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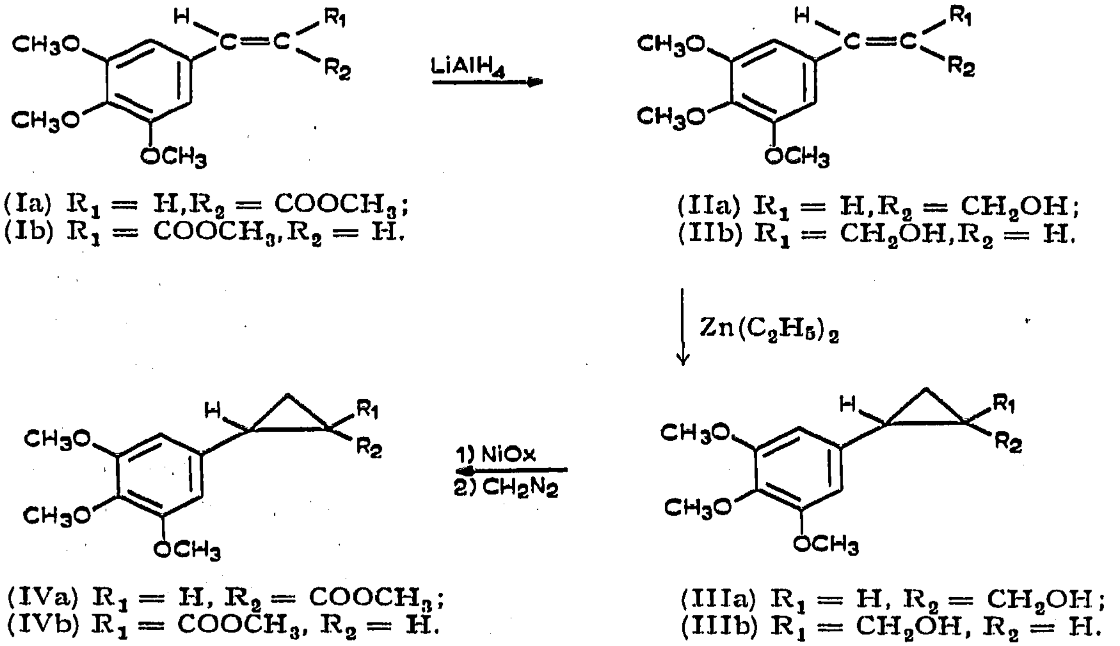
Thin-layer chromatographic separations of some geometric isomers

During the course of synthesis of some alicyclic analogues of mescaline[1] we were able to establish the composition of a series of intermediate *cis–trans* isomers (Ia,b–IVa,b) using thin-layer chromatography (TLC).



(Ia) $R_1 = H, R_2 = COOCH_3$;
(Ib) $R_1 = COOCH_3, R_2 = H$.

(IIa) $R_1 = H, R_2 = CH_2OH$;
(IIb) $R_1 = CH_2OH, R_2 = H$.

(IVa) $R_1 = H$, $R_2 = COOCH_3$;
(IVb) $R_1 = COOCH_3$, $R_2 = H$.

(IIIa) $R_1 = H$, $R_2 = CH_2OH$;
(IIIb) $R_1 = CH_2OH$, $R_2 = H$.

We wish to describe some phenomena which emerged from this study.

Experimental

TLC plates consisted of a 0.25-mm coating of Silica Gel H (Merck, Darmstadt, G.F.R.) applied as a slurry (30 g and 65 ml of water) using a Desaga spreader. The plates were air-dried and used without heat activation. Samples were applied 2 cm from the bottom of the plate and were developed to a length of 15 cm, at room temperature, using the following solvent systems: A, petroleum ether (b.p. 30–60°)–acetone (3:1); B, benzene–ethyl acetate (4:1); C, benzene–ethyl acetate (3:2); D, petroleum ether (b.p. 30–60°)–acetone (7:1); E, petroleum ether (b.p. 30–60°)–methanol (6:1). The developed plates were exposed to iodine vapour to detect the spots.

Results and discussion

Table I shows the R_F values of compounds I–IV. The *cis*-isomers, Ia–IIIa, have higher R_F values than their *trans*-counterparts (Ib–IIIb) whereas within the pair IVa, b the *trans*-isomer has the higher values in all solvent systems studied. PALAMEREVA *et al.*[2] reported that within 37 pairs of diastereoisomers, the *erythro*-isomer invariably has the higher R_F value relative to the *threo*-isomer. They therefore proposed that the relative configurations of such isomers could be assessed using TLC. Our finding of an R_F-inversion amongst the related and relatively small series of compounds I–IV suggests that TLC is not of general predictive value in distinguishing between geometric isomers.

TABLE I

R_F VALUES OF A SERIES OF *cis,trans*-ISOMERS

TLC of *cis*-isomers (Ia–IVa) and corresponding *trans*-isomers (Ib–IVb) using solvent systems A–E mentioned in text.

Compound	*R_F values*				
	Solvent system				
	A	*B*	*C*	*D*	*E*
Ia	0.69	0.70	0.86	0.49	0.47
Ib	0.66	0.68	0.86	0.40	0.35
IIa	0.28	0.09	0.49	—	—
IIb	0.23	0.09	0.46	—	—
IIIa	0.27	0.07	0.43	—	—
IIIb	0.24	0.07	0.43	—	—
IVa	0.63	0.57	0.80	0.35	0.26
IVb	0.65	0.65	0.84	0.43	0.38

Table I also shows that the olefins (I and II) usually have higher R_F values than their corresponding cyclopropane analogues (IV and III, respectively). Since olefins are considered to be more polar than cyclopropanes, factors other than polarity must be the determinants in these separations.

We conclude that one must be cautious in the utilization of TLC for other than a valuable but nonetheless empirical analytical method.

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