Tetrahedron Letters No.19, pp. 2313-2315, 1968. Pergamon Press. Printed in Great Britain.

VINYL RADICALS

HOMOLYTIC AROMATIC SUBSTITUTION WITH 1-CYCLOHEX-1-ENYL RADICALS

P. Spagnolo and M. Tiecco
Istituto di Chimica Organica e di Chimica Industriale della
Università, Bologna, Italy.

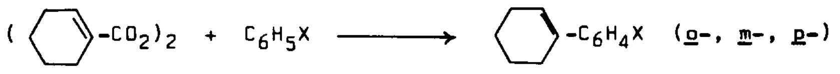
(Received in UK 24 January 1968; accepted for publication 12 February 1968)

Vinyl radicals have recently received the attention of many workers, whose interest was focused on the configurational stability of such radicals <u>via</u> a study of hydrogen (1) and halogen (2) abstraction reactions.

We wish, now, to report the results of a study intended to determine the ability of vinyl radicals to effect homolytic aromatic substitution. In order to generate styryl radicals, the cobaltous chloride catalized reaction of methylmagnesium iodide with β-bromostyrene (3) was employed. The reaction, carried out in benzene, used as a solvent diluent, failed to give stilbenes and only styrene and methylstyrenes were produced. In contrast, the same reaction, applied to 1-bromocyclohex-1-ene, afforded a good yield of 1-phenylcyclohex- ene, whose formation may be taken as indicative of the intermediacy of 1-cyclohex-1-enyl free radicals. These radicals were also generated from the peroxide (I) of cyclohex-1-ene-1-carboxylic acid, prepared from the corresponding acid chloride by reaction with ethereal hydrogen peroxide and pyridine at -20° (m.p. 42-3° on recrystallization from methanol. Found: C, 65.96; H, 7.19% - $C_{14}H_{18}O_4$ requires C, 67.01; H, 7.25% . $\nu(CCl_4)$ 1752 cm^{-1}).

The decomposition of the peroxide (I) in benzene, at 80° for 24 hours, afforded cyclohex-1-ene-1-carboxylic acid, cyclohexene, 1-phenylcyclohex-1-ene and some carbonyl containing polymeric material. Decomposition of (I) in cumene gave dicumyl, as the major product, together with cyclohexene and cyclohex-1-ene-1-carboxylic acid; gas chromatographic analysis of the reaction mixture showed that it contained small amounts of the three 1-(<u>o</u>-, <u>m</u>-, <u>p</u>-isopropylphenyl)cyclohex-1-ene isomers.

Experiments were then carried out using other monosubstituted benzenes as solvents; in all cases a mixture of isomers was obtained, the ratios of which were determined by g.l.c. They are summarized in Table 1.



(I)

$X = -CH_3,\ -C(CH_3)_3,\ -OCH_3$

The reactivities of the benzene derivatives C_6H_5X, relative to benzene ($^{X}_{H}K$) towards substitution by 1-cyclohex-1-enyl radicals, were determined by competitive experiments in which equimolecolar C_6H_5X / benzene mixtures were allowed to compete for 1-cyclohex-1-enyl radicals. Analysis by g.l.c. of the reaction mixtures allowed the values of $^{X}_{H}K$, reported in Table 1, to be determined from the relative amounts of 1-arylcyclohex-1-enes and 1-phenylcyclohex-1-ene.

TABLE 1

Isomer ratios and relative reactivities in homolytic aromatic 1-cyclohex-1-enylation (a).

Aromatic Solvent	1-Arylcyclohex-1-enes			$^{X}_{H}K$
C_6H_5X	Ortho%	Meta%	Para%	
$C_6H_5CH_3$ (b)	67	- 33	-	1.2
$C_6H_5C(CH_3)_3$	20	60	20	0.75
$C_6H_5OCH_3$	68	16	16	1.5

a) Determined by g.l.c. using a 10% FFAP column. Identification of products was effected by a comparison of the g.l.c. retention times with those of authentic specimens prepared as described in the literature.

b) Meta and para isomers were not resolved under the experimental conditions used. Dibenzyl was also present.

The values reported in Table 1 may be taken as a clear indication of the homolytic nature of the aromatic substitution, since they are not very different from the corresponding values reported for the substitution by phenyl radicals (3,4). The data on isomer ratios and relative reactivities indicate that no unusual properties can be associated with 1-cyclohex-1-enyl radicals with regard to homolytic aromatic substitution.

REFERENCES

1) (a) J.A. Kampmeier and R.M. Fantazier, J.Am.Chem.Soc., **88**, 1959, 5219 (1966);
   (b) L.A. Singer and N.P. Kong, J.Am.Chem.Soc., **88**, 5213 (1966); Tetrahedron Letters, 2089 (1966); 643 (1967);
   (c) G.D. Sargent and M.W. Browne, J.Am.Chem.Soc., **89**, 2788 (1967).

2) O. Simamura, K. Tokumaru and H. Yui, Tetrahedron Letters, 5141 (1966).

3) D.I. Davies, D.H. Hey and M. Tiecco, J.Chem.Soc., 7062 (1965) and references cited therein.

4) (a) D.H. Hey, S. Orman, and G.H. Williams, J.Chem.Soc., 565 (1961);
   (b) D.R. Angood, Ph.D. Thesis, London (1952);
   (c) C.S. Rondestvedt and H.S. Blanchard, J.Org.Chem., **21**, 229 (1956).