Tetrahedron Letters No. 42, pp. 3927 - 3930, 1971. Pergamon Press. Printed in Great Britain.

ACIDITY OF HYDROCARBONS. XLI.
KINETIC ACIDITIES OF BRIDGEHEAD HYDROGENS IN BENZOTRIPTYCENE AND ETHENOANTHRACENE TOWARDS CESIUM CYCLOHEXYLAMIDE

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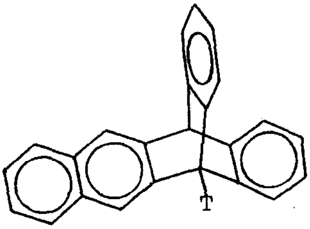
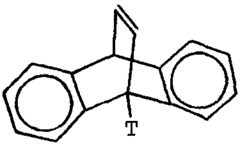
(Received in USA 3 August 1971; received in UK for publication 20 September 1971)

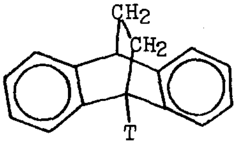
We have shown recently (1) that the kinetic acidity of the bridgehead position of triptycene, I, can be quantitatively accounted for on the basis of the s-character in the C-H bond as measured by $J_{^{13}C-H}$, and by the inductive field effect of the aryl carbons as measured by $\Sigma 1/r$. The success of the $\Sigma 1/r$ field effect function prompted a further test by extension to two derivatives of I obtained by adding and removing a benzene ring, respectively: benzo[b]triptycene, II, and 9,10-dihydro-9,10-ethenoanthracene, III.



II-t



III-t



IV-t

Anthracene-9-*t* and -9-*d*(*t*) were prepared by quenching the reaction product of 9-bromoanthracene and butyllithium with the appropriate water. Anthracene-9-*t* with Wittig's method (2) using 1,4-endoxynaphthalene gave II-*t*, mp 263-4° (lit. (2) 257.8°). The Diels-Alder adduct of anthracene-9-*d*(*t*) and maleic anhydride was prepared in refluxing benzene and converted to the corresponding dicarboxylic acid, mp 265.5-267.5° (lit. (3) 251-3°). This acid was decarboxylated with $Pb(OAc)_4$ in pyridine following the general procedure of Cimarusti and Wolinsky (4 to give III-*d*,*t*, mp 120-1° (lit. (5) 118.5-119°). The saturated compound was also prepared for comparison by hydrogenation of II-*t* with Pd/C to give 9,10-dihydro-9,10-ethanoanthracene-9-*t*, IV-*t*.

Exchange kinetics were run with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA) following our usual procedure (1). The experimental results are summarized in Table I. Since the relative reactivities of benzene-*t*, toluene-2-*t* and mesitylene-2-*t* are known (6), the rates were converted to the relative tritium exchange reactivities in Table II.

These structures are so closely related to triptycene it seems reasonable to assume that the reaction mechanism for base-catalyzed exchange is the same in this series, although we note that the primary isotope effect, $k_D/k_T = 1.5$ for III, is somewhat lower than the value 2.2 found for triptycene (1). We further assume that the hybridization of the bridgehead C-H is the same as in triptycene and that the only important effect on rate is the difference in inductive effects. The experimental results agree qualitatively with such a view. Addition of more electron-attracting aromatic carbons as in II gives a rate increase. In fact, the rate increase of 2-fold for the change I → II is comparable to the 1.7-fold increase for the comparable change of *aromatic* C-H's, 1-naphthalene → 1-anthracene (7). III-*t* is less reactive than I-*t* as expected from the removal of four π-carbons.

The inductive effect was treated quantitatively with the $\Sigma\, 1/r$ function, in which r is the distance between the acidic carbon and each π-carbon in the system. To calculate the effect on rate with no new parameters we use the slope of the linear correlation established previously for polycyclic aryl hydrogens (7):

TABLE I

Kinetic Results with CsCHA/CHA at 25.0° ± 0.05°

Run	Compound	[RH] m/l	[CsCHA] m/l	$10^5\ k_T$[a] sec^{-1}
GRZ357	II-*t*	0.0016	~ 0.012	54.7 ± 1.6
	Benzene-*t*	.083		111 ± 6
MJM279	Toluene-2-*t*	.098	.027	16.5 ± 0.4
	III-*d*,*t*	.0032		3.70 ± 0.21[b]
MJM397	Mesitylene-2-*t*	.051	.049	4.38 ± 0.15
	IV-*t*	.0029		0.107 ± 0.012

(a) Pseudo first order rate constant.

(b) k_D = 5.38 ± 0.12.

TABLE II

Relative Rates and Σ 1/r Correlation

Compound	Rel. Rate	$\Sigma\ 1/r$, Å^{-1}	Calcd Rel. Rate
Benzene-*t*	4.2	2.66	
Triptycene-9-*t*	1	6.66	(1)
II-*t*	2.0	7.35	2.7
III-*t*	0.20	5.52	0.19
IV-*t*	0.0013	4.44	0.041

$$d \log k = 0.624\ d(\Sigma\ 1/r) \qquad \text{eq. 1}$$

Calculated values for Σ 1/r using reasonable geometries based on the known geometry of triptycenes (8) are summarized in Table II together with the predicted rates relative to triptycene derived from eq. 1. The agreement for the addition or removal of a benzo-group is remarkably good, considering the different character of a triptycyl anion compared to an aryl anion and the drastic approximations inherent in the simple Σ 1/r treatment. This simple field effect approach appears to be generally useful in evaluating the effect of a distant sp^2 carbon on an in-plane lone pair.

For IV, however, in which we have a saturated ethano-bridge, the experimental rate is much lower than that calculated. In this case an additional factor must be operating; this factor is undoubtedly in the σ-bond system, inasmuch as the $\Sigma\, 1/r$ treatment appears to account satisfactorily for the π-system. The $C_{methylene}$-$C_{bridgehead}$ bond in this case is approximately C_{sp^3}-$C_{bridgehead}$ and is effectively electron-donating and carbanion-destabilizing compared to the C_{sp^2}-$C_{bridgehead}$ bond present in the other systems. According to this analysis, such a σ-bonding difference is equivalent to 1.5 powers of ten in reactivity in the present exchange reaction.

Acknowledgement. This research was supported in part by grant GM-12855 of the National Institutes of Health, U.S. Public Health Service. We also thank the National Science Foundation and the National Institutes of Health for predoctoral fellowships to M. J. Maskornick, 1965-68, and to G. R. Ziegler, 1964-66, respectively.

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