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CARBON-13 ESR COUPLING CONSTANTS OF PERSISTENT AND STABILIZED ALLYL RADICALS

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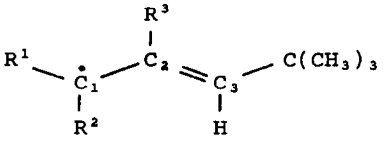
In a recent paper Ingold et al. 1) pointed out that allyl radicals in gaining persistence by steric hindrance lose their stabilization by resonance. In the course of our work on sterically hindered allyl 2) and aza-allyl 3) radicals we have prepared a series of "stabilized" 1) allyl radicals, two of which are "persistent" 1) even at room temperature 4). This persistence enabled us to measure ^{13}C-ESR coupling constants of delocalized allyl radicals for the first time

1,1,3-tri-tert-butylallyl 1a and 1,3-di-tert-butyl-1-isopropylallyl radical 2a and their deuterated analogs 1b and 2b were generated by reductive cleavage with K/Na alloy of the 3,5-di-tert-butyl-benzoate and oxalic diester 6) of the corresponding allyl alcohols at room temperature. The less persistent radicals 1,2,3-tri-tert-butylallyl 3, 1,3-di-tert-butyl-(2-pentadeuterophenyl)-allyl 4 and 1,3-di-tert-butylallyl 5 were produced from the corresponding allyl bromides by abstraction of bromine atoms with photochemically generated trimethylstannyl radicals. The ESR-data of the new radicals are shown in the table.

The persistence of 1 and 2 must be caused by steric screening of the high spin density at C_3 by the endo tert-butyl and isopropyl groups at C_1.

Comparison of the a^H values of 1 and 2 with those of the planar radical 5 shows that 1 is slightly twisted at the C_1-C_2 bond while 2 is nearly planar. From the almost identical $a^H_{C_3}$ values of 4 and 5 a planar conformation can be deduced for 4. Taking into account the known effect of alkyl substituents to increase a^C to about 2 % (CH_3: a^C = 38,34 G; CH_2-CH_3: a^C = 39,07 G) 7) one can predict the a^C values of the unsubstituted allyl radical to be $a^C_{1,3}$ = 22,3 and a^C_2 = 16,9 G. These data are in part considerably different from the results of INDO



ESR coupling constants a)

					a^H			a^C		
	R^1	R^2	R^3	temp. b)	C_1	C_2	C_3	C_1	C_2	C_3
1a	$C(CH_3)_3$	$C(CH_3)_2$	H	25		5.7	12.3	-	-	-
1b	$C(CD_3)_3$	$C(CD_3)_3$	H	25		5.6	12.3	26.0	16.9	20.9
2a	$C(CH_3)_3$	$CH(CH_3)_2$	H	25		4.3	13.1	-	-	-
2b	$C(CD_3)_3$	$CH(CD_3)_3$	H	-40	1.1 c)	4.2	13.1	24.0	16.8	23.0
3	H	$C(CH_3)_3$	$C(CH_3)_3$	-20	13.6	-	13.6	23.9	16.8	23.9
4	H	$C(CH_3)_3$	C_6D_5	-20	14.8 d)	-	13.3 d)	22.8	17.0	22.8
5	$C(CH_3)_3$	H	H	-20	13.4	3.8	13.4	-	-	-

a) in Gauss = 10^{-4} T; b) in °C; 1a,b, 2a in benzene, 2b, 3, 4, 5 in cyclopentane; c) methin proton; d) at -40°

calculations ($C_{1,3}$: 28,0; C_2: -16,6) 8) and semiempirical calculations using the Karplus Fraenkel relationship ($C_{1,3}$: 25,8; C_2: -23,0) 9). A detailed discussion including the conformations of radicals 1-4 will be given in a full paper.

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References

1) D. Griller, J.W. Cooper and K.U. Ingold, J.Amer.Chem.Soc.,97, 4269 (1975)

2a) H. Regenstein and A. Berndt, Angew.Chem., Int.Ed. 13, 145 (1974)
b) H. Regenstein, W. Ahrens and A. Berndt, Tetrahedron 31, (1975), in press

3) W. Ahrens and A. Berndt, Tetrahedron Lett. 3141 (1973); 2295 (1975)

4) the long known persistent allyl radicals of the tetraphenylallyl type 5) owe their persistence to delocalization into the aromatic rings too

5) K. Watanabe, J. Jamauchi, H. Ohya-Nishiguchi, Y. Deguchi and H. Takaki, Bull.Chem.Soc.Jap. 45, 371 (1972) and literature cited therein

6) K. Schreiner and A. Berndt, Angew.Chem., Int.Ed. 13, 144 (1974)

7) R.W. Fessenden, J.Phys.Chem. 71, 74 (1967)

8) J.A. Pople, D.L. Beveridge and P.A. Dobosh, J.Amer.Chem.Soc. 90, 4201 (1968)

9) G.N. LaMar, "NMR of paramagnetic molecules", Ed. by G.N. LaMar, Academic Press, New York 1973, p. 103