by ^{19}F NMR and GLC. Products **4**, **6**, and **7** almost disappeared, while the amounts of products **5** and **8** were strongly diminished. The effect of the free-radical scavengers is evident from the table.

Registry No. **1a**, 501-65-5; **1b**, 536-74-3; **1c**, 4250-82-2; **1d**, 4250-81-1; **1e**, 673-32-5; **2a**, 14210-91-4; **2b**, 14210-92-5; **2c**, 110097-44-4; **2d**, 110097-45-5; **2e**, 14320-36-6; **3a**, 365-01-5; **3b**, 395-01-7; **3c**, 110097-46-6; **3d**, 58534-47-7; **3e**, 703-17-3; **4e**, 110097-47-7; **5d**, 110097-48-8; **5e**, 29548-91-2; **6d**, 29114-66-7; **6e**, 21120-36-5; **7d**, 110097-49-9; **7e**, 21120-43-4; **8d**, 20895-66-3; **8e**, 579-07-7.

Computation of the Structures of the Phenyl and Benzyl Radicals with the UHF Method

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In a recent note Pacansky, Liu, and DeFrees[1] reported computations on the structures of the phenyl and benzyl radicals. The results were obtained by using the restricted open-shell Hartree–Fock method (ROHF), and they were based on a slightly improved version of the GAUSSIAN 82 program package,[2] making use of 4-31G basis sets. It was noted that the use of the corresponding unrestricted Hartree–Fock method (UHF) produces results with S^2 expectation values that are considerably larger than $^3/_4$. Such values imply a certain amount of spin contamination, and it was therefore argued that the UHF method is not appropriate for calculating the structures of the phenyl and benzyl radicals.

Farnell, Pople, and Radom[3] compared the geometries derived from UHF and ROHF computations for a set of small molecules. It was found that the ROHF results are usually in better agreement with experimental data than the UHF results, especially when the spin contamination in the UHF function is significant. Improving the quality of the basis sets in the computation leads to a decrease in the spin contamination in the UHF function and to a better agreement between the UHF and the ROHF geometries.

It was also noted by Farnell, Pople, and Radom[3] that the UHF method is more convenient than the ROHF method. We had similar experiences. We found that there are many situations where the UHF computations converge, while the ROHF computations do not converge. We feel therefore that it may be of interest to compare the geometries of the phenyl and benzyl radicals derived by means of the UHF procedure with the geometries derived by Pacansky, Liu, and DeFrees[1] by means of the ROHF method. If the two sets of geometries turn out to be similar, then we might be encouraged to use the UHF procedure also for geometry predictions in situations where the ROHF method does not converge.

In order to investigate the matter we performed a set of structure calculations of the phenyl and benzyl radicals with the GAUSSIAN 82 program package,[2] using the UHF method. In the case of the phenyl radical we used the 6-31G basis set and in the case of the benzyl radical we used the 4-31G basis set. Those are the largest basis sets for which the UHF computations converge. We compare our results with the structures that were reported in ref 1 using the ROHF procedure. Here the 4-31G basis set was used in both the phenyl and the benzyl computations.

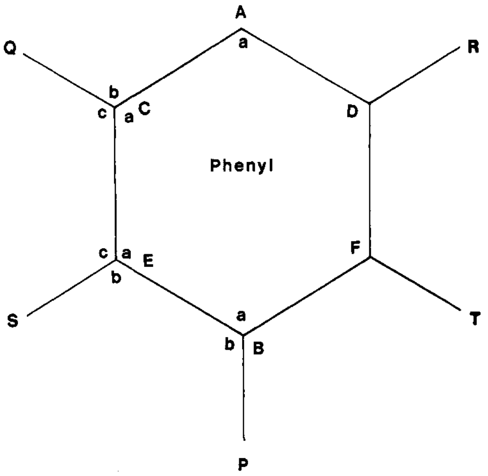

Figure 1. Structure and definitions of bond lengths and bond angles of the phenyl radical.

Table I. Bond Lengths and Bond Angles of the Phenyl Radical Obtained from a UHF Computation with a 6-31G Basis Set and the Same Quantities Obtained from a Previously Reported ROHF Computation with a 4-31G Basis Set[1] (Bond Lengths and Bond Angles Defined in Figure 1)

	UHF	ROHF
	Bond Lengths, Å	
AC	1.392	1.371
BE	1.406	1.387
CE	1.404	1.390
BP	1.073	1.072
CQ	1.072	1.071
ES	1.073	1.072
	Bond Angles, Deg	
a_A	124.5	124.8
a_B	120.8	120.6
a_C	117.3	117.2
a_E	120.0	120.1
b_B	119.6	119.7
b_C	121.6	121.7
b_E	120.0	120.1

Table II. Bond Lengths and Bond Angles of the Benzyl Radical Derived from a UHF Computation with a 4-31G Basis Set and the Same Quantities Derived from a Previously Reported ROHF Computation with a 4-31G Basis Set[1] (Bond Lengths and Bond Angles Are Defined in Figure 2)

	UHF	ROHF
	Bond Lengths, Å	
AC	1.426	1.396
BE	1.402	1.384
CE	1.389	1.380
AG	1.403	1.447
BP	1.072	1.072
CQ	1.073	1.073
ES	1.072	1.072
GU	1.072	1.070
	Bond Angles, Deg	
a_A	117.4	118.0
a_B	119.7	119.6
a_C	121.1	120.9
a_E	120.4	120.3
a_G	118.5	118.2
b_A	121.3	121.0
b_B	120.2	120.2
b_C	118.9	119.3
b_E	119.8	120.0
b_G	121.3	120.9

The various results for the phenyl radical are reported in Table I, and the results for the benzyl radical are reported

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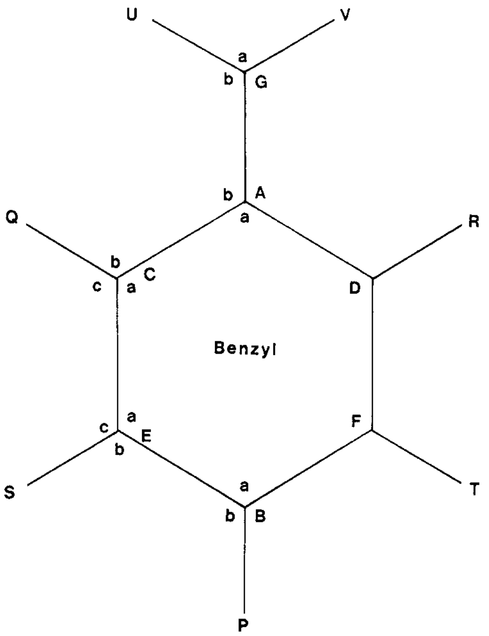

Figure 2. Structure and definitions of bond lengths and bond angles of the benzyl radical.

Table III. Expectation Values $\langle H \rangle$ of the Hamiltonian H_{op} and Expectation Values $\langle S^2 \rangle$ of the Spin Operator S^2 with Respect to the Wave Functions Ψ_{UHF} and Ψ_{ROHF} of the Phenyl and Benzyl Radicals

	phenyl	benzyl
$\langle H \rangle_{UHF}$	−229.988346	−268.761460
$\langle H \rangle_{ROHF}$	−229.725501	−265.837128
$\langle S^2 \rangle_{UHF}$	1.4970	1.4194
$\langle S^2 \rangle_{ROHF}$	0.7500	0.7500

in Table II. The bond lengths are expressed in terms of angstroms and the bond angles are expressed in terms of degrees. The bond lengths and bond angles of the phenyl radical are defined in Figure 1, and the corresponding quantities of the benzyl radical are defined in Figure 2.

Experimental data on the structures of the phenyl and benzyl radicals do not seem to be available, and it is not possible to decide which of the two sets of theoretical results, UHF or ROHF, are closer to experiment. On the other hand, the two sets of theoretical values are fairly similar. The root mean square deviation of the bond lengths is 0.014 Å for the phenyl radical, and it is 0.018 Å for the benzyl radical. The largest discrepancy is 0.04 Å for the CC bond length AG between the ring and the methyl group in the benzyl radical. The UHF bond lengths are generally a bit longer than the ROHF bond lengths, which is consistent with the results derived by Farnell, Pople, and Radom.[3] It follows also from the data in Tables I and II that the difference between the UHF and the ROHF bond angle predictions are quite small, especially if we bear in mind that the margin of error in the computed bond angles is usually taken as 0.1 or 0.2°. We feel that the agreement between the two sets of geometry predictions is good enough to encourage the use of the UHF method in those situations where the ROHF method is not feasible.

In Table III we list the expectation values $\langle H \rangle$ and $\langle S^2 \rangle$ of the Hamiltonian operator H_{op} and of the spin operator S^2 with respect to the UHF wave functions. It follows from the variational principle that the UHF energy should always be lower than the corresponding ROHF energy. In the case of the phenyl radical, we use a slightly better basis set than Pacansky, Liu, and DeFrees[1] (6-31G versus 4-31G), and our energy is somewhat lower than theirs. In the case of the benzyl radical, we used the same basis set as Pacansky, Liu, and DeFrees,[1] namely 4-31G, and we were surprised to find that our UHF energy was lower by more than 3 hartree. We rechecked our result, and we also found that it is consistent with previously obtained 3-21G results so that we have no further explanation for this large discrepancy.

The spin contamination of the UHF wave functions may not be quite as bad as it seems from the data reported in Table III. According to a simple argument, similar to a recent analysis by Schlegel,[4] we may expand Ψ_{UHF} as

$$\Psi_{UHF} = {}^2\Psi + {}^4\Psi + {}^6\Psi + {}^8\Psi + ... \qquad (1)$$

We define the normalization integrals

$$N_k = \langle {}^k\Psi | {}^k\Psi \rangle \qquad (2)$$

and we have

$$1 = N_2 + N_4 + N_6 + ... \qquad (3)$$

since Ψ_{UHF} is normalized to unity. The expectation value $\langle S^2 \rangle_{UHF}$ is then given by

$$\langle S^2 \rangle_{UHF} = \langle \Psi_{UHF} | S^2 | \Psi_{UHF} \rangle = \tfrac{3}{4}N_2 + \tfrac{15}{4}N_4 + \tfrac{35}{4}N_6 + ... = \tfrac{3}{4} + 3N_4 + 8N_6 + ... \qquad (4)$$

It is easily derived from the $\langle S^2 \rangle_{UHF}$ values for phenyl and benzyl in Table III that the spin contamination is at worst 25% for phenyl and 22% for benzyl if all of the spin contamination is concentrated in the quartet spin state.

In using the GAUSSIAN 82 program package[2] for computations on organic radicals, we have found[5] that the UHF computations converge more readily than the corresponding ROHF computations. It is therefore useful to have some information about the relation between geometry predictions derived from UHF and from ROHF computations. Even though the amount of information that we present here is rather limited, it encourages us to use the UHF procedure for geometry predictions of aromatic radicals and radical anions in situations where the ROHF procedure does not converge.

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Registry No. Phenyl radical, 2396-01-2; benzyl radical, 2154-56-5.

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Reaction of Organometallic Reagents with Ethyl Trifluoroacetate and Diethyl Oxalate. Formation of Trifluoromethyl Ketones and α-Keto Esters via Stable Tetrahedral Adducts

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In conjunction with our studies designed to evaluate the effect of the trifluoromethyl group on free radical stabilities, we had need for a variety of trifluoromethyl ketones, $RCOCF_3$. The primary method for preparation of these