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ASYMMETRIC INDUCTION IN CARBENOID REACTION
BY MEANS OF A DISSYMMETRIC COPPER CHELATE

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Preparative value of modified carbenes produced by copper catalyzed decomposition of diazoalkanes is due to their highly discriminative reactivity. In view of the complex nature of heterogeneous catalysis previously recorded (1), we have been examining the effects of soluble copper catalysts which have known geometry in solution. Diphenylcarbene produced by thermal decomposition of diphenyldiazomethane in the presence of bis(acetylacetonato)copper(II) is completely devoid of radical character but shows remarkably electrophilic reactivity (2,3). The proposed explanation involves intermediary occurrence of carbene-copper complex in which the carbene moiety is bonded to the metal as a fifth ligand (4).

The present communication should supposedly provide independent evidences for this proposal and these were derived from two kinds of carbenoid reactions, viz., addition to C=C bond and insertion to C-O bond. Ethyl diazoacetate was smoothly decomposed in styrene (1:3 mole ratio) at

58-60° in the presence of bis[N-(R)-α-phenylethylsalicylaldiminato]copper(II) (I) (5). The reaction gave 72% yield of an optically active mixture of cis and trans isomers of ethyl 2-phenylcyclopropanecarboxylate (IIa and IIIa). The mixture was separated by vpc on Apiezon L column into pure components, the cis/trans ratio being ca. 1:2.3. Hydrolysis with 8% potassium hydroxide solution at room temperature gave respective, optically active acids IIb and IIIb. Similar reactions were carried out with the copper chelate I having N-(S)-α-phenylethyl group (5), and the optical data of resulting products were summarized in Table I. Based on the recorded rotations and absolute configurations of IIIb (6), the optical yields of 1R,2R- and 1S,2S-acids produced in excess are calculated to be 6% in both cases.

The reaction of ethyl diazoacetate with 2-phenyloxetane (1:5 mole ratio) results in ring-enlargement yielding a cis-trans mixture of ethyl 3-phenyltetrahydrofuran-2-carboxylate (7). It has been discovered that catalytic decomposition of methyl diazoacetate in the presence of I with N-(R)-α-phenylethyl group at 58-60° modifies the reaction so as to yield an optically active mixture of IVa and Va in 85% yield, the cis/trans ratio being ca. 1:2 (8). Vpc separation on Apiezon L-Silicone DC QF-1 column gave the pure isomers, which were carefully hydrolyzed to yield cis- and trans-3-phenyltetrahydrofuran-2-carboxylic acids (IVb and Vb), respectively, both in optically active form. Reaction in the presence of I having N-(S)-α-phenylethyl group gave products with comparable magnitude but different sign of rotation as shown in Table I.

Table I. Asymmetric Synthesis with Alkoxycarbonylcarbene

Product[a]	M.p., °C (B.p., °C/mm)	α_D^{25} [b] obsd.	*c* mg/ml	$[\alpha]_D^{25}$ deg
With N-(*R*)-α-phenylethyl-substituted chelate I[c]				
IIa + IIIa	(90-95/2)	+0.656	101.1	+13.0
IIa	oil	+0.065	70.0	+1.86
IIIa	36-38	+0.644	71.4	+18.0
IIb	98-101	+0.075	51.0	+2.94
IIIb	88.5-89.5	+0.800	69.8	+22.9
IVa + Va	(92-93/0.08)	+0.253	102.0	+4.96
IVa	oil	+0.054	20.2	+5.35
Va	oil	+0.098	41.4	+4.73
IVb	140-143	+0.050	20.6	+4.85
$Vb \cdot H_2O$	69-71	+0.082	41.0	+4.00
With N-(*S*)-α-phenylethyl-substituted chelate I[c]				
IIa + IIIa	(90-95/2)	-0.682	104.9	-13.0
IIa	oil	-0.064	67.8	-1.89
IIIa	36-38	-0.636	69.2	-18.4
IIb	97-101	-0.071	50.5	-2.81
IIIb	88-89	-0.798	70.2	-22.8
IVa + Va	(92-93/0.08)	-0.241	100.0	-4.82
IVa	oil	-0.058	20.4	-5.69
Va	oil	-0.092	40.4	-4.55
IVb	140-143	-0.052	21.0	-4.95
$Vb \cdot H_2O$	68-70	-0.083	42.0	-3.95

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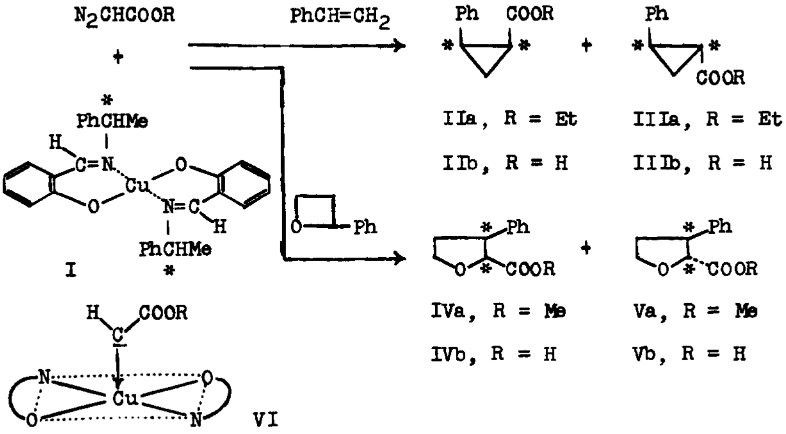
a. All products gave correct elemental analyeses. IR spectra in solutions were completely superimposable on those of inactive authentic specimen (6). b. All rotatory values were measured in chloroform solutions with 0.5 dm cells.
c. I (used in 0.009 mole ratio to diazoacetate) was recovered more than 70%.



In the absence of the chelate I no reaction was observed between the substrates and diazoacetate at 58-60°. UV (9) and/or IR evidences indicated the absence of any detectable interaction of the chelate I with either olefinic or ethereal substrate. Strong coordination of bases such as pyridine (4) to the chelate I destroyed the catalytic activity. The reasonable account for the dissymmetric alkoxycarbonylcarbene reactions must be given by assuming the formation of a reactive complex which should result from nucleophilic attack by diazoacetate at the open coordination site of the chelate I and following elimination of nitrogen (10, 11). In this complex the carbene is bonded transiently to copper as a fifth ligand in dissymmetric atmosphere as this is tentatively shown by VI. The recorded non-planarity of the original chelate complex I (5) may imply considerably distorted geometry of VI from regular square-pyramidal one. Correlation of the asymmetry of N-α-phenylethyl group with the absolute configuration of the resulting cyclopropanecarboxylic acid becomes rather equivocal under such circumstances and should be discussed fully in the future.

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