

ACIDITY OF HYDROCARBONS. XXXVI. KINETIC ACIDITY OF [2.2]-PARACYCLOPHANE.

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Both types of hydrogen in [2.2]-paracyclophane (PC) present unusual features that lend interest to a study of hydrocarbon acidities. The aryl hydrogens are present in a benzene ring known to be bent (1) and the benzylic position has seriously impaired conjugation with the aromatic rings. The kinetic acidities of these hydrogens were determined in our usual manner (2) by tritium exchange with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA). In the first run, incorporation of tritium from CHA-N-*t* gave a rate 0.53 that of benzene for one set of PC hydrogens (Table I). The second set exchanged too slowly for measurement in this way. In order to determine which set had the reactivity measured and to establish the relative reactivity of the slow set, the two specifically tritiated hydrocarbons were prepared as follows for protodetritiation studies.

[2.2]-Paracyclophane-4-*t* (PC-4-*t*) was prepared by metalating 4-bromo-[2.2]-paracyclophane (3) with butyllithium in ether at 0° and quenching with tritiated water. [2.2]-Paracyclophane-1-*t* (PC-1-*t*) was prepared from toluene- α -*t* and the synthesis of Winberg, et al. (4): *p*-chloromethyltoluene- α -*t* from the reaction with zinc chloride and formaldehyde was converted with trimethylamine to the quaternary salt which with aqueous sodium hydroxide gave the tritiated cyclophane (5). The exchange rates with CsCHA are summarized in Table I.

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TABLE I
CsCHA Exchange of [2.2]-Paracyclophane at 25°

Run no.	Hydrocarbon R-T	Concn. M	[CsCHA] M	$10^5 k_T$ sec ⁻¹	k_T/k_{PhT}
395	Benzene ^a	0.103	~0.006	171	0.53
	PC	.0018		90	
433	Benzene- <i>t</i>	.27	.023	69	0.45
	PC-4- <i>t</i>	.0024		31	
479	Mesitylene-2- <i>t</i>	.10	.081	5.1	0.0062 ^b
	PC-1- <i>t</i>	.0024		2.4	

- (a) A tritiodeprotonation run using cyclohexylamine-N-*t*. Only the rate of the more reactive position in PC was determined. This run also contained norbornene.
- (b) The relative reactivities of mesitylene-2-*t* and benzene-*t* are reported in reference 6.

Note that the more reactive set are the aryl hydrogens which are about 0.5 as reactive as in benzene. The inductive effect of the methylene bridges can be modeled approximately by using partial rate factors derived from the reactivities of aryl hydrogens in toluene (6) -- this leads to a relative rate of ~0.1. The second benzene ring is expected to provide a rate-enhancing inductive effect although the magnitude is difficult to estimate because of the shielding effect of π -electrons. However, the magnitude is surely not large-- note that the 2-position in triptycene, in which similar effects can operate, is only 2.8 times as reactive as benzene (2b). Thus, the observed reactivity is not far from that expected by these effects. There is but little that can be attributed to any changes in s-character of the C-H bond or to conjugation with the bent ring as was found in 1,6-methanocyclodecapentaene (7).

The benzylic positions in PC are far less reactive than normal, as is to be expected from their rather extreme geometry. Nevertheless, the reactivity of 6.2×10^{-3} benzene or 6×10^{-5} α -toluene (8) is substantially greater than that expected for normal alkane hydrogens; this reactivity is 5.6×10^5 that of

the saturated hydrogens in cyclohexane (9). From the reactivity of the bridge-head position of triptycene (2b), each benzene ring in the α -position has a rate-enhancing inductive effect of about 1.5 powers of ten; hence, we may estimate the effect in the β -position to be about 0.5 log units. Thus, the two benzene rings in PC would provide a total inductive enhancement of about 2 powers of ten; the remaining 3.7 powers of ten enhancement of PC over cyclohexane is then to be attributed to some other factor. One such factor is an enhanced s-character in the benzylic C-H bond; however, the $J_{13\text{C-H}}$ value of 129.7 Hz (10) of the methylene C-H corresponds to a rate enhancement of 0.8 log units. The remaining enhancement of almost 3 powers of ten is then attributed to conjugation with a benzene ring despite the unfavorable geometry; on this basis, conjugation of the PC-1 carbanion in the exchange transition state is about 1/3 as effective as that for toluene.

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