NOTES

POLAROGRAPHY OF 7-BENZONORBORNENONES¹

Hiroshi Tanida, Hiroshi Miyazaki, and Hiroyuki Ishitobi

Polarographic half-wave reduction potential distinguishes between aryl ketones and alkyl ketones. The reduction under neutral or acidic conditions is believed to involve a free radical process, followed by dimerization (pinacol formation) (1-3). As shown in previous papers (4), reactivity at the 7-position of benzonorbornenes demonstrated a typical homobenzylic conjugation; direct conjugate interaction was shown between the



 C_7 carbonium ion formed in acetolysis of anti-7-benzonorbornenyl *p*-bromobenzenesulfonate and the aromatic ring. Interest in a radical reaction at this position led us to measure half-wave reduction potentials $(-E_{\frac{1}{2}})$ of benzonorbornen-7-one (I) and 4'-substituted derivatives (II-VI).

The Oppenauer oxidation of the 4'-substituted anti-7-benzonornenols (4) provided the materials used in this study. The $-E_{\frac{1}{2}}$'s measured under neutral conditions (see Experimental section), where a one-electron reduction process was observed for acetophenone, are summarized in Table I. For comparison, the results of benzonorbornen-2-one (VII), acetophenone, cyclohexanone, and cyclopentanone under the same conditions are also listed. The most significant result was that the $-E_{\frac{1}{2}}$ of the 7-ketones (I-VI) was almost the same as that of acetophenone; on the other hand, the 2-ketone (VII) did not yield a result similar to that of acetophenone, but instead resembled cyclohexanone and cyclo-

TABLE I								
Half-wave potentials (saturated calomel electrode) and limiting currents								
of benzonorbornenones								

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Compound	$-E_{rac{1}{2}}$, V	<i>i</i> 1, μA	Concentration \times 10 ³ , moles/l
I	1.653	0.35	5,38
II	1,637	0.37	5.13
III	1.638	0.19	5.19
IV	1.614	0.32	5.07
v	1.623	0.43	4.97
VI	1.621	0.89	5.31
VII	No wave		
Acetophenone	1.616	9.43	5.93
Cyclohexanone	No wave		
Cyclopentanone	No wave		

¹Paper XI of a series on bicyclic systems; for paper X see H. Tanida and R. Muneyuki, J. Am. Chem. Soc., in press.

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pentanone. Therefore, one might be able to argue that the 7-ketones behave as a kind of aryl ketone. However, the limiting current of 7-ketones was very small for reasons that cannot be explained at present. No significant substituent effect was observed.





Absence of anchimeric assistance in the homolytic reactions of 2-norbornyl and 2norbornenyl systems has recently been demonstrated by several workers (5). In this connection, the indication of phenyl participation in the polarographic reduction reported here may be of interest in considering a radical reaction at the 7-position of the norbornenyl system.

EXPERIMENTAL

Melting points were taken by capillary and are corrected; boiling points are uncorrected.

Materials

4'-Methoxy-, 4'-methyl-, 4'-chloro-, and 4'-bromo-benzonorbornen-7-one (II, III, IV, and V) were prepared by the Oppenauer oxidation of the corresponding anti-alcohols (4) according to the procedure of Bartlett and Giddings (6) which was used for the preparation of I. The cyano compound (VI) was prepared by refluxing a solution of V and cuprous cyanide in dimethylformamide (7). Properties and analyses of the new 7-ketones prepared in this study are listed in Table II.

TABLE II

4'-Substituted benzonorbornen-7-ones (I)

	Melting or boiling point (mm), °C			% carbon		% hydrogen	
4'-Substituent		$n_{\rm D}$ (temp., °C)	Formula	Calcd.	Found	Calcd.	Found
CH ₃ O CH ₃ H	$ \begin{array}{c} 140^{*} (1) \\ 101-102 (1) \\ 126 (16) \end{array} $	$\begin{array}{c} 1.5632 \ (25.7) \\ 1.5547 \ (23) \\ 1.5597 \ (27.8) \end{array}$	$\begin{array}{c} C_{12}H_{12}O_2\\ C_{12}H_{12}O\end{array}$	76.57 83.69	76.76 83.75	$\begin{array}{c} 6.43 \\ 7.02 \end{array}$	$6.68 \\ 7.08$
Cl Br CN	109 (2) 130* (1) 107–108	1.5748 (28.0) 1.5953 (28.3) Crystal	C11H9OCl C11H9OBr C12H9ON	$\begin{array}{c} 68.58 \\ 55.72 \\ 78.67 \end{array}$	$\begin{array}{c} 68.47 \\ 56.00 \\ 78.50 \end{array}$	$4.71 \\ 3.83 \\ 4.95$	$\begin{array}{r} 4.97 \\ 3.89 \\ 5.08 \end{array}$

*Bath temperature.

Polarography

The half-wave reduction potentials were measured on a Yanagimoto pen-recording polarograph, model 102. The dropping mercury electrode that was used had the following characteristics in distilled water under an open circuit: m = 0.865 mg/s; n = 70 cm; t = 4.33 s. The supporting electrolytic solution was prepared by mixing 10 ml of 95% ethanol, 0.01% gelatin solution, and 1 N lithium chloride solution, adjusted to a total volume of 20 ml. Dissolved oxygen was removed from the solutions by bubbling nitrogen gas through them for 10 min. A saturated calomel electrode was used as an external reference electrode and the measurements were made in triplicate at 25 ± 0.1 °C.

Under acidic conditions (supporting electrolytic solution prepared by mixing 10 ml of 95% ethanol, 0.01% gelatin solution, and 10 ml of pH = 3.59 buffer), the wave of I became blurred. For acetophenone, $E_{\rm f}=-1.273$ V and $i_{\rm d}=7.16~\mu{\rm A}~(5.64\times10^{-3}~{\rm mole/l})$ were observed.

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GAS CHROMATOGRAPHY OF ESTRONE AND RELATED COMPOUNDS

RAFAEL MONTALVO AND OWEN H. WHEELER

Gas chromatography at high temperatures has been used widely for the analysis of mixtures of steroids (1). The liquid phases most generally used are the nonpolar SE-30 silicone gum (2) and the polar QF-1 fluorinated alkyl silicone (3). However, only a few measurements have been reported on estrone, estradiol, and estrone methyl ether (4, 5).

This note reports a study of the retention times of estrone and a series of its derivatives, principally those substituted in ring A, on QF-1 and SE-30 columns (Table I), both as the free compounds and as their trimethylsilyl ethers (4).

The retention times (R_t) on the QF-1 column depend on the polarity of the compound, and methylation in position-3 reduced the R_t values. Similarly, estrolactone showed a greatly increased R_t value, whereas 17-deoxyestrone gave a low retention time.

Hydroxylation in position-2 of estradiol increased the R_t value to about twice that of estradiol, as did hydroxylation at position-16, although a 4-hydroxyl substituent caused an increase of only about 70%. The retention time for 2-acetoxy substitution was also greater than that for the 4-isomer. These differences are probably steric in origin, since a 2,3-disubstituted compound can be absorbed more easily in a direction along the length of the steroid molecule.

The trimethylsilyl ethers had lower values of R_t on the QF-1 column (Table I) than did the corresponding free compounds. Estradiol gave two peaks, one of the monoether and the second of the diether. However, the derivatives of 4-hydroxyestradiol and 4-hydroxyestrone showed only one peak.

The usefulness of the QF-1 column in separating estrone derivatives was shown by the fact that a commercial sample of estradiol monoacetate was readily analyzed as estradiol (33%), estradiol 3-acetate (25%), estradiol 17β -acetate (22%), and estradiol diacetate (20%). A sample of Werbin's dilactone (6) showed the following peaks (and relative areas): 6.3 (2%), 7.5 (2%), 9.0 (6%), and 9.4 min (90%). The compound may be a mixture of isomers, as originally suggested (6), although the peaks of low retention time are probably the result of decomposition.

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