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**ON THE STEREOSELECTIVITY OF STOBBE CONDENSATION WITH ORTHO
SUBSTITUTED AROMATIC ALDEHYDES: THE (E, Z) CONFIGURATION OF
MONOBENZYLIDENESUCCINATES AND DIBENZYLIDENESUCCINIC ANHYDRIDES**

A. S. R. ANJANEYULU, P. RAGHU, K. V. RAMAKRISHNA RAO, CH. V. M. SASTRY,
P. UMASUNDARI and P. SATYANARAYANA
Department of Chemistry, Andhra University, Waltair 530 003, India.

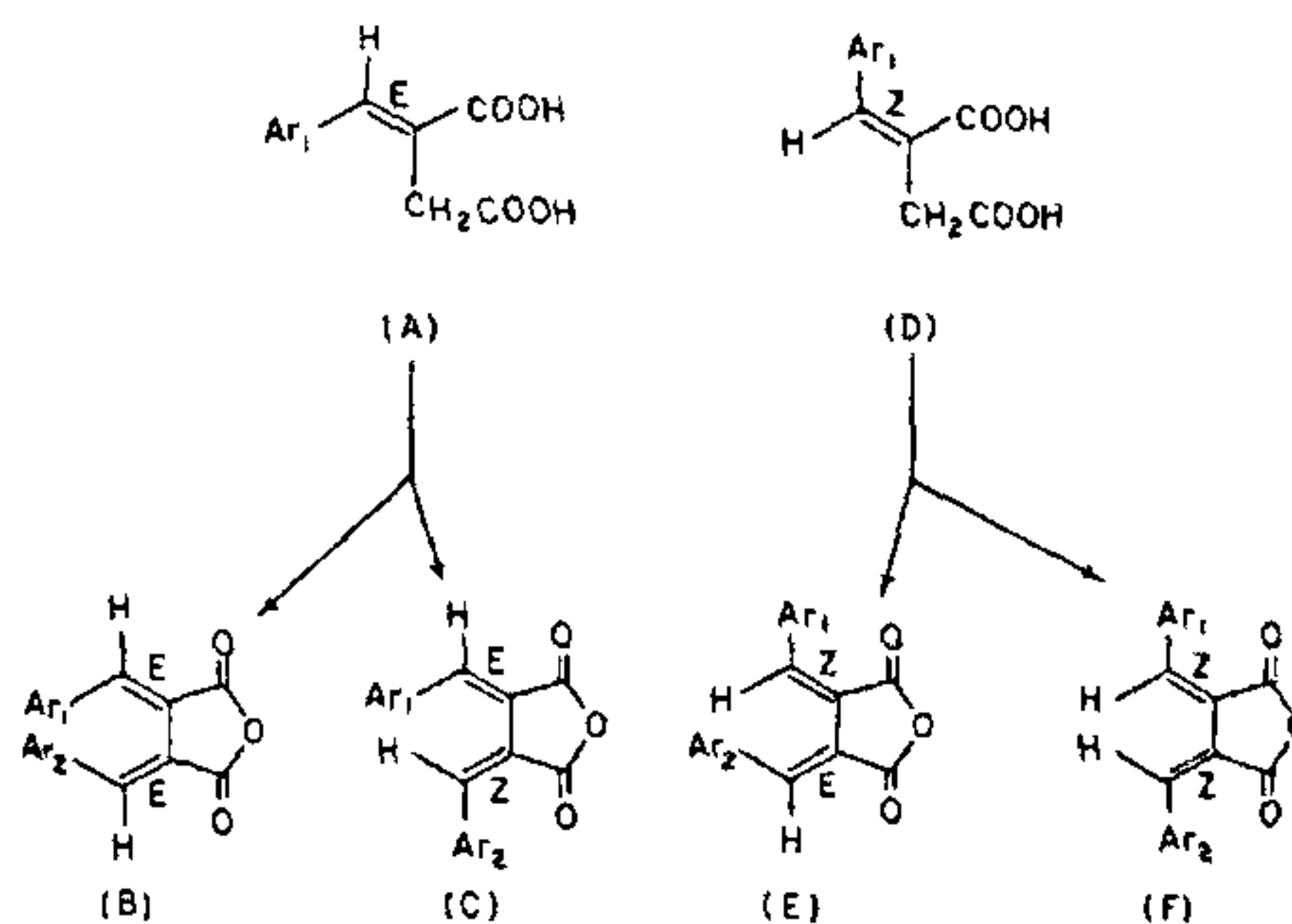
ABSTRACT

The geometrical configuration (E or Z) of several monobenzylidenesuccinates and dibenzylidenesuccinic anhydrides has been established unequivocally by a study of their respective PMR spectra. The Stobbe condensation between mono-ortho substituted or ortho unsubstituted aromatic aldehydes has been found to be stereoselective in giving only the (E)-monobenzylidenesuccinates. The second Stobbe reaction involving the (E)-monobenzylidenesuccinates and ortho monosubstituted or ortho unsubstituted aromatic aldehydes has been found to be stereoselective giving only the (E,E)-derivatives.

STOBBE condensation of aromatic aldehydes with dimethyl succinate in the presence of a base like tertiary butoxide or methoxide gives monobenzylidenesuccinic half-esters¹ or acids². The monobenzylidenesuccinates when subjected to further Stobbe condensation give dibenzylidene half-esters or diacids respectively. The diacids on heating with acetyl chloride give the corresponding anhydrides (V). Theoretically speaking, two geometrical isomers (E or Z) (A or D, chart I) are possible with monobenzylidenesuccinates and from them four isomers (E,E, E,Z, Z,E and Z,Z) (B, C, E, and F) are possible with dibenzylidene derivatives. When the aryl groups are identical ($Ar_1 = Ar_2$), the number of isomers reduces to three ($C \equiv E$).

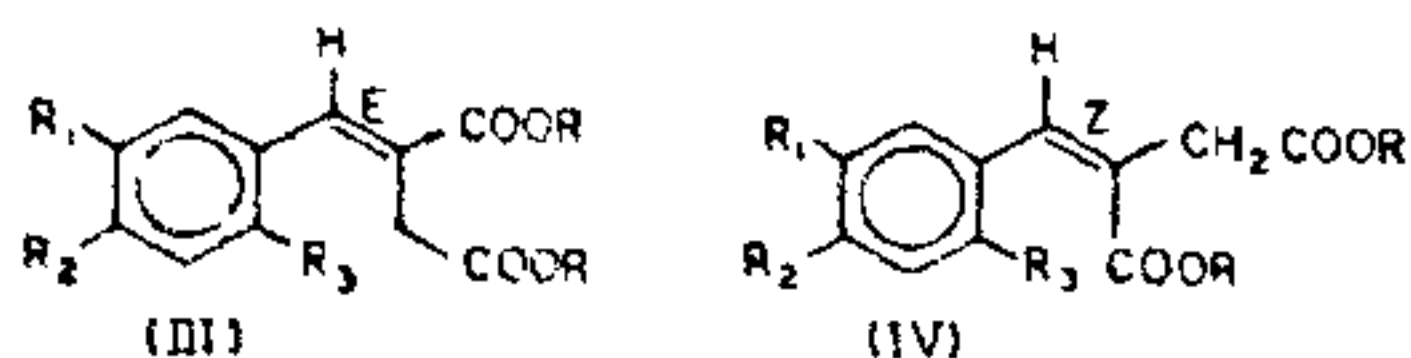
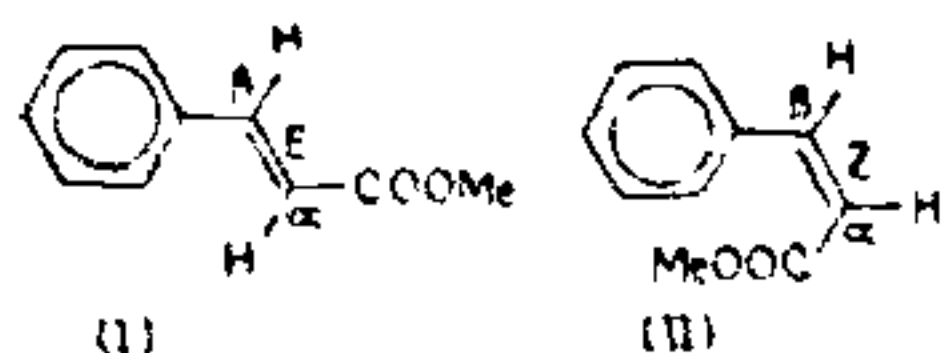
During the course of our investigation, for over some years, on synthetic experiments in lignans³⁻⁹ a number of these mono and di-Stobbe products have been prepared as intermediates. The geometrical configuration of these isomers at the respective double bonds has not been unequivocally established, although assumptions have been made by analogies, occasionally wrongly, in these as well other labora-

Chart I

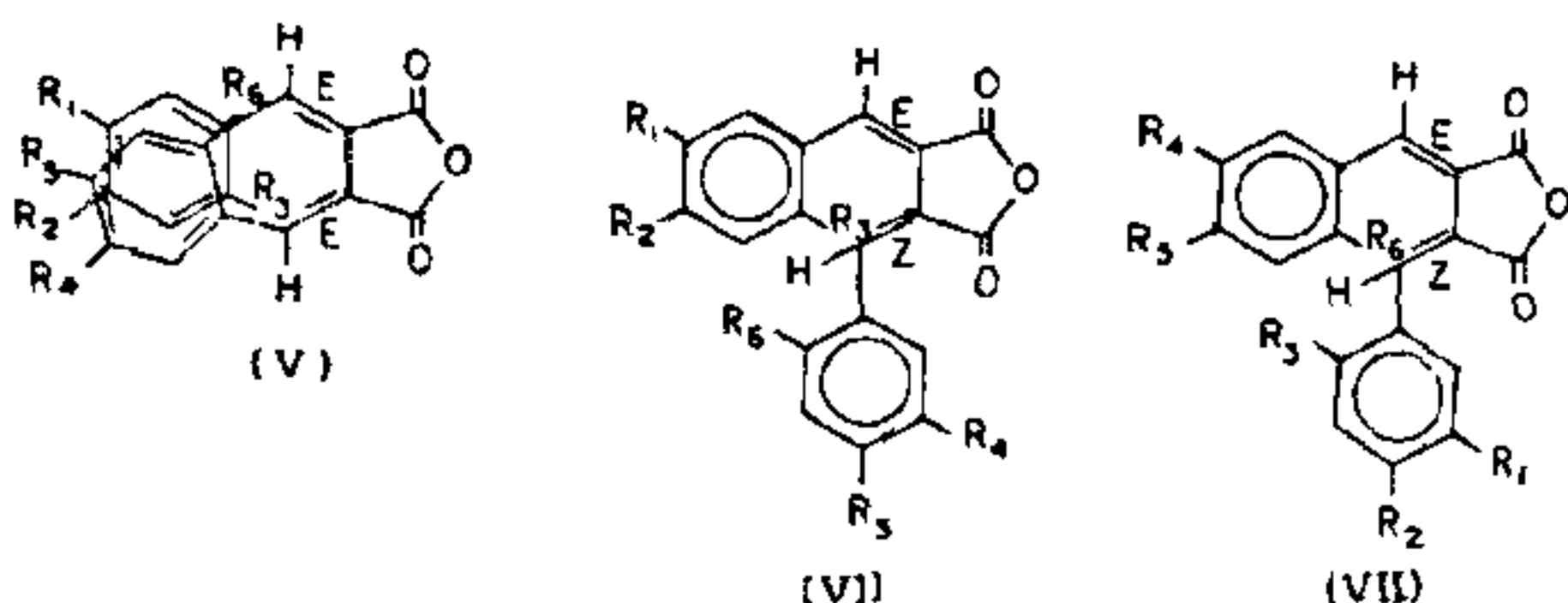


tories^{10-14a, b} on similar derivatives. A detailed study on these derivatives has now been made and the geometrical configuration at the respective double bonds has been established with the help of PMR spectral data and with an understanding on the mechanism of the Stobbe condensation.

Chart II

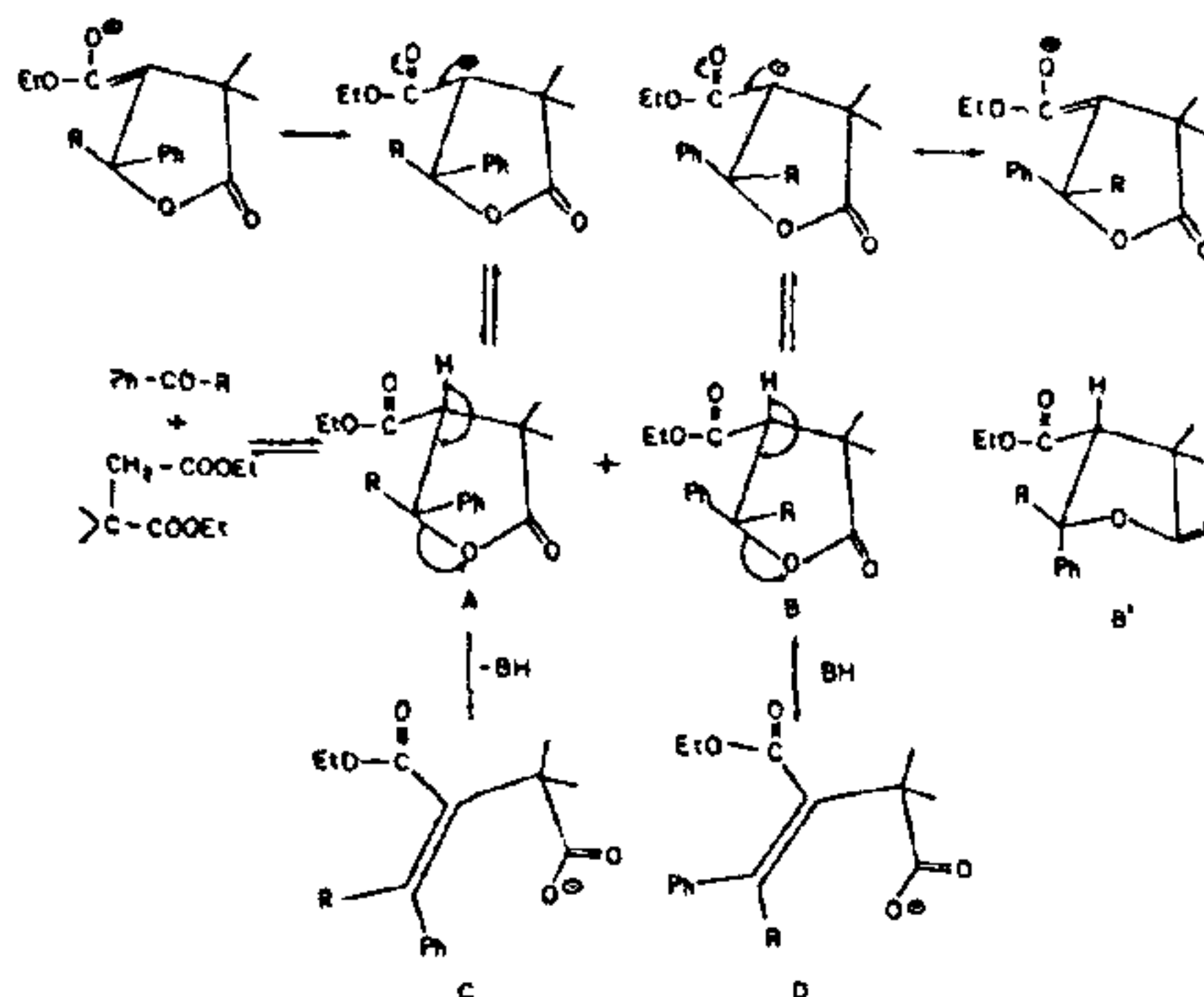


- a $R_1 = R_2 = \text{OMe}$, $R_3 = \text{H}$, $R = \text{Me}$
 b $R_1, R_2 = -\text{OCH}_2\text{O}-$, $R_3 = \text{H}$, $R = \text{Me}$
 c $R_1 = R_2 = R_3 = \text{OMe}$, $R = \text{Me}$
 d $R_1 = R_2 = \text{OMe}$, $R_3 = \text{Br}$, $R = \text{Me}$
 e $R_1, R_2 = -\text{OCH}_2\text{O}-$, $R_3 = \text{Br}$, $R = \text{Et}$



- a $R_1 = R_2 = R_4 = R_5 = \text{OMe}$, $R_3 = R_6 = \text{H}$
 b $R_1, R_2 = R_4, R_5 = -\text{OCH}_2\text{O}-$, $R_3 = R_6 = \text{H}$
 c $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = \text{OMe}$
 d $R_1 = R_2 = \text{OMe}$, $R_4, R_5 = -\text{OCH}_2\text{O}-$, $R_3 = R_6 = \text{H}$
 e $R_1 = R_2 = R_4 = R_5 = R_6 = \text{OMe}$, $R_3 = \text{H}$
 f $R_1 = R_2 = R_4 = R_5 = R_6 = \text{OMe}$, $R_3 = \text{Br}$
 g $R_1 = R_2 = R_4 = R_5 = \text{OMe}$, $R_3 = R_6 = \text{Br}$
 h $R_1, R_2 = R_4, R_5 = -\text{OCH}_2\text{O}-$, $R_3 = R_6 = \text{Br}$

Chart III



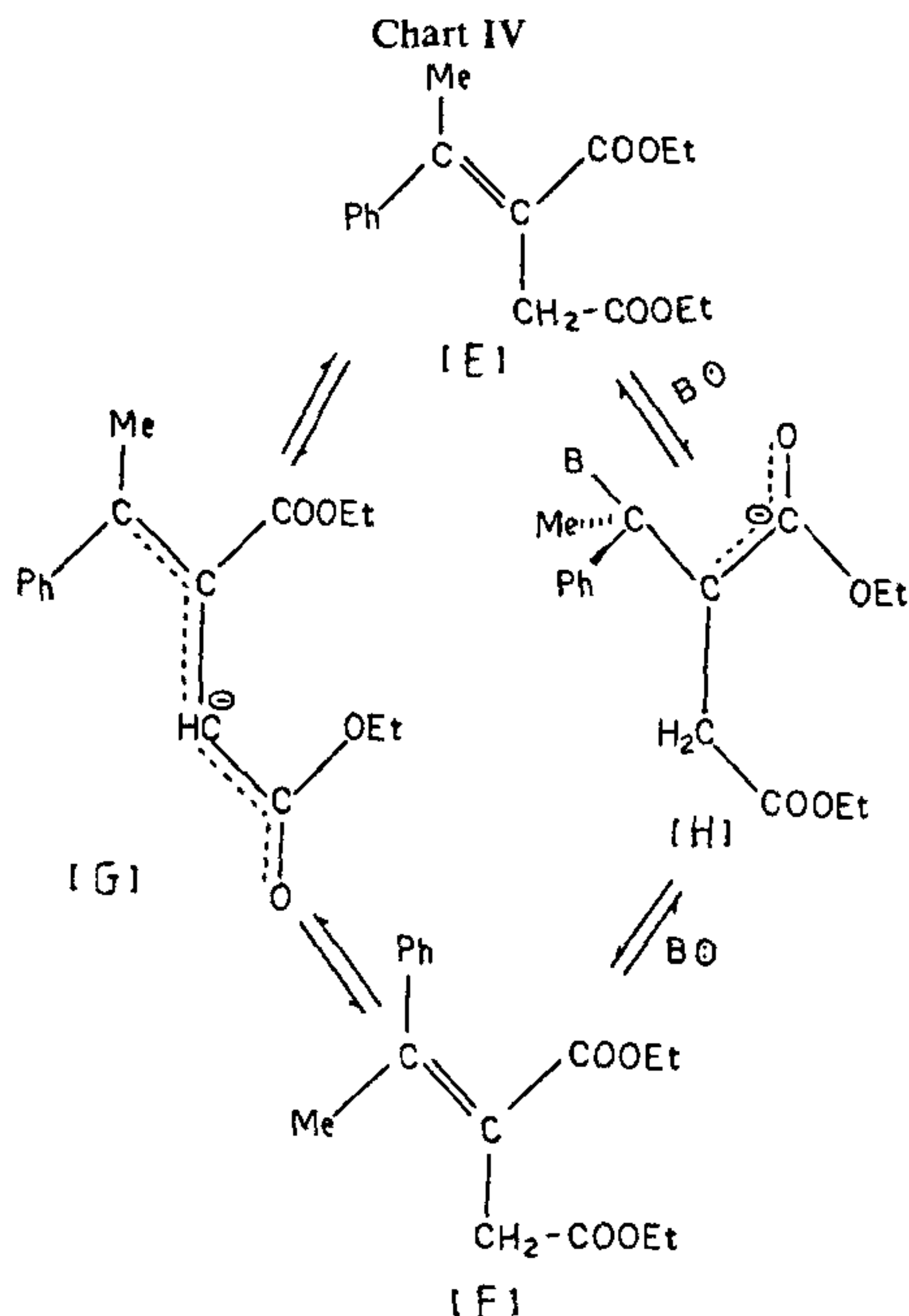
reaction might be expected to yield diastereoisomeric lactones (A and B, $R = \text{H}$) of which only A can adopt the anti-periplanar conformation favoured for E2/E1CB mechanism giving a transition state with no eclipsing effects between the phenyl and ester groups, allowing for maximum overlap of the developing p -orbitals. Lactone B in the analogous conformation gives rise to an unfavourable transition state having steric interactions between the eclipsing phenyl and ester groups, thus preventing coplanarity and overlap of the forming p -orbitals. Conformer B' lacks the necessary transoid arrangement between the parts of the eliminant, thus lactone (B) does not undergo elimination to yield the (Z)-benzylidenesuccinic half-ester anion (D, $R = \text{H}$) but gives back the reactants which can recombine to give the lactone (A) which undergoes eventual elimination yielding only the 'E' isomer.

It was also noticed that the Stobbe condensation of aryl-ketones (C and D, $R = \text{CH}_3$, chart III) will not show that much of stereoselectivity and give a 1:1 mixture of E and Z isomers. The lack of stereoselectivity was also noticed in the case of 2,6-disubstituted aromatic aldehydes¹⁶⁻¹⁸. In the above examples conformer B (Chart III) acquires similar stability as that of A giving rise to mixtures of E and Z isomers.

In the case of aromatic ketones, the Stobbe products formed were found to isomerise under the experimental conditions with equilibration of the E and Z isomers (chart IV) through the succinate anion (G) or by reversible addition elimination of base giving the conjugate base (H). Such $E \rightleftharpoons Z$ isomerisations were however not noticed with the products from simple

The 'E' or 'Z' configuration of the cinnamic acid derivatives (I and II, chart II) or the monobenzylidene succinic acid derivatives (III and IV, chart II) can be distinguished by the chemical shift of the olefinic proton. In the isomers of E configuration (A, Chart I), the olefinic proton (β) which is *cis* to the carboxy carbonyl appears beyond 7.5 ppm, deshielded by about 0.5 to 1 ppm compared to that in the isomers of 'Z' configuration (D, chart I) where the same is *trans* to the carboxy carbonyl^{15, 16}. Similar consideration of the olefinic proton at the other double bond can establish the configuration of the dibenzylidenesuccinic acid derivatives formed^{15, 16} (table 2).

The Stobbe condensation involving simple aromatic aldehydes with no ortho-substituent was stereoselective giving only the E isomer of the monobenzylidene succinic acid derivative. The stereoselectivity noticed was explained by Heller *et al.*^{16, 18} by a mechanism involving 'overlap control' analogous to that proposed by Zimmermann^{19, 20} and to that given by Johnson *et al.*²¹ for Stobbe reaction (chart III). The Stobbe



aromatic aldehydes, probably because of the greater stability of the E isomers.

The PMR spectral data for five monobenzylidene succinates (IIIa to e) have now been obtained and recorded (table 1). From the chemical shifts of the olefinic proton noticed in each case, the monobenzylidene succinates were confirmed to have the E configuration. The formation of Stobbe products in quantitative yields establish the stereoselectivity of the reaction and also rule out the $E \rightleftharpoons Z$ isomerisation during the reaction. It may be remarked here that the aldehydes used in examples (IIIc to e) are ortho-substituted, in one (IIIc), a methoxyl and in the other two (III d and e), bromine atoms.

The Stobbe reaction involving aromatic aldehydes with single ortho-substituent has thus been found to be stereoselective as much as with ortho-unsubstituted aldehydes and unlike ortho-disubstituted aromatic aldehydes, where the formation of E and Z isomers were noticed¹⁶⁻¹⁸.

The PMR spectral data of dibenzylidene succinic anhydrides (Va to h) obtained in our course of study have been recorded in table 2. From the chemical shifts of the two olefinic protons the configuration of the two double bonds in each case was E,E only (V). Further, it is significant to note that the two protons appeared as a single peak, understandably, in cases (Va, b, c, g and h)

Table 1 PMR values of monobenzylidene succinates

Compound	—CH ₂ —	Methoxyls	Methylene-dioxy	Aromatic	Olefinic (β -H)	Ref.
I	—	—	—	—	7.69 (d, J = 16 Hz)	16
II	—	—	—	—	6.93 (d, J = 12 Hz)	15
IIIa(E) (Previous)	—	—	—	—	7.82, s	15
IV(Z) (Previous)	—	—	—	—	6.76 (merged t.) (J = 1 Hz)	15
IIIa (Present)	3.44(s, 2H)	3.63(s, 3H) 3.74(s, 6H) 3.77(s, 3H)	—	6.74–6.83 (m, 3H)	7.65(s, 1H)	
IIIb	3.48(s, 2H)	3.69(s, 3H) 3.77(s, 3H)	5.92(s, 2H)	6.75(s, 3H)	7.70(s, 1H)	
IIIc	3.50(s, 2H)	3.69(s, 3H) 3.79(s, 9H) 3.88(s, 3H)	—	6.48(s, 1H) 6.88(s, 1H)	7.92(s, 1H)	
III d	3.36(s, 2H)	3.67(s, 3H) 3.74(s, 3H) 3.78(s, 3H) 4.02(s, 3H)	—	6.95(s, 1H) 6.92(s, 1H)	7.79(s, 1H)	
IIIe	3.22(s, 2H)	1.28t(—OCH ₂ CH ₃) 4.15q(—OCH ₂ CH ₃)	5.90 (s, 2H)	6.78(s, 1H) 6.94(s, 1H)	7.58(s, 1H)	

Table 2 PMR values of the dibenzylidenesuccinic anhydrides

Compound	Methoxyls	Methylenedioxy	Aromatic	Olefinic
Va	3.50 (s, 6H) 3.80 (s, 6H)	—	6.41–6.65 (6H)	7.78 (s, 2H)
Vb	—	5.85 (s, 4H)	6.16–6.54 (6H)	7.77 (s, 2H)
Vc	3.83 (s, 12H) 3.98 (s, 6H)	—	6.04–6.53 (4H)	8.30 (s, 2H)
Vd	3.62 (s, 3H) 3.80 (s, 3H)	5.99 (s, 2H)	6.05–6.55 (6H)	7.70 (s, 1H) 7.79 (s, 1H)
Ve	3.36 (s, 3H) 3.50 (s, 3H) 3.79 (s, 6H)	—	6.01–6.63 (5H)	7.74 (s, 1H) 8.05 (s, 1H)
Vf	3.82 (s, 3H) 3.35 (s, 3H) 3.45 (s, 3H) 3.76 (s, 3H)	—	5.80–6.84 (4H)	7.83 (s, 1H) 8.04 (s, 1H)
Vg	3.80 (s, 6H) 3.96 (s, 6H)	—	6.18 (s, 2H) 7.14 (s, 2H)	8.23 (s, 2H)
Vh	—	5.93 (s, 4H)	7.00 (s, 2H) 7.32 (s, 2H)	8.14 (s, 2H)

with identical aryl rings and as two separate peaks in the examples (Vd, e and f) having different aryl rings.

Thus the second Stobbe reaction has been found to be equally stereoselective as much as the first Stobbe reaction with ortho-unsubstituted or mono ortho-substituted (-OMe or -Br) aromatic aldehydes. E \rightleftharpoons Z isomerisation of the dibenzylidene derivatives under the reaction conditions was also ruled out in view of the high yields reported. The assumption that E,E isomers cannot be formed because of steric factors was rejected as untenable¹⁶ by preparing some highly crowded and yet stable derivatives¹⁶.

The di-Stobbe products (Va-h) described in this paper have thus been proved to have (E,E) configuration although they have been hitherto assumed to have (E,Z) configuration as represented in (VI or VII). The E,E anhydrides were, however, found to isomerise to E,Z isomers (VI or VII) at reaction temperatures above 180°C before undergoing thermally allowed electrocyclic dis-rotatory ring closure to yield the corresponding 1-phenylnaphthalene-2, 3-dicarboxy-anhydrides.

ACKNOWLEDGEMENT

The authors are grateful to the CSIR for financial assistance.

6 July 1983; Revised 13 September 1983

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DISCOVERY OF ARCHAEOCYATHA IN THE UPPER KROL CARBONATES, MUSSOORIE HILLS, UTTAR PRADESH, INDIA

I. B. SINGH and VIBHUTI RAI

Geology Department, Lucknow University, Lucknow 226 007, India.

ABSTRACT

Well-developed Archaeocyatha-bearing carbonates are recorded for the first time from the uppermost part of Krol sediments (Krol-E), mostly in the form of thin lensoid and flat layers interbedded with algal mat carbonates. The Archaeocyatha occur together with calcareous algae and stromatolite-algal mats making a biogenic rock-building biotope. The group Archaeocyatha is restricted only upto Cambrian, mostly Lower Cambrian, making topmost part of Krol-E to belong to Lower Cambrian age. Consequently, the overlying Tal Formation (excluding Shell Limestone = Nilkanth Formation of Late Cretaceous age) also becomes of Cambrian age.

INTRODUCTION

TRADITIONALLY, the Krol belt is supposed to represent a continuous sequence of Palaeozoic – Mesozoic age, wherein the Krol Formation is assigned a Permo – Carboniferous – Triassic age^{1,2}. However, these sediments though representing deposits of well-oxygenated shallow tidal sea, surprisingly lack metazoan fossils, and Singh³⁻⁵ proposed that Krol Formation represented deposits of Late Precambrian age, while Tal Formation may extend into Cambrian^{6,7}. Lately, the stromatolites of Krol sediments of Nainital hills have been assigned a Late Vendian age⁷. Further, shelly microfossils are recorded by several workers from the Lower Tal phosphorite sediments, but given rather contradictory ages by different workers⁸⁻¹². Bhatt *et al*¹³ discuss the age significance of these shelly microfossils of mostly phosphate, and consider them to be of Tommotian age (Lower Cambrian, Trilobite lacking basal part). However, many workers still adhere to the traditional presumed Mesozoic age of Krol – Tal succession¹⁴.

Area

The Archaeocyatha-bearing bands are present in the topmost *ca* 10 m of carbonates just below the Chert Member of Tal Formation in the surface outcrop of Krol sediments near Maldeota phosphorite mine of P P C L, Dehradun (figures 7, 8).

Archaeocyatha of Krol Carbonate

The individual skeleton of Archaeocyatha, the cup is fundamentally an inverted cone, mostly having two fairly widely spaced walls and a central cavity. The walls are perforate and are connected across the inner space (intervallum) by perforate radial longitudinal plates (septa), by radial rods, by perforate transverse plates (tabulae) or dissepiments¹⁵.

Several samples from the bands, containing the Archaeocyatha were sliced and cut at various angles to reconstruct its morphology. In transverse section, the cups show semicircular outline exhibiting a broad intervallum transversed by several perforated septa