

DIMETHYL 2-PHENYL-1, 1-CYCLOBUTANE- AND CYCLO- HEXANEDICARBOXYLATES & RELATED COMPOUNDS. NMR EVIDENCE FOR THE GREATER PROXIMITY OF THE 1, 2-*cis*- GROUPS OF THE CYCLOBUTANE SERIES

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ABSTRACT

Based mainly on the relative chemical shift data of ester methyl protons, it has been shown that the 1,2-*cis* groups (Ph, CO₂Me and H, CO₂Me) of dimethyl 2-phenyl-1, 1-cyclobutanedicarboxylate and related compounds are more convergent and the 1,2-*trans* groups (Ph, CO₂Me) are more divergent than in the corresponding cyclohexane compounds.

INTRODUCTION

Recently we had occasion to prepare dimethyl 2-phenyl-1, 1-cyclobutanedicarboxylate (III) required for elaboration to a natural product.¹ We followed essentially the intramolecular cyclization procedure of Burger^{2,3} for its preparation, except for the use of Makosza's catalyst⁴ and aqueous conditions, for the cyclization of methyl 2-carbomethoxy-5-bromo-5-phenylpentanoate (IIa) which in turn was obtained from Ia by treatment with N-bromosuccinimide. By an analogous intramolecular cyclization of IIb (DMF-K₂CO₃) we also prepared in good yield dimethyl 2-phenyl-1, 1-cyclohexanedicarboxylate⁵ (IV).

2. PRESENT FINDINGS

The NMR study of the two diesters (III and IV), the half ester-acids (V and VI) and the *trans* esters (VII and VIII) (Table I) brought to light some interesting features which are discussed in this communication.

The spread in the chemical shift values ($\Delta \delta$ CO₂Me) of the carbomethoxymethyl protons of the cyclobutane diester (III) and the cyclohexane diester (IV) presented revealing contrast. In the cyclohexane diester the π -cloud of the phenyl group appears to affect the chemical shifts of the

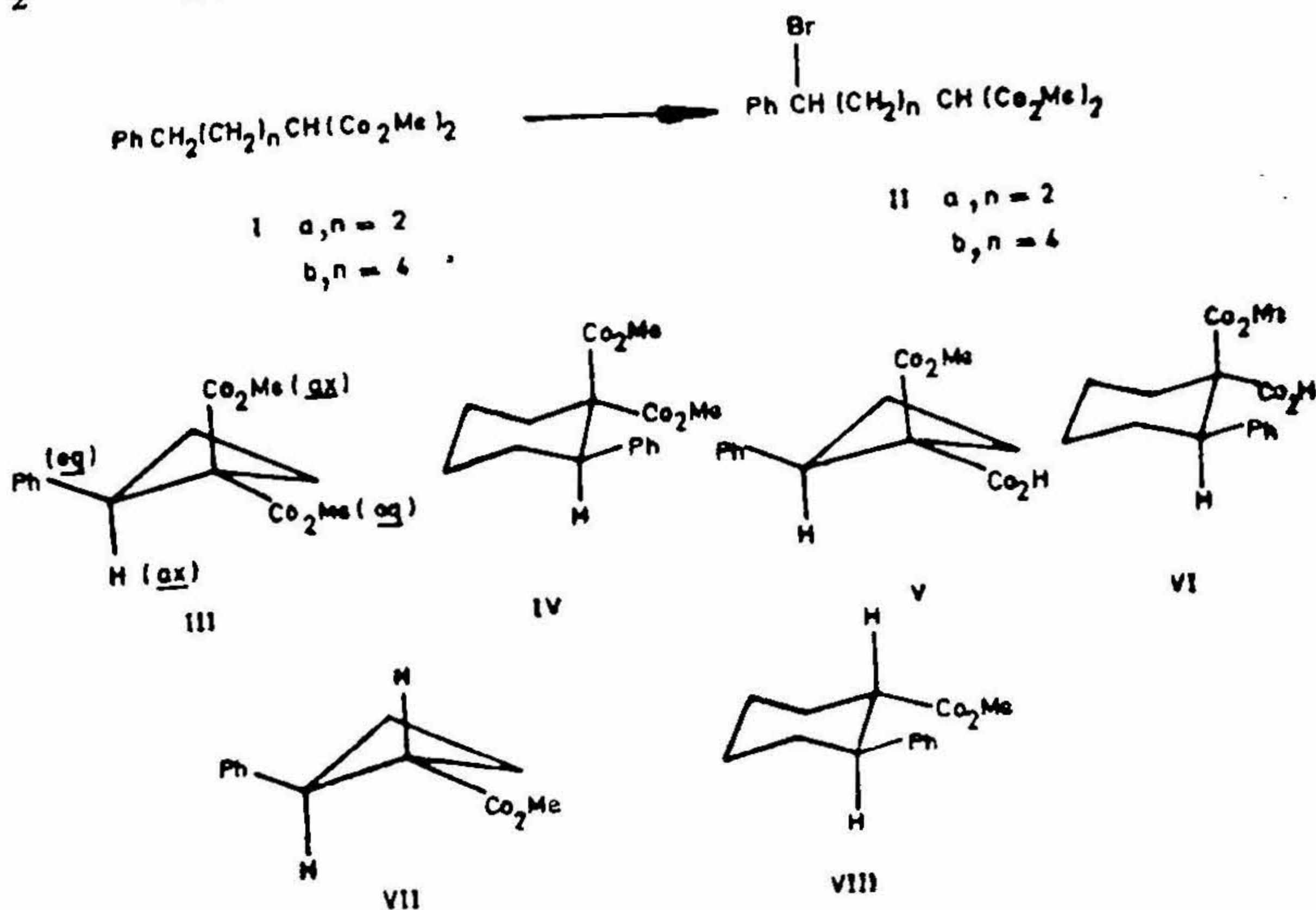


TABLE I
Chemical shift data of the esters III to VIII

Compound	NMR 100 MHz; CDCl_3 ; Chemical shifts in δ values from TMS as zero					
	$ax\text{-CO}_2\text{Me}$ (s)	$eq\text{-CO}_2\text{Me}$ (s)	$\Delta\delta \text{CO}_2\text{Me}$	$ax\text{-Ph-C-H}$ 	Upfield shift of $ax\text{-CO}_2\text{Me}$ with respect to $\text{CH}_2(\text{CO}_2\text{Me})_2$	Shift of $eq\text{-CO}_2\text{Me}$ with respect to $\text{CH}_2(\text{CO}_2\text{Me})_2$
III	3.28	3.82	0.54	4.42(m)	0.47	0.07
IV	3.52	3.56	0.04	3.20(dd)	0.23	0.19
V	3.30	0.27	4.38(m)	0.45
VI	3.57		3.29(dd)	0.18	---
VII	3.69	0.31	---	0.06
VIII	---	3.38		---	---	0.37

$\text{H}_2\text{C}(\text{CO}_2\text{Me})_2$: 3.75 (s)

ester methyl protons to almost equal extent ($\Delta \delta \text{CO}_2\text{Me} = 0.04$), while in the cyclobutane diester, the anisotropic effect is thirteen times more pronounced ($\Delta \delta \text{CO}_2\text{Me} = 0.54^*$). The magnitude of the relative upfield shift of the axial CO_2Me signal (3.28) of III with respect to $\text{CH}_2(\text{CO}_2\text{Me})_2$ (3.75) may be regarded as a qualitative measure of the proximity of the shielding *cis*-2-phenyl group⁶ in III. From this one may conclude that the phenyl group, assumed to be equatorial³, and the *cis*-axial CO_2Me are more proximate in the cyclobutane diester (III) than in the cyclohexane diester (IV). An inspection of the CO_2Me signals of the half ester-acids V and VI derived from III and IV by saponification using one equivalent of aqueous potassium hydroxide and assigned the given structures on the basis of preferential nucleophilic attack on the less hindered equatorial carbonyl, also confirms this conclusion.

A comparison of the $\delta \text{CO}_2\text{Me}$ values of the *trans*-esters VII and VIII demonstrates the closer proximity of the phenyl and the *trans*- CO_2Me groups in the cyclohexane compound than in the corresponding cyclobutane compound.

The lower $|\delta \text{eq-}\text{CO}_2\text{Me} \text{ of VII}^\dagger \sim \delta \text{CH}_2(\text{CO}_2\text{Me})_2|$ value (0.06) and the higher $|\delta \text{eq-}\text{CO}_2\text{Me} \text{ of VIII}^\ddagger \sim \delta \text{CH}_2(\text{CO}_2\text{Me})_2|$ value (0.37) suggest that while in VII the phenyl group exercises practically little influence on the chemical shift of the *trans*- CO_2Me , it has considerable upfield shifting influence in VIII.

In the cyclobutane compounds III and V, the axial methine proton ($\text{Ph}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{H}$) is relatively shifted far downfield (4.42 and 4.38 δ) compared to the cyclohexane compounds IV and VI (3.20 and 3.29 δ). This is attributable to the greater proximity of the deshielding $\text{CO}_2\text{Me}/\text{CO}_2\text{H}$ groups *cis* to the methine proton in III and V.

Thus it is clear from the above data and discussion, that in the cyclobutane compounds of this series, the 1,2-*cis* groups (Ph, CO_2Me , and H, CO_2Me) are more convergent and the 1,2-*trans* group (Ph, CO_2Me) are more divergent than in the corresponding cyclohexane compounds.

* That the spread of this magnitude (0.54) is not due to conformational difference of the two ester groups (*ax*- $\text{CO}_2\text{Me} \sim \text{eq-}\text{CO}_2\text{Me}$) is evident from the data available for the diester of 3-phenylcyclobutane-1,1-dicarboxylic acid.²

† The *trans* ester was derived from the half ester-acid V by decarboxylation with pyridine followed by equilibration with sodium methoxide.¹

It would be of interest to study similar effects in dimethyl 2-phenyl-1,1-dicarboxylates, their half ester-acids, etc., of 3-, 5- and 7- membered ring systems.

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