

reciprocal plots of k_0^{-1} or k_{ψ}^{-1} vs $[\text{acetone}]^{-1}$ have been found to be linear with intercept on the ordinate indicating that both the uncatalyzed and micellar-catalyzed oxidations proceed via complex formation obeying Michaelis-Menten kinetics. The rate law is therefore of the form,

$$\frac{1}{k_0} \text{ or } \frac{1}{k_{\psi}} = \frac{1}{k_t} + \frac{1}{k_t K [\text{acetone}]}$$

The values of k_t and K have been evaluated from the intercept and slope of the Michaelis-Menten plots. The value of k_t is found to be $4.7 \times 10^{-4} \text{ s}^{-1}$ for the uncatalyzed as well as the micellar reaction. But K is found to be greater for the micellar reaction, $K = 2.1 \text{ mol}^{-1} \text{ dm}^3$ for the uncatalyzed Ce(IV)-acetone reaction and $K = 2.7 \text{ mol}^{-1} \text{ dm}^3$ for the micellar-catalyzed oxidation. These data show clearly that the rate acceleration is due to an increase in equilibrium constant for complex formation, i.e., the stability of Ce(IV)-acetone complex is increased, in presence of micelles.

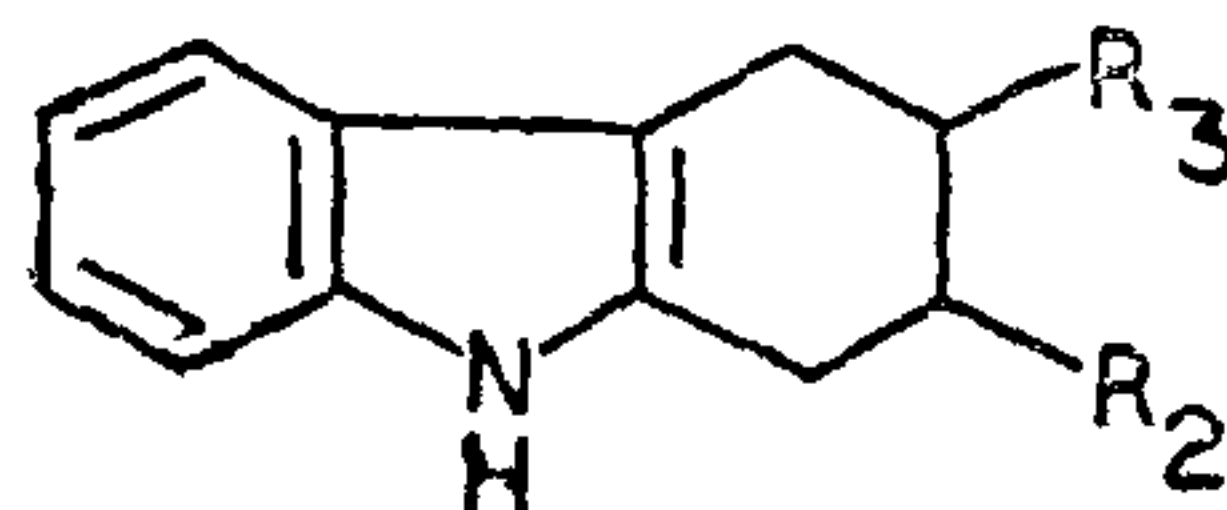
Department of Physical Chemistry,
University of Madras,
A.C. College Campus,
Madras 600 025, July 27, 1979.

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SOME NEW BIS-TETRAHYDROCARBAZOLYL METHANE DERIVATIVES AND THEIR ANTIMICROBIAL PROPERTIES WITH RESPECT TO THOSE OF THE CORRESPONDING TETRAHYDROCARBAZOLES

PREVIOUS report reveals that the condensation of carbazole with formaldehyde takes place at 9-position rather than 3-position, if the 9-position remains unblocked¹. On this ground we prepared three new bis-tetrahydrocarbazolyl methane derivatives (IV, V and VI) from the corresponding tetrahydrocarbazole derivatives (I, II and III)².

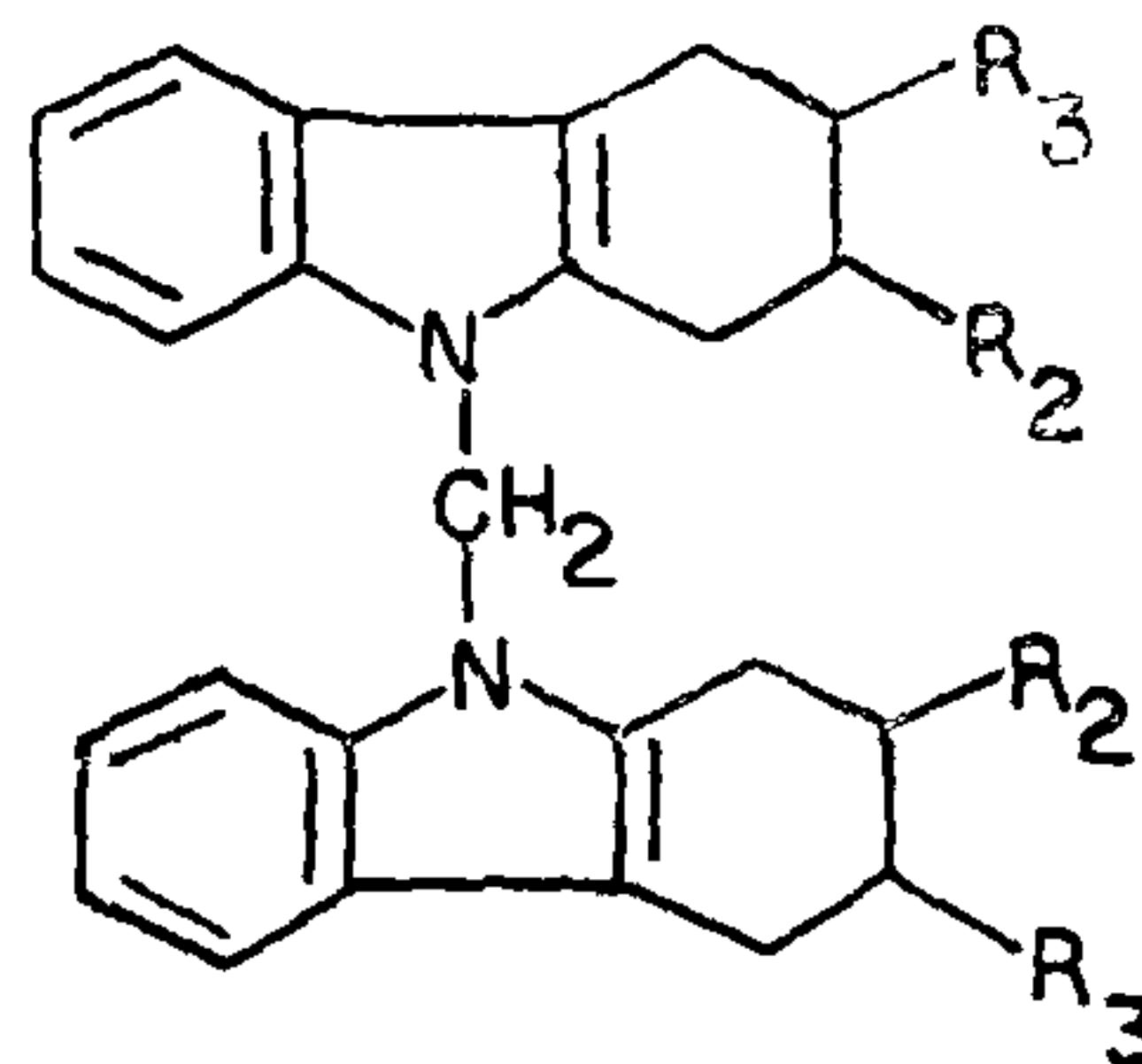
Recent comparative studies of the pesticidal properties of some tetrahydrocarbazole derivatives along with carbazoles show that due to the presence of partially reduced moiety the pesticidal properties of tetrahydrocarbazoles are enhanced². Now we report the studies of the antimicrobial properties of three new bis-tetrahydrocarbazolyl methane derivatives with those of the corresponding tetrahydrocarbazole derivatives,



(I) $R_2 = R_3 = \text{H}$

(II) $R_2 = \text{CH}_3$, $R_3 = \text{H}$

(III) $R_2 = \text{H}$, $R_3 = \text{CH}_3$



(IV) $R_2 = R_3 = \text{H}$

(V) $R_2 = \text{CH}_3$, $R_3 = \text{H}$

(VI) $R_2 = \text{H}$, $R_3 = \text{CH}_3$

The following procedure was adopted for the preparation of bis-tetrahydrocarbazolyl methane derivatives:

Paraformaldehyde was added to the acetic acid solution of the tetrahydrocarbazole derivative (I, II or III) and boiled for 2-3 minutes. After boiling small amount of 4% concentrated sulphuric acid in acetic acid was added when a precipitate was obtained. The product on crystallisation gave white crystals of bis-tetrahydrocarbazolyl methane derivative (IV, V or VI). Crystallising medium for bis-(9-(1,2,3,4-tetrahydrocarbatolyl)) methane (IV), m.p. 145°C , was cyclohexane, whereas bis-(9-2 methyl, 1,2,3,4-tetrahydrocarbazolyl)-methane (V), m.p. 175°C , and bis-(9-(3-methyl, 1,2,3,4-tetrahydrocarbazolyl)) methane (VI), m.p. 165°C , were crystallised from ethyl acetate and petroleum ether ($40^\circ\text{--}60^\circ \text{C}$) mixture. Compounds (IV, V or VI) are soluble in cyclohexane, benzene, chloroform and ethyl acetate, but very slightly soluble in alcohol. Homogeneity of the compounds were studied by t.l.c.

Analytical data and IR spectral data are presented in Table I.

IR spectra of the compounds (IV, V and VI) show the absence of peak of $-\text{NH}-$ group near about 3400 cm^{-1} , which was present in the spectra of the corresponding tetrahydrocarbazoles (I, II and III).

TABLE I

Compound	m.p.	Analytical data		IR (Wavelength in cm^{-1})
(IV)	145° C	Found :	C 84.60% H 6.91% N 3.55%	2930, 1610, 1455, 730
		Calculated for $\text{C}_{26}\text{H}_{26}\text{N}_2$:	C 84.74% H 7.34% N 7.9%	
(I)	118° C			3420, 1620, 1470, 740
(V)	175° C	Found :	C 84.47% H 8.25% N 6.85%	2920, 1610, 1450, 730
		Calculated for $\text{C}_{27}\text{H}_{30}\text{N}_2$:	C 84.81% N 7.85% N 7.32%	
(II)	114° C			3350, 1610, 1470, 757
(VI)	165° C	Found :	C 84.30% H 8.33% N 6.88%	2920, 1610, 1455, 730
		Calculated for $\text{C}_{27}\text{H}_{30}\text{N}_2$:	C 84.81% H 7.85% N 7.32%	
(III)	111° C			3400, 1640, 1445, 730

Moreover, the band at 2920, or 2930 cm^{-1} of IV, V and VI show the presence of >N-CH-N< , which is absent in I, II and III. So it is evident that the condensation takes place at the 9-position of the tetrahydrocarbazoles and not at the 3-position.

The N.M.R. spectra (90 Mz in CDCl_3) of IV, V and VI also show the absence of $-\text{NH}-$ proton, but the presence of $-\text{CH}_2-$ protons are found at about 5.2δ in all cases. NMR spectra also account for all the 26 protons present in IV and 39 protons present in V or VI. Hence the new bis-(9-tetrahydrocarbazolyl) methane derivatives should be represented by the structures (IV), (V) and (VI).

Studies of the antimicrobial properties of the bis-(9-tetrahydrocarbazolyl) methanes (IV, V and VI) with those of the corresponding tetrahydrocarbazoles

(I, II and III) were carried out by agar disc method. The inhibitory effect of the compounds were studied *in vitro* against the following microbes :

(a) *Microsporum gypseum*, (b) *Candida albicans*, (c) *Epidermophyton floccosum*, (d) *Trichophyton rubrum*, (e) *Alternaria solani*, (f) *Aspergillus niger*, (g) *Helminthosporium sativum*, (h) *Curvularia lunata*, (i) *Escherichia coli* and (j) *Staphylococcus aureus*.

The agar medium was first inoculated with a 24 hours old culture of the test-organism. Filter paper discs, after proper saturation with the solution of the bis-(9-tetrahydrocarbazolyl) methane derivatives (IV, V or VI) at the concentration of 1 mg/ml in benzene, were placed on the agar plate. Similar experiments were performed with the tetrahydrocarbazole derivatives (I, II and III). Control in benzene was run side by side. The zone of inhibition around the discs

with respect to control were measured after an incubation period of 24 hours at $35 \pm 1^\circ \text{C}$.

The bio-assay clearly shows that the activity of bis-(9-tetrahydrocarbazolyl) methane derivatives (IV, V and VI) is much lower than those of the corresponding tetrahydrocarbazole derivatives (I, II and III).

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Department of Chemistry,
Visva-Bharati,
Santiniketan 731 235,
West Bengal, India,
August 13, 1979.

B. P. DAS.
(Miss) B. CHOUDHURY.

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HYDROTHERMAL SYNTHESIS OF OOLITHS

Introduction

HYDROTHERMAL phase equilibria studies were being carried out in this laboratory in the system $\text{Y}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ using oxalic acid and formic acid as source of CO_2 and H_2O , in the system. During the initial random runs made across the temperature range of $150\text{--}800^\circ \text{C}$ at low pressures (50–500 atmospheres), certain unusual development of oolitic textures were noticed, in addition to the development of several yttrium carbonate hydrates isostructural with natural minerals, when formic acid is used. The intention of the present note is to report for the first time, the synthesis of oololiths under hydrothermal condition and to discuss the probable mechanism of the development of oolitic textures.

Experimental

$\text{Y}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--H}_2\text{O--CO}_2$ system was studied by taking $\text{Y}_2\text{O}_3/\text{Fe}_2\text{O}_3$ in the ratio 3 : 5 and concentrated formic acid as the source of CO_2 and H_2O . About 100 mg of well ground $\text{Y}_2\text{O}_3/\text{Fe}_2\text{O}_3$ mixture is taken in platinum ampoules (5 cm length, 5 mm ID and 2 mm wall thickness). The ampoules are sealed by crimping the open end with 3 jaw chuck and welding with arc welding unit. Leak in the ampoules is checked through extended heating before the experiment and checking the weight after the run. Tuttle type cold seal vessels are used with Tempress Hydrothermal unit HR-IB-4. Runs were conducted for 90–100 hours, and the vessels are quenched after the run, to room temperature before venting out the pressure. The vessels are introduced in the pre-heated furnaces with distilled water as pressure trans-

mitting fluid. The product after the run is washed with hot distilled water and identified by X-ray powder diffraction method (114.6 mm camera with Co K α radiation).

Results and Discussion

Although a large number of experiments are conducted both with oxalic acid and formic acid, we are presently reporting only the results of a few selected experiments with formic acid. The formation of oololiths takes place at 200°C (Table I).

TABLE I
Details of hydrothermal experiments in
 $\text{Y}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--HCOOH}$ system

Temperature ($^\circ \text{C}$)	Pressure (psi)	Product
150	1000	$\text{C}_2\text{H}_2\text{FeO}_4 \cdot 2\text{H}_2\text{O} + \alpha\text{-Fe}_2\text{O}_3 + \text{Y}(\text{HCOO})_3$
200	4500	$\text{FeCO}_3 + \text{Y}(\text{OH})\text{CO}_3\text{--A}$ (Oololiths)
250	500	$\text{Fe}_3\text{O}_4 + \text{Y}(\text{OH})\text{CO}_3\text{--A}$
485	6250	$\text{Fe}_3\text{O}_4 + \text{Y}_2\text{O}_2\text{CO}_3\text{--Type II}$
680	4000	$\text{YFeO}_3 + \text{Fe}_3\text{O}_4$
785	6500	$\text{YFeO}_3 + \text{Fe}_3\text{O}_4$

At 780°C YFeO_3 (orthorhombic) and Fe_3O_4 (magnetite) are the stable phases, while at lower temperatures, Fe_3O_4 and $\text{Y}_2\text{O}_2\text{CO}_3\text{--II}$ (hexagonal) are the stable solids. Experiments below 300°C yield a stable carbonate phase, $\text{Y}(\text{OH})\text{CO}_3\text{--A}$ (orthorhombic) isostructural with natural mineral ancylite along with $\text{FeCO}_3\text{--siderite}$ phase. Good single crystals of these compounds have been obtained. Experiments below 200°C yield $\text{Fe}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Y}(\text{HCOO})_3$ along with $\alpha\text{-Fe}_2\text{O}_3$ as stable phases. In addition to the carbonate phase, unusual, spherical oololiths are also formed. Some of them are loose while some are intimately clustered and joined (Figs. 1 and 2 respectively). Most of the oololiths are found broken into exact hemispheres (Fig. 3). X-ray analysis of the crushed oololiths showed the presence of siderite and ancylite. The core of the oololiths is either of ancylite or of siderite. In certain oololiths upto seven rhythmic layers can be clearly seen with sharp demarcation. Single crystals of ancylite-like phases are found to grow on the external surface of the outermost shell which, invariably, is of ancylite composition. Figure 4 shows a number of hollow broken shells made entirely of ancylite composition. Analysis of the sample was not possible for want of bulk material.