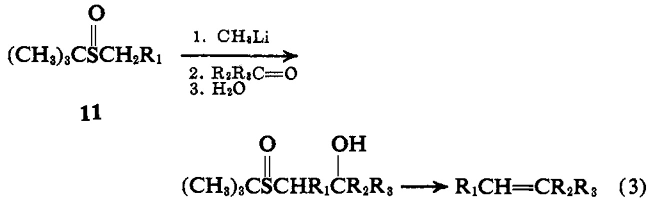

$$(\text{CH}_3)_3\text{C}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{CH}_2\text{R}_1 \xrightarrow[\substack{2.\ \text{R}_2\text{R}_3\text{C=O} \\ 3.\ \text{H}_2\text{O}}]{1.\ \text{CH}_3\text{Li}}$$

11

$$(\text{CH}_3)_3\text{C}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{CHR}_1\overset{\text{OH}}{\overset{|}{\text{C}}}\text{R}_2\text{R}_3 \longrightarrow \text{R}_1\text{CH=CR}_2\text{R}_3 \quad (3)$$

spectively, of the Wittig reaction. An earlier, rather limited Wittig-like olefin synthesis based on sulfur as the heteroatom involved the thermal decomposition of β-hydroxy sulfinamides.[11]

In order to evaluate the potential of the hydroxy sulfoxide route, we have carried out the preparation of a number of representative olefins. In general, the yields of the required adducts **3** from **11** were highly satisfactory. The best olefin yields are obtained when trisubstituted olefins are formed; fair to good yields were observed for the mono- and disubstituted olefins. In one example, a tetrasubstituted olefin was obtained in 53% yield.[12]

When isomeric olefins can be produced in the overall sequence, the *E*/*Z* ratio is determined by the diastereomer ratio due to the asymmetry at the two adjacent carbon atoms obtained in the condensation reaction of the lithio derivatives of **11** with carbonyl compounds.[13] In the limited examples we have carried out, this ratio is generally not greater than 7:3. In most instances, we have found that the diastereomers were readily separable by column chromatography. Decomposition of each purified isomer led to isomerically pure olefin. β-Sultines leading to the trans olefins decomposed more readily than those leading to the cis isomer.

Acknowledgment. The financial assistance of the National Research Council of Canada is gratefully acknowledged.

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(12) Tetrasubstituted olefin will probably not be formed in much greater than 50% yield from the appropiate β-hydroxy sulfoxides since the sulfoxide bond is flanked by two tertiary carbon atoms and cleavage of either C–S bond can occur, one leading to β-sultines (olefins) and the other to sulfinate esters.

(13) The configuration at the sulfur has no bearing on the *E*/*Z* ratio.

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Di- and Tri-*tert*-butylmethyl, Two Aliphatic Radicals of Unusual Stability[1]

Sir:

The stability of carbon radicals such as triphenylmethyl,[2] Koelsch's radical,[3] tetraphenylallyl,[4] and pentaphenylcyclopentadienyl[5] depends on a combination of steric hindrance to dimerization and a lowering of the energy of the orbital containing the free electron by rehybridization within a π system. We wish to report preliminary results that show nonbonded interactions alone are sufficient to confer remarkable stability on some carbon radicals derived from alkanes and their silicon analogs.

We prepared radicals **1–4** in concentrations of 1–10 μ*M* by photolysis directly in the cavity of an epr spectrometer of degassed solutions of the parent hydrocarbons dissolved in di-*tert*-butyl peroxide. From **1**-H and **3**-H we also observed less stable primary alkyl radicals, and from **2**-H two other radicals were formed on prolonged photolysis. The most stable of the above species is **4**, which has previously been prepared[6] by reaction of triethylsilyl radicals with $(\text{Me}_3\text{Si})_3\text{CBr}$, under which conditions it had a half-life of 5 sec at −40°. Under our own conditions, where reaction with solvent is slow or absent, the radical persists for several days in dilute solution at 25°. At higher temperatures (50–90°) first-order decay kinetics were observed yielding the expression k (sec^{-1}) = $10^{12.3}$ exp $(-24{,}100\ \text{cal}/RT)$.

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2t\text{-BuO}\cdot$$

$$t\text{-BuO}\cdot + \text{RH} \longrightarrow \text{R}\cdot + t\text{-BuOH}$$

$\text{R}\cdot = \text{Me}_3\text{C}\dot{\text{C}}\text{HCMe}_3$	$\text{Me}_3\text{Si}\dot{\text{C}}\text{HSiMe}_3$	$(\text{Me}_3\text{C})_3\text{C}\cdot$	$(\text{Me}_3\text{Si})_3\text{C}\cdot$
1	**2**	**3**	**4**
a_H 21.89 G	a_H 15.2		
g 2.0027	2.0034	2.0026	2.0027

2,2,4,4-Tetramethyl-3-pentyl (**1**) is stable at 10^{-5} *M* in solution below about −30°. Between −30 and −130° the signal appeared to decrease reversibly, but comparison of the double integral with that of 2,2,6,6-tetramethylpiperidine-*N*-oxyl solutions indicated that anisotropic line broadening rather than dimerization was largely responsible for the effect. Between 10 and 65° the decay can be expressed as k (sec^{-1}) = $10^{12.0}$ exp$(-18{,}900\ \text{cal}/RT)$. At 25° the half-life is 50 sec and did not change on dilution with CFCl_3.

Radical **1** was also prepared by photolysis of di-*tert*-butylmethyl chloride in the presence of hexamethylditin and in the presence of di-*tert*-butyl peroxide and trimethylsilane. In these two systems the lifetime of **1** was greatly reduced but the signal was more intense and it was easy to resolve coupling by the methyl protons, $a_\text{H}^{\text{CH}_3} = 0.68$ G, and by the methyl ^{13}C, $a_{(^{13}\text{C})}^{\text{CH}_3} = 11.7$ G. (For comparison in **4**, $a_\text{H}^{\text{CH}_3} = 0.375$ G and $a_{(^{13}\text{C})}^{\text{CH}_3} = 5.2$ G[6]).

Tri-*tert*-butylmethyl (**3**) was observed as a broad singlet on photolysis of a single solution of a few milligrams of the methane in the peroxide. The decay rates were not of a definite order and depended on the length of photolysis, but we estimate the stability of **3** to be comparable to that of **1**.

A weak doublet assigned structure **2** was the first of several radicals formed from **2**-H and peroxide. The decay of **2** was extremely rapid and apparently second order with $2k_t = 10^{8.6 \pm 0.5}\ M^{-1}\ \text{sec}^{-1}$.

It is clear from these results that whereas α substitution of aliphatic carbon radicals has only a minor effect on the bimolecular termination rate,[7] extensive β substitution can totally inhibit such bimolecular reactions. This occurs even when, as in **1**, the radical is on a sec-

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(1) Issued as N.R.C.C. No. 13231.

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ondary carbon.[8] The stability of **1** and **3** may, of course, be partly due to their inability to disproportionate to olefin and alkane. Our results demonstrate in a direct fashion that alkyl shifts in carbon radicals are slow (or they are disfavored at equilibrium), and our decay rates in those cases where they are first order may be interpreted as minimum values for this rearrangement. Chemical evidence had previously supported this contention.[9,10]

The mechanism of decay of these radicals is not yet known. The obvious possibilities are inter- or intramolecular hydrogen abstraction or methyl elimination. In a preliminary attempt to study the products from **1** we treated *t*-Bu_2CHCl with sodium. The reaction was slow and it required 90 min of refluxing in octane to produce a change in the vpc trace. After this time only a small portion of the chloride had reacted. A number of products had formed, some with short and some with long retention times. One product had the retention time of 2,2,4-trimethyl-3-pentene. One of three peaks with a long retention time had a mass spectral pattern consistent with the formation of a dimer of **1** or *t*-$Bu_2CH_2C(Me_2)\dot{C}H_2$, though no parent ion was formed so the molecular weight could not be determined. However, this product, along with some other products of similar volatility, was also formed when *t*-Bu_2CH_2 was allowed to react with *tert*-butoxy (from di-*tert*-butyl hyponitrite) at ambient temperatures and when chlorinated *t*-Bu_2CH_2 (primary:secondary, 6:1) was allowed to react with sodium.

The rapid, bimolecular, decay of **2** appears anomalous. Perhaps the methyl groups in **2** are better able to avoid each other when **2** dimerizes than when **1** attempts to do so, because of the larger size of the silicon atoms. We are actively studying these and other similar aliphatic radicals.

Acknowledgment. We are extremely grateful to Professor Martin Stiles for providing the sample of tri-*tert*-butylmethane for these experiments.

[8] However, the $Me_3C\dot{C}H_2$ radical and other primary alkyl radicals as well as $Me_3C\dot{C}Me_2$ decay by rapid bimolecular processes.[7]

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[11] N.R.C.C. Postdoctoral Fellow 1971–1972.

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Preparation of Di-π-cyclooctatetraene Complexes of Uranium, Thorium, and Plutonium by Direct Reaction of the Metals with Cyclooctatetraene[1]

Sir:

We report the practical preparation of the di-π-cyclooctatetraene complexes of uranium, thorium, and plutonium by direct reaction of the finely divided metals with cyclooctatetraene. These organometallic sandwich compounds have been prepared previously by reaction of cyclooctatetraene dianion with UCl_4,[2] $ThCl_4$,[3] and $[(C_2H_5)_4N]_2PuCl_6$,[4] respectively, in accord with the common preparation of metallocene compounds by reaction of a ligand anion with a metal salt.

Previous preparations of metallocenes from the free metal include the treatment of magnesium[5] or iron[6] with cyclopentadiene at 300–600° to produce $Mg(C_5H_5)_2$ and $Fe(C_5H_5)_2$, respectively, in reactions that may require the prior formation of cyclopentadienyl salts with liberation of hydrogen. A more direct transition metal analogy to our synthesis is the preparation of dibenzenechromium, $Cr(C_6H_6)_2$, in centigram amounts by the co-condensation of vapors of chromium and benzene onto a cold surface.[7]

The present experiments made use of pyrophoric uranium prepared from uranium hydride as described by Seaborg and Katz.[8] Several cycles of formation and decomposition of the hydride gave a finely divided reactive metal.

Reactions were generally run in sealed Pyrex tubes with care taken to exclude air and water. Uranium hydride was formed and decomposed on a vacuum line, and dried and degassed cyclooctatetraene was condensed into an intermediate volumetrically calibrated tube and then onto the uranium. The Pyrex tube containing the uranium–cyclooctatetraene mixture was sealed off and heated in a tube furnance. Yields of $U(C_8H_8)_2$ were determined by triturating the sample with tetrahydrofuran under an inert atmosphere and measuring the absorbance of the 615-nm peak. The presence of uranocene was established unambiguously by the characteristic cascade of bands in the 600–700-nm region.[2] The reaction could be run with either uranium or cyclooctatetraene as the limiting reagent. The highest yield observed, 57%, was obtained in an experiment with excess uranium at 150° for 2.5 hr. The product was also isolated by sublimation from the crude reaction mixture.

An interesting and significant feature of this preparation is the apparent catalytic effect of traces of mercury. Yields were low in the complete absence of mercury; the presence of a mercury manometer on the vacuum line is sufficient to provide the catalytic effect. One especially noteworthy feature of this effect is that previous studies of the mercury–uranium system[9] indicate that their mutual solubility is very small.

The analogous thorium compound, di-π-cyclooctatetraenethorium(IV) or thorocene[3] was formed in the same fashion *via* heating finely divided thorium metal, prepared from thorium hydride, with cyclooctatetraene at 150°. Due to its relative insolubility the thorocene formed was characterized by placing the reaction product inside a quartz cuvette and subliming a thin film of thorocene on the walls of the cuvette. The thorocene isolated in this manner showed a uv spectrum identical

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