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THE DIMER OF 2-METHYL-1,1-DIPHENYLPROPYL RADICALS AND ITS REACTIVITY[1)+)]

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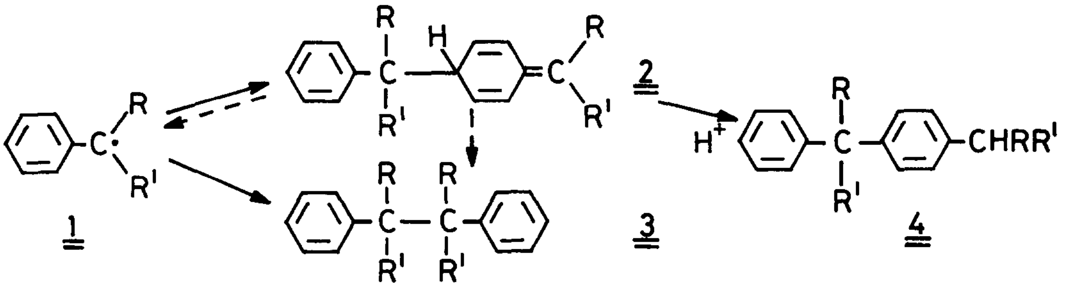
Abstract: The title radicals dimerize to an α,p-dimer 2 and not to an α,α-dimer 3 as previously[8] assumed. The structure of the dimers of t-benzhydryl radicals $Ph_2\dot{C}R$ in general is strongly dependent on the bulkiness of the R group.

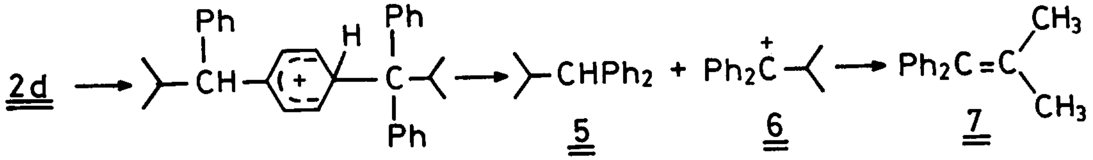
Benzyl type radicals 1 can dimerize to form either α,α-dimers 3 or α,p-dimers 2[2]. The latter dimerisation process seems to be favoured by bulky groups R and R' in 1. Only the α,p-dimers of 1a[2-4], 1b[5] and 1c[5] have been isolated in crystalline state, but no α,p-dimer of a benzhydryl type radical[4]. The isolation of α,p-dimers is frequently prevented by their fast transformation into α,α-dimers 3 by reversible dissociation[2,6] to 1 or by a radical chain process[7]. In addition 2 is easily oxidized by air to an hydroperoxide[2,5] or tautomerized to the aromatic species 4 under acid catalysis[2,5,7]. The instability of 2 has been taken therefore as a characteristic feature to distinguish between 2 and the more stable α,α-dimer 3 [2,4a,b]. It will be shown in this communication that this simple rule does not hold for the dimers of t-benzhydryl radicals 1 ($R=C_6H_5$, R'=alkyl).



	a	b	c	d	e
R	C_6H_5		$c-C_6H_{11}$	C_6H_5	C_6H_5
R'	C_6H_5		$c-C_6H_5$	$2-C_3H_7$	C_2H_5

When we repeated K. Zieglers procedure for the preparation of 3d[8)], we obtained a product with the reported melting point[8)], *which turned out, however, to be the α,p-dimer 2d* according to its spectra. 3e in contrast was obtained by the same procedure without interference of 2e. The uv absorption of 2d in cyclohexane at 270 nm(log ε = 4.17) is in agreement with literature values for other α,p-dimers[4,5)]. The well resolved ^{1}H-nmr spectrum is shown in fig. 1. The chemical shifts of the olefinic protons at δ=4.59-6.65 ppm ($J_{b,d}=J_{c,e}$= 10.7 Hz; $J_{a,b}=J_{a,c}$= 2.6 Hz) and of the double allylic H at δ = 4.32 ppm are of the expected magnitude[3b,4,5,9)]. The poor signal to noise ratio of the ^{13}C-nmr spectrum recorded at -30°C in $CDCl_3$ prevented a complete analysis. Three aromatic C-signals and one additional for the exo-methylene carbon appeared in the region of quaternary aromatic carbons (138.9-141.9 ppm), and one signal in the region of quaternary aliphatic carbons[10)] (61.5 ppm).

After 2d was kept at 22°C in a benzene solution of thiophenol (10 vol.%) for 16 h, 80% 2-methyl-1,1-diphenylpropane 5 was then analyzed by GC, indicating homolytic cleavage of 2d into radicals 1d and their trapping by thiophenol. After treatment with 2 vol.% CF_3COOH in CH_2Cl_2 at -10 to 20°C isomerisation 2d → 4d was *not* observed but instead 2-methyl-1,1-diphenylpropane 5 and 2-methyl-1.1-diphenylpropene 7 (∿1:1 ratio) were formed immediately as main products according to GC and nmr analysis. A retro Friedel Crafts reaction



which is favoured by the stability of the carbeniumion 6 appears to be responsible for this. For 2a an analogous cleavage was reported under $SbCl_5$ catalysis[3b)], but this reaction was never observed for α,p-dimers of benzyl radicals.

In summary, the relative stability of α,α-dimers 3 and α,p-dimers 2 is not so much dependent on the semibenzene - benzene energy difference of ca. 7-8 kcal/mole[3b)] as on the difference in ground state strain[11)]. The correlations in fig. 2 point out that the dimers of t-benzhydryl radicals are divided into two groups according to the varying response of their thermal stability to the bulk of the R group as expressed by the steric substituent constants $\mathcal{S}_f$[12)] of the fragment Ph_2CR. It follows from fig.2 that, in contrast to Zieglers original view[8)], the dimers of 1-cyclopentyl-, 1-cyclohexyl- and 1-t-butylbenzhydryl radicals are also α,p-dimers 2. The steric substituent constants $\mathcal{S}_f$[12)] have accordingly high predictive power for the preferred dimer structure in this series. The stabilities of the α,α-dimers 3 respond much more sensitively to the bulkiness of R than that of the α,p-dimers 2 do.

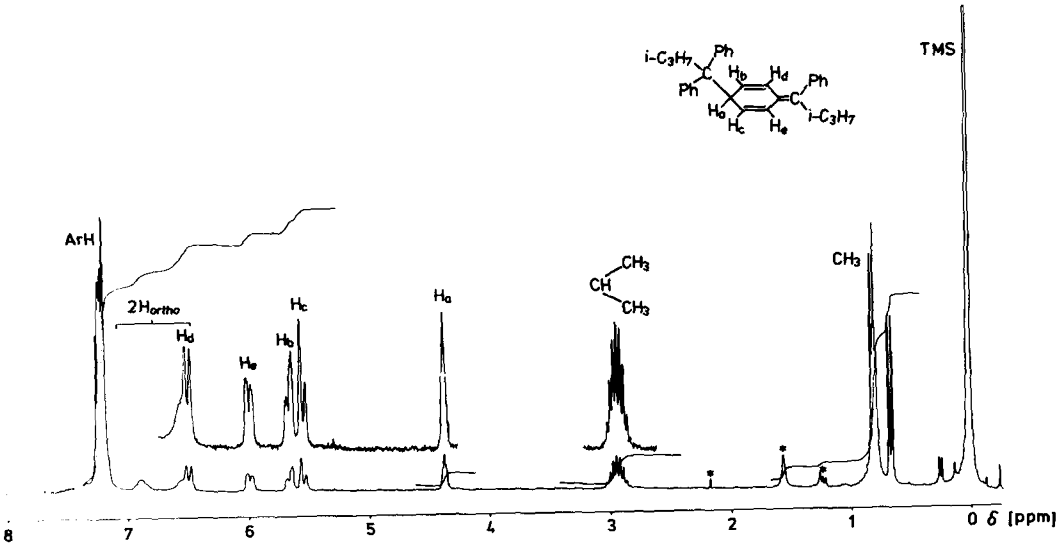


Fig.1 ^{1}H nmr spectrum of 2d in CDCl$_3$ (250 MHz) (*) impurity

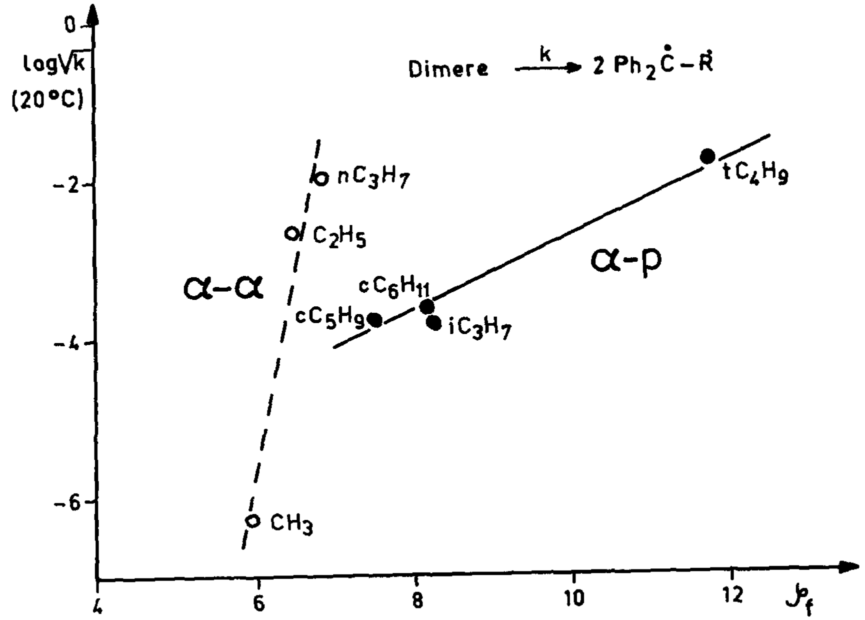


Fig. 2 Relationships between thermal stability (log $\sqrt{k}$)8,9) of α,α-dimers (○) or α,p-dimers (●) of t-benzhydryl radicals Ph$_2\dot{C}$R and steric substituent constants $\mathcal{S}_f$ 12) of the Ph$_2\dot{C}$R fragments. R groups are shown in the fig.

References

+) This paper is dedicated to Prof. A. Steinhofer on the occasion of his 75th birthday.

1. Thermolabile Hydrocarbons XXIII; for paper XXII see G. Kratt, H.-D. Beckhaus and C. Rüchardt, Chem.Ber.,in preparation.
2. J.M. McBride, Tetrahedron **30**, 2009 (1974); K.J. Skinner, H.S. Hochster and J.M. McBride, J.Am.Chem.Soc. **96**, 4301 (1974).
3.
   - 3a) H.A. Staab, H. Brettschneider and H. Brunner, Chem.Ber. **103**, 1101 (1970).
   - 3b) H. Volz, W. Lotsch and H.-W. Schnell, Tetrahedron **26**, 5343 (1970).
   - 3c) For an X-ray analysis of **2a** see J. Allemand and R. Gerdil, Acta Cryst. **B34**, 2214 (1978); for an X-ray analysis of a related α,α-dimer see M. Stein, W. Winter and A. Rieker, Angew.Chem. **90**, 737 (1978), Angew.Chem.,Int.Ed.Engl. **17**, 692 (1978); see also E. Osawa, Y. Onuki and K. Mislow, J.Am.Chem.Soc. **103**, 7475 (1981).
4. for solution work see
   - 4a) H. Lankamp, W. Th. Nauta and C. McLean, Tetrahedron **1968**, 249.
   - 4b) J. Coops, W.Th. Nauta, M.J.E. Ernsting and A.C. Faber, Rec.trav. chim. **59**, 1109 (1940) and further papers in this series.
   - 4c) C.S.W. Hook, Tetrahedron **1975**, 3321.
   - 4d) W.B. Smith, G.D. Branum and C. Saint, J.Org.Chem.,in print.
5. G. Kratt, H.-D. Beckhaus, H.J. Lindner and C. Rüchardt, Chem.Ber., in print.
6. see also Dissertation H.-D. Beckhaus, Universität Freiburg 1975.
7. H. Langhals and H. Fischer, Chem.Ber. **111**, 543 (1978).
8. K. Ziegler, A. Seib, K. Knoevennagel, P. Herte and F. Andreas, Liebigs Ann.Chem. **551**, 150 (1942).
9. for details see Diplomarbeit J. Schaetzer, Universität Freiburg 1983.
10. M.I. Watskins and G.A. Olah, J.Am.Chem.Soc. **103**, 6566 (1981).
11. see also C. Rüchardt and H.-D. Beckhaus, Angew.Chem. **92**, 417 (1980); Angew.Chem.,Int.Ed.Engl. **19**, 429 (1980).
12. H.-D. Beckhaus, Angew.Chem. **90**, 633 (1978); Angew.Chem.,Int.Ed.Engl. **17**, 593 (1978).

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