resolution mass spectrometry.

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Hydrogen Abstraction by Thiyl Radicals

Sir:

Data are available on the selectivity and polar character of most common free radicals,[1] but the thiyl radical, a ubiquitous species in organic chemistry[2] and radiation biology,[3] is a notable exception. Hydrogen abstraction by thiyl radicals from organic substrates (eq 1) is well documented.[2a,d,4] However, a quantitative study of this reaction has not been published, although work by Walling and Rabinowitz[4] and by van Zwet and Kooyman[5,6] has provided important semiquantitative data. Kellogg, in a recent review,[2a] has stated that it will be difficult to obtain quantitative data on reaction 1 because of its reversibility.

$$RS\cdot + QH \xrightarrow{k_H} RSH + Q\cdot \qquad (1)$$

A method for the quantitative study of eq 1 is presented here; the method was conceived in order to take advantage of the very reversibility of eq 1 which has hindered previous studies. The key of this method is to utilize tritium-labeled thiol (RSH*) as a solvent; in this milieu, Q· radicals generated in eq 1 abstract hydrogen from RSH* to re-form the substrate QH* which is now tritium labeled (eq 2). The level of radioactivity in the recovered QH* can be related to the specific rate constant for eq 1. Tritium isotope effects are involved in the calculation, but they can be evaluated independently.[7,8] Because there are no data in the literature with which to test our method, we have developed two kinetic schemes for the determination of relative values of k_H (eq 1).

$$Q\cdot + RSH^* \longrightarrow QH^* + RS\cdot \qquad (2)$$

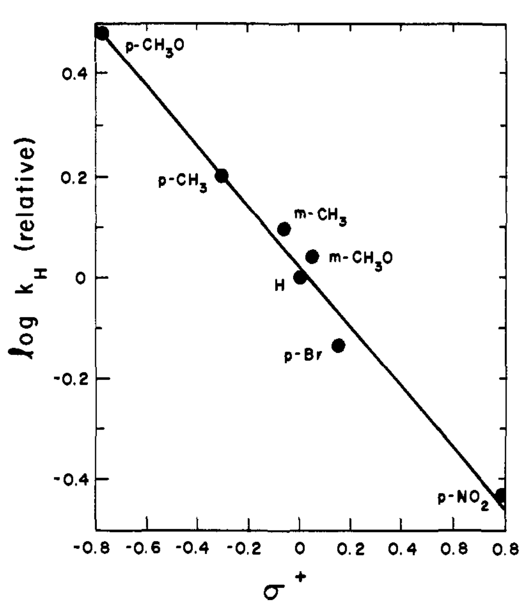

Figure 1. A plot of relative values of k_H (eq 1) *vs.* Hammett σ^+ constants.

Table I gives data on the cyclohexanethiyl radical.

Table I. Relative Rate Constants per Reactive Hydrogen for Hydrogen Abstraction by the Cyclohexanethiyl Radical at 80° [a]

Hydrogen donor	n^b	Relative k_H^c	
		Scheme I	Scheme II
Anisole	3	≪0.032	
m-Xylene	6	0.043	0.048
Mesitylene	9	0.057	
p-Xylene	6	0.066	
p-Nitroethylbenzene	2	0.37	
p-Bromoethylbenzene	2	0.73	
Ethylbenzene	2	(1.0)	(1.0)
m-Ethylanisole	2	1.1	
m-Ethyltoluene	2	1.25[d]	
p-Ethyltoluene	2	1.6[d]	
p-Ethylanisole	2	3.0	
Diphenylmethane	2	1.5	
Cumene	1	6.3	6.6
p-Cymene	1	8.8	

[a] These data have *not* been corrected for the ratio of isotope effects.[7,13] [b] Number of reactive hydrogens assumed. [c] Reproducibility suggests these data are accurate to ±5%. [d] k_H applies to secondary benzylic position.

A Hammett plot[9] of the data for substituted ethylbenzenes at 80° gives an excellent correlation using σ^+ with

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$\rho^+ = -0.59$ (correlation coefficient, $r = 0.997$) and a poorer correlation with σ ($\rho = -0.77$, $r = 0.944$).

Our first scheme for determining k_{H} values involves thermal homolysis of AIBN in solvent RSH* containing two hydrogen donors, QH and $\mathrm{Q^0H}$. The radicals from the initiator convert a fraction of the thiol to thiyl radicals[7,8,10–12] which abstract hydrogen from QH or $\mathrm{Q^0H}$ (eq 1 and 3). The Q· and $\mathrm{Q}\cdot^0$ radicals

$$\mathrm{RS}\cdot + \mathrm{Q^0H} \xrightarrow{k_{\mathrm{H}^0}} \mathrm{RSH} + \mathrm{Q}\cdot^0 \qquad (3)$$

$$\mathrm{Q}\cdot^0 + \mathrm{RSH^*} \longrightarrow \mathrm{Q^0H^*} + \mathrm{RS}\cdot \qquad (4)$$

then undergo reactions 2 and 4 and become labeled. Kinetic analysis leads to eq 5, where A_{QH} and $A_{\mathrm{Q^0H}}$ are the molar specific activities of the recovered substrates and I and I^0 are the isotope effects $k_{\mathrm{H}}/k_{\mathrm{T}}$ on eq 2 and 4, respectively.[13]

$$k_{\mathrm{H}}/k_{\mathrm{H}^0} = (I/I^0)(A_{\mathrm{QH}}/A_{\mathrm{Q^0H}}) \qquad (5)$$

In the second scheme, triphenyl phosphite (TPP) replaces one of the hydrogen donors.[14]

$$\mathrm{RS}\cdot + \mathrm{(PhO)_3P} \xrightarrow{k_{\mathrm{P}}} \mathrm{R}\cdot + \mathrm{(PhO)_3PS} \qquad (6)$$

$$\mathrm{R}\cdot + \mathrm{RSH^*} \longrightarrow \mathrm{RH^*} + \mathrm{RS}\cdot \qquad (7)$$

Kinetic analysis yields eq 8, where A_{RSH} is the molar

$$A_{\mathrm{QH}}[\mathrm{TPP}] = (k_{\mathrm{H}}/k_{\mathrm{P}})(I^{-1})(A_{\mathrm{RSH}})[\mathrm{RH}] \qquad (8)$$

specific activity of the thiol and [RH] is the *total* yield of cyclohexane. A plot of A_{QH}[TPP] *vs.* [RH] at constant thiol activity yields a straight line with zero intercept and a slope which is proportional to k_{H}. Data from such plots for two substrates yield relative k_{H} values (eq 9).

$$k_{\mathrm{H}}/k_{\mathrm{H}}^0 = (I/I^0)(\text{slope for QH plot})/(\text{slope for Q}^0\text{H plot}) \qquad (9)$$

The assumptions made in deriving the kinetic expressions, eq 5 and 9, are as follows. (1) [RSH] $\gg$ [RST]. (2) Only a small fraction of the QH becomes labeled. Both requirements 1 and 2 were satisfied in our work. (3) A steady state in the concentration of Q· radicals obtains. (4) Only the listed reactions are involved in the formation of the products studied. This was demonstrated by showing that extensive variation in the reaction variables (including replacing AIBN by *tert*-butyl peroxycyclohexanecarboxylate) does not affect the relative values of k_{H}.

Controls also were performed in which the value of $(k_{\mathrm{H}})_{\mathrm{A}}/(k_{\mathrm{H}})_{\mathrm{B}}$ obtained from direct competition between substrates A and B was compared with the results of two separate cross-competitions, one involving A and C (a third substrate) and another between B and C. These direct and indirect measures of $(k_{\mathrm{H}})_{\mathrm{A}}/(k_{\mathrm{H}})_{\mathrm{B}}$ always were in good agreement.

(5) Q· and $\mathrm{Q}\cdot^0$ radicals are not involved in termination processes. This was verified for cumyl radicals by detailed product studies using glpc of reaction mixtures similar to those from scheme I in Table I but containing cumene as the only hydrogen donor. The amounts of $\mathrm{C_6H_{11}SC(CH_3)_2Ph}$, $\mathrm{C_6H_{11}SCH_2CH(CH_3)Ph}$, and bicumyl account for less than 1% of the cumyl radicals formed in a sample. The data also show that the yield of isobutyronitrile was twice that of dicyclohexyl disulfide, indicating that dimerization of the thiyl radicals is the only significant termination reaction occurring in these systems.

Our ρ^+ value of -0.59 can be compared with $\rho^+ = -0.86$ obtained for abstraction by atomic bromine,[15] and $\rho^+ = -0.53$ for abstraction by trichloromethyl radicals[15] (all three ρ values apply to ethylbenzenes at 80°).[16,17] These three ρ values are of interest in the light of the recent novel and ingenious suggestions of Zavitsas.[18–20]

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Photo-CIDNP Detection of Transient Intermediates. The Enol of Acetophenone

Sir:

CIDNP studies are ideally suited to reveal the presence of thermally unstable products of radical reactions.[1] The large intensity enhancements in CIDNP spectra result from polarization in newly formed product molecules (and decay with $\mathrm{T_1}$) so that, unlike most physical techniques, it is the concentration of recently formed species, rather than the total concentration of the species, that is important. We now report an example of this CIDNP application in the detection of the enol formed during the photolysis of acetophenone.

Hydrogen abstraction reactions of the triplet excited state of acetophenone (**1**) have long been known to lead to reductive dimerization of the ketone.[2] Recently,[3] a novel hydrogen abstraction from phenol (**2**) by acetophenone was reported to lead to 1,2-dibenzoylethane (**3**) as well as acetophenone pinacol in high yield. The

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