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ORGANOMETALLIC ANALOGUES OF N-CYCLOALKYL BENZAMIDES

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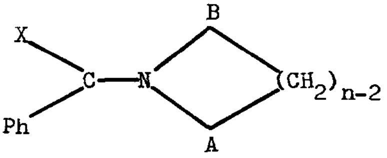
We have prepared a series of benzamide analogues, $Ph\cdot CX\cdot N(CH_2)_n$, ($X = Cr(CO)_5$; n = 2-6), Ia-e (see Table) which are planar in the region of the nitrogen atom. These compounds are sources of carbenoid intermediates and bear a formal relationship to the low temperature forms of some 2,5-bisaminated-1,4-benzoquinones described recently (1). The use of ASIS data and spin decoupling in these rotationally rigid systems provides a specific assignment of the α-CH_2 proton resonances in the n.m.r. spectra of Ia-e recorded at 100MHz (internal TMS) as follows:

TABLE



		A		B		$(CH_2)_{n-2}$		
	n	δ	Δ	δ	Δ	δ	Δ	ν
Ia	2	-266	134	-320	102	-	-	1570
Ib	3	-390	99	-482	72	-239	119	1535
Ic	4	-321	79	-424	44	-204	97	1504
Id	5	-338	70	-444	51	-178	65	1512
Ie	6	-348	55	-437	39	-140	36	1527

δ(Hz) refers to $CDCl_3$ solution. $\Delta \equiv [\delta(C_6D_6) - \delta(CDCl_3)]$(Hz).

Concentration (n.m.r.) = 0.38±0.02 mmole/ml.

$\nu \equiv \nu(C\text{-}N)(cm^{-1})$ recorded in $CHCl_3$ solution.

The effect of ring size (n) upon the magnitude and variation of both δ and Δ for the ring protons is substantial and is in contrast to the results obtained on β-lactams(2). We have also recorded the spectra of some of these compounds in pyridine and in C_6F_6 solution(3). In Ic, for example, $[\delta(C_6D_6) - \delta(C_6F_6)]$ has the values 109, 71 and 126 Hz respectively, for the ring proton multiplets. The inertness and the absence of hydrogen make C_6F_6 a useful alternative to $CDCl_3$ for n.m.r.

The variation of ν with n indicates that the contribution of X, via (d→p)π bonding, to the C-N linkage is variable and may be contrary to the donor action of the nitrogen. The infrared and n.m.r. results together are best interpreted in terms of conformational effects rather than some index of basicity. This interpretation has been applied to the free amines $HN(CH_2)_n$ in which, however, the nitrogen atom may be free to invert(4).

Whereas the compounds Ia-d are all formed rapidly and almost quantitatively in the reaction between Ph·CX·OEt,II, and the amine $HN(CH_2)_n$,(n=2-5), in ether solution under anaerobic conditions(5), the reaction between II and $HN(CH_2)_6$,III, proceeds slowly under identical conditions to give Ie and both cis and trans isomers of $Ph{\cdot}CX{\cdot}NHC_6H_{13}$,IV, which were prepared unambiguously from n-hexylamine and II. The ratio Ie:IV at equilibrium is approximately 1:2. Minor products of the reaction are [III·X] and $Ph{\cdot}CX{\cdot}NC_6H_{12}O$, which latter is still under investigation. The formation of IV from Ie is the first example of this type of homogeneous hydrogenolysis involving a saturated heterocyclic compound. Molecular models suggest that the origin of this process may be an unfavourable interaction between the α-CH_2 groups and the group X in certain orientations of the heterocyclic ring of Ie.

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