

TABLE I  
Analysis, conductance and infrared spectral data (cm<sup>-1</sup>)

Compound	% Cd		% N		% Halogen		$\Lambda_m$ mhos cm <sup>2</sup>	$\nu$ (C≡N)
	Found	Reqd.	Found	Reqd.	Found	Reqd.		
L	..	..	66.22	66.61	..	..	..	2200
[CdL <sub>2</sub> Ci <sub>2</sub> ]	31.58	31.98	31.58	31.86	19.63	20.17	12.0	2180
[CdL <sub>2</sub> Br <sub>2</sub> ]	25.21	25.52	21.24	25.43	35.88	36.29	8.5	2185
[CdL <sub>2</sub> I <sub>2</sub> ]	20.82	21.03	20.64	20.96	47.28	47.50	7.0	2180
[CdL <sub>2</sub> (SCN) <sub>2</sub> ]	28.05	28.34	34.95	35.30	..	..	10.4	2180
[CdL <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	27.36	27.78	34.38	34.60	..	..	5.0	2185
[CdL <sub>2</sub> (Ac) <sub>2</sub> ]	27.83	28.20	27.83	28.10	..	..	8.5	2180
[CdL <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	17.07	17.35	34.28	34.59	..	..	145.6	2180

L = Dicyandiamide.

Dicyandiamide contains primary, secondary and tertiary nitrogen atoms as possible bonding sites to metal ions. The band observed at 2200 cm<sup>-1</sup> in the ligand is attributable to  $\nu$ (C≡N) vibration. In the complexes, this band has been shifted to lower frequency region  $\sim$  2180 cm<sup>-1</sup>, which indirectly supports the bonding of tertiary N-atom of C≡N group to the cadmium ion. The appearance of a strong band at 3200 cm<sup>-1</sup> assignable to  $\nu$ (NH) vibration both in ligand and complexes suggests the non-coordination of -NH group and hence dicyandiamide acts as a monodentate ligand.

From analysis, conductance and IR spectral studies, the compounds are presumably tetra coordinated involving a tetrahedral environment around the metal ion.

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### SURFACE HETEROGENEITY AND ELOVICH EQUATION

GRADIENT changes observed in the treatment of adsorption kinetic data through Elovich equation<sup>1-3</sup>

$$\frac{dq}{dt} = ae^{-aq} \quad (1)$$

where  $q$  is the amount adsorbed in ml NTP at time  $t$  have been the subject of critical examination in recent times and it is concluded that the breaks observed in Elovich plots are due to inherent nature of the mathematical form of the equation<sup>4</sup> and not due to changes in adsorption mechanism at the point at which the change in gradient occurs. The purpose of this communication, is therefore, to analyse the same kinetic data through both Elovich equation and by a procedure<sup>5</sup> which can directly give the values of activation energy for adsorption and desorption simultaneously and to assess how far the gradient changes are due to changes in adsorption mechanism.

Hydrogen chemisorption kinetic data used for such an analysis have been obtained on a ZnO-MeO<sub>3</sub> catalyst (the surface of this catalyst has been shown to be heterogeneous through temperature jump chemisorption of hydrogen<sup>6</sup>) in a conventional volumetric adsorption apparatus by recording the volume uptake  $a$ . a function of time at various temperatures in the range 300 to 360° C.

The procedure used for the evaluation of the values of rate constants for adsorption and desorption processes is based upon the simple theory that the adsorption rate at any fixed value of coverage ( $\theta$ ) is given by

$$\left[ \frac{dq}{dt} \right]_{\theta} = k_a f(1-\theta)p - k_d f(\theta) \quad (2)$$

where  $k_a$  and  $k_d$  are adsorption and desorption rate constants. A plot of  $dq/dt$  at any fixed coverage will

then be a linear function of pressure, the slope and the intercept can be used to evaluate the values of  $k_a$  and  $k_d$ . The values of activation energy for adsorption and desorption at various surface coverages were computed through the Arrhenius equation and are given in Table I. The same kinetic data were analysed through Elovich equation and the corresponding Elovich parameters are given in Table II. The variation of the heat of adsorption (proportional to the difference in the activation energy values) with coverage is shown in Fig. 1. It is seen that the values of  $q_a$ , the value of the volume adsorbed at the point of gradient

TABLE I

Values of activation energy for adsorption and desorption of hydrogen on coprecipitated 1:1 ZnO-MnO<sub>3</sub> catalyst

Volume adsorbed at NTP (ml)	Surface coverage ( $\theta$ )	Values of activation energy in kcal/mole		$(E_d - E_a)$ kcal/mole
		Adsorption ( $E_a$ )	Desorption ( $E_d$ )	
0.25	0.150	57.2	84.7	27.5
0.30	0.179	36.1	61.1	25.0
0.35	0.209	30.9	42.2	11.3
0.40	0.239	38.1	45.8	7.7
0.45	0.269	41.6	50.9	9.3
0.50	0.299	44.1	52.3	8.2

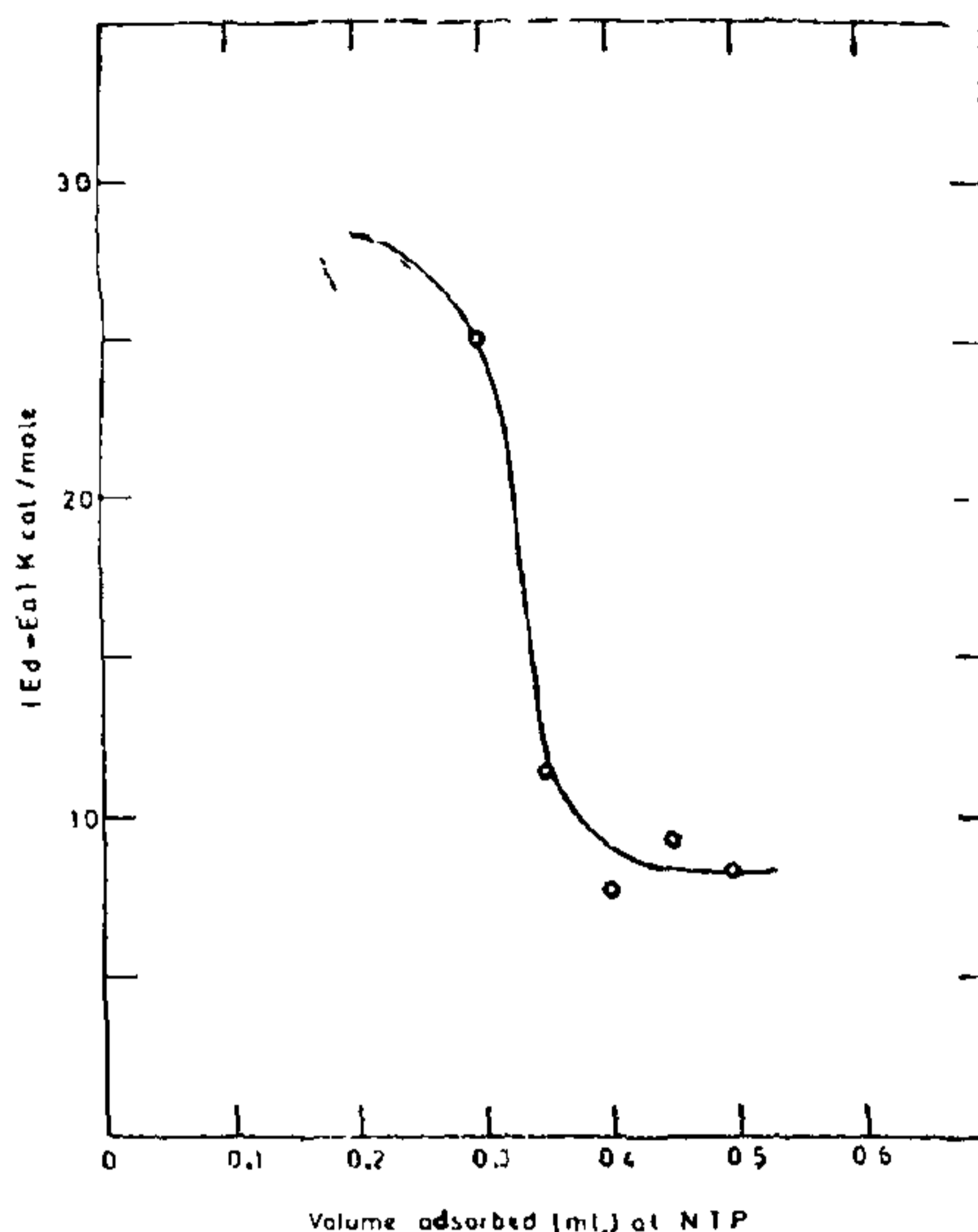


FIG. 1. Variation of the difference in the values of activation energy for adsorption and desorption of hydrogen on ZnO-MnO<sub>3</sub> catalyst as a function of the amount adsorbed.

TABLE II

Values of the Elovich parameters for the chemisorption of hydrogen on ZnO-MnO<sub>3</sub> catalyst

Temp. (C)	Equilibrium pressure (cm)	$a_1$	$t_{01}$	$a_1$	$q_b$	$a_2$	$t_{02}$	$a_2$
300	31.4	43.95	$2.583 \times 10^{-4}$	88.120	0.270	9.4891	3.100	0.03299
	33.2	46.21	$1.854 \times 10^{-4}$	116.700	0.270	4.6714	12.940	0.02714
	42.5	23.11	$2.481 \times 10^{-2}$	1.744	0.310	5.2258	7.050	0.02714
320	24.3	31.39	$1.588 \times 10^{-2}$	2.006	0.217	10.2721	1.476	0.06598
	28.5	23.52	$2.378 \times 10^{-2}$	1.788	0.265	8.2842	1.542	0.07828
	32.7	25.56	$8.193 \times 10^{-3}$	4.775	0.290	6.2395	2.341	0.06844
	42.5	17.03	$1.416 \times 10^{-2}$	4.146	0.427	4.7563	2.734	0.07692
340	22.7	18.66	$4.351 \times 10^{-2}$	1.232	0.282	9.0137	0.661	0.1678
	26.2	18.16	$7.868 \times 10^{-2}$	0.699	0.250	7.0364	1.392	0.1020
	29.5	17.33	$3.718 \times 10^{-2}$	1.552	0.300	8.5170	0.503	0.2332
	33.4	11.39	$1.025 \times 10^{-1}$	0.857	0.398	6.0477	0.914	0.1810
360	21.8	18.28	$3.727 \times 10^{-2}$	1.468	0.400	4.8668	8.919	0.0230
	23.7	17.39	$3.086 \times 10^{-2}$	1.863	0.364	8.1550	0.920	0.1332
	26.4	19.72	$1.012 \times 10^{-2}$	5.012	0.370	7.4386	0.964	0.1395
	33.6	22.08	$2.578 \times 10^{-3}$	17.560	0.387	5.4073	1.603	0.154

$a_1, a_1, t_{01}$  and  $a_2, a_2, t_{02}$  refer to values of Elovich parameters in the two segments of Elovich plot respectively.  $q_b$  — the amount of hydrogen adsorbed in ml NTP at the point of break in the Elovich Plot.

change in the Elovich plot [ $q$  vs  $\log t$ ] lie in the range 0.25 to 0.40 ml. From Fig. 1 it is clear that there is a sharp decrease in the value of  $(E_d - E_a)$  value in this range. After this range, the value of  $(E_d - E_a)$  remains almost constant with coverage showing that a set of sites of low energy content is involved in the adsorption process, while in the initial stages the process involves sites of high energy content thus giving rise to high heat of adsorption. It appears, therefore, that the gradient changes in Elovich plots are denoting the changes in the adsorption mechanism and the sites involved in the adsorption process.

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### N-DEBENZYLYATION OF BENZIMIDAZOLE DERIVATIVES

A NUMBER of reagents such as Na in liq.  $\text{NH}_3$ ,  $\text{H}_2/\text{pd-C}$ ,  $\text{AcOH}/\text{PtO}_2$ , Raney nickel,  $\text{HBr}$ , con.  $\text{H}_2\text{SO}_4$ , etc., have been used for N-debenzylation<sup>1-4</sup>. In view of the elaborate procedures required for the above methods it was considered desirable to explore simpler methods for debenzylation. For this purpose the pyrolysis of 1-benzyl-2-phenylbenzimidazole (I,  $\text{R}=\text{Ph}$ ,  $\text{X}=\text{H}$ ) was undertaken. Its pyrolysis at temperatures above  $330^\circ$  gave 2-phenylbenzimidazole (II,  $\text{R}=\text{Ph}$ ,  $\text{X}=\text{H}$ ) in 56% yield. However, on pyrolysis of I ( $\text{R}=\text{Ph}$ ,  $\text{X}=\text{H}$ ) in refluxing diphenylether (b.p.  $258^\circ\text{C}$ ) in the presence of benzoyl peroxide the starting material was recovered unchanged indicating that cleavage of the N-C bond is not proceeding through a free radical mechanism. Heating I ( $\text{R}=\text{Ph}$ ,  $\text{X}=\text{H}$ ) in the presence of catalytic amounts of  $\text{I}_2$  to  $250^\circ$  or refluxing in diphenylether resulted in the formation of 2-phenylbenzimidazole in about 67% yield. 1-Benzyl and 1-benzyl-2-methylbenzimidazoles (I,  $\text{X}=\text{H}$ ,  $\text{R}=\text{H}$  and  $\text{CH}_3$ ) were also found to undergo debenzylation under similar conditions. In the case of the former, in addition to the product of debenzylation, a significant amount of benzimidazolone (III,  $\text{X}=\text{H}$ ) was obtained.

Formation of corresponding benzimidazolones in addition to debenzylation products was also observed on refluxing 1-benzyl-5-methyl and 1-benzyl-5-chlorobenzimidazole (I,  $\text{R}=\text{H}$ ,  $\text{X}=\text{CH}_3$  and  $\text{Cl}$ ). Formation of benzimidazolones appears to be the main side reaction in the debenzylation of N-benzylbenzimidazoles unsubstituted in 2 position.

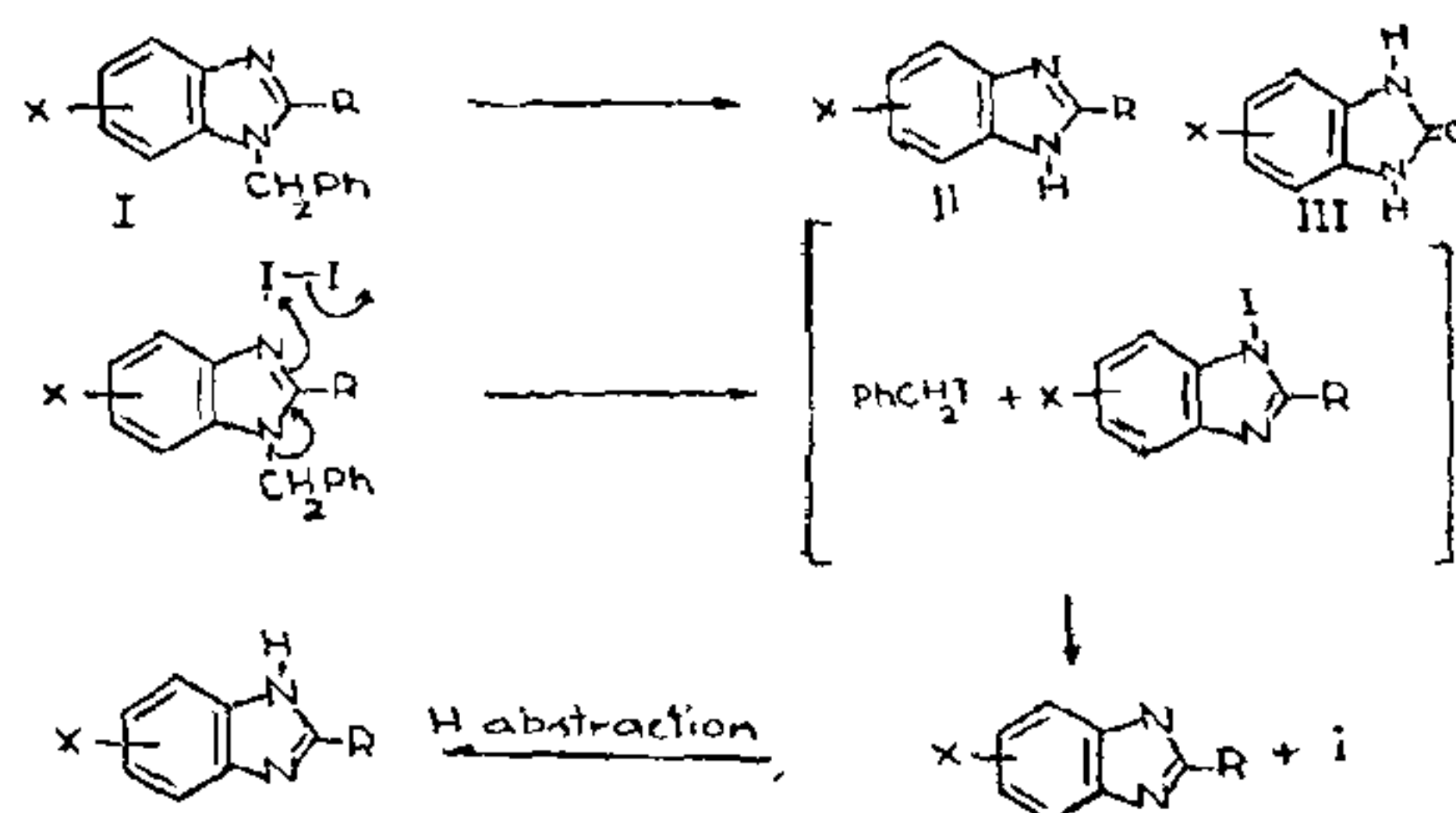


CHART I

However, refluxing 1-benzylbenzimidazole and its 5-methyl and 5-chloro analogues in decalin for 5 h in the presence of  $\text{I}_2$  resulted in the exclusive formation of corresponding debenzylation products. The generality of the iodine catalysed debenzylation in refluxing decalin has been established by the formation of a number of N-H free benzimidazoles in satisfactory yields (Table I) from the corresponding 1-benzylbenzimidazoles. The products of debenzylation have been characterised by comparison with authentic samples<sup>5-10</sup>. The probable mechanism of debenzylation is shown in the chart.

TABLE I  
% Yield of products of debenzylation of (I) by  $\text{I}_2$  in boiling decalin

Sl. No.	1-Benzylbenzimidazole (I)		Debenzylation Product (II)	
	R	X	M.P. °C	Yield%
1.	Ph	H	290 <sup>5</sup>	89
2.	CH <sub>3</sub>	H	176 <sup>6</sup>	70
3.	H	H	170 <sup>6</sup>	70.5
4.	Ph	CH <sub>3</sub>	240 <sup>7</sup>	91
5.	CH <sub>3</sub>	CH <sub>3</sub>	203 <sup>8</sup>	80.8
6.	H	CH <sub>3</sub>	114 <sup>9</sup>	75
7.	Ph	Cl	210 <sup>7</sup>	71
8.	CH <sub>3</sub>	Cl	203 <sup>9</sup>	65
9.	H	Cl	126 <sup>10</sup>	40

Attempts to debenzylate 1-benzyl, 1-benzyl-2-methyl, 1-benzyl-2-phenyl-5-nitrobenzimidazoles (I,  $\text{X}=\text{NO}_2$ ,  $\text{R}=\text{H}$ ,  $\text{CH}_3$  and  $\text{Ph}$ ) by iodine in boiling decalin were unsuccessful. This might perhaps be due to the lower basic strength of the tertiary nitrogen in these benzi-