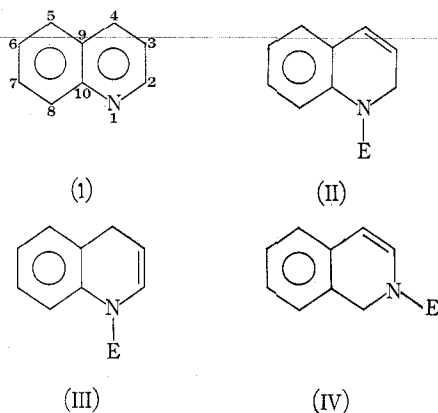


SHORT COMMUNICATIONS

MECHANISM OF ELECTROPHILIC SUBSTITUTION IN QUINOLINE AND ISOQUINOLINE*

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Recently, several mechanisms (Dewar and Maitlis 1957; Brown 1958; Brown and Harcourt 1959; Eisch 1959) have been proposed to account for the predominant substitution of quinoline (I) at the 3-position by certain electrophils. Some of these involved the initial formation of either 1,2-dihydroquinoline (Dewar and Maitlis 1957) or 1,4-dihydroquinoline (Eisch 1959) systems (II) and (III). These in turn were postulated to be attacked by the electrophil at the carbon atom of greatest π -electron density. A Hückel molecular orbital treatment (Brown and Harcourt 1959) suggested that system (III) rather than (II) or (I) was the substrate attacked by the electrophil since only for (III)



was the π -electron density greatest at the 3-position for what were considered to be physically reasonable values of the hetero-atom and auxiliary inductive parameters (h and h'). These were $h=2$, $h'=0.2$, and were based on considerations of both the simple Hückel (Brown and Coller 1959) and the more elaborate VESCF studies (Brown and Heffernan 1959*a*, 1959*b*) of secondary nitrogen heterocycles. For these parameters (and a wide range of others) the π -electron densities of (II) were greatest at the 6- and 8-positions rather than the 3-position.

We have now carried out the more elaborate VESCF calculations, which do not depend on arbitrary choices of hamiltonian matrix elements, on the above intermediates (II) and (III), and on the 1,2-dihydroisoquinolinium system (IV)

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TABLE 1
 ELECTRON DENSITIES

	1,2-Dihydroquinoline		1,4-Dihydroquinoline		1,2-Dihydroisoquinoline	
	Hückel $h=2, h'=0.2$	VESCF <i>BJ</i>	Hückel $h=2, h'=0.2$	VESCF <i>BJ</i>	Hückel $h=2, h'=0.2$	VESCF <i>BJ</i>
1	1.902	1.883	1.807	1.814		
2			1.007	1.022	1.879	1.868
3	1.020	1.026	1.098	1.073	0.976	0.998
4	0.997	1.000			1.095	1.082
5	1.000	1.004	0.999	1.003	1.019	1.010
6	1.024	1.021	1.022	1.017	1.000	1.003
7	0.997	1.004	0.999	1.005	1.017	1.012
8	1.033	1.040	1.026	1.036	1.000	1.006
9	1.027	1.037	1.026	1.029	0.994	0.997
10	0.999	0.986	1.015	1.001	1.019	1.023

which has also been postulated as an intermediate to account for certain electrophilic substitutions at the 4-position of isoquinoline (Brown and Harcourt 1960). The charge distributions thus obtained (Table 1) show very good agreement indeed with those obtained from the above Hückel calculations thus providing further support for the above choice of h and h' for the secondary nitrogen atoms, that is, that they reproduce the VESCF charges reasonably well. The VESCF method used has been referred to as procedure *BJ* in earlier calculations (Brown and Heffernan 1959*b*).

Both the Hückel and VESCF charge distributions suggest that of the two postulated addition-substitution mechanisms for quinoline, that involving intermediate (III) is preferable since only for (III) is the charge greatest at the 3-position.

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