

New Addition Reactions. (II)

Addition of Aliphatic Epoxides to Schiff Bases

Ryohei ODA, Masaya OKANO, Shohei TOKIURA, and Akira MIYASU

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By the stannic chloride-catalyzed addition of aliphatic epoxides to Schiff bases, various oxazolidines have been obtained. For example, the reaction of propylene oxide with N-t-butylazomethine and benzalaniline afforded 3-t-butyl-5-methyl-oxazolidine and 5-methyl-2,3-diphenyloxazolidine in 24% and 30% yields, respectively. The use of boron trifluoride as a catalyst resulted in a lower yield of the desired adduct.

New Addition Reactions. (III)

Addition of Aliphatic Epoxides to Nitriles

Ryohei ODA, Masaya OKANO, Shohei TOKIURA, and Fujio MISUMI

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Upon treatment of aliphatic epoxides with aliphatic or aromatic nitriles in cold concentrated sulfuric acid, the formation of the cyclic adducts, 2,4- and/or 2,5-disubstituted 2-oxazolines, has been observed in low yields (below 20%). The reaction of acetonitrile with propylene oxide gave a mixture of 2,4- and 2,5-dimethyl-2-oxazoline (70:30), while the reaction with epichlorohydrin afforded only 4- (or 5-) chloromethyl-2-methyl-2-oxazoline.

Partial Asymmetric Synthesis in the Conjugate Addition of a Grignard Reagent to an α, β -Unsaturated Ester

YUZO INOUE and H. M. WALBORSKY

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In the series of our asymmetric synthesis studies, a successful asymmetric synthesis in a Diels-Alder condensation has recently been reported (H. M. Walborsky, L. Barash and T. C. Davis, *J. Org. Chem.*, **26**, 4778 (1961)) and the resemblance in mechanism suggested the possibility of asymmetric synthesis in the conjugate addition of a Grignard reagent to an α, β -unsaturated ester.

The addition of phenylmagnesium bromide to (-)-menthyl crotonate resulted

ABSTRACTS

in the formation of *S*-(+)-3-phenylbutyric acid and, furthermore, when this reaction was catalyzed by catalytic amounts of cuprous or cupric chlorides, the reaction products had the *R*-(-)-configuration.

3-Phenylbutyric Acid

Run	Catalyst ^a	% Yield	$[\alpha]^{25}_D$ ^b	% Optical ^c yield
1	—	46.1	+3.1°	5.4
2	Cu ₂ Cl ₂	63.5	-5.9	10.2
3	—	53.0	+3.7	6.9
4	Cu ₂ Cl ₂	60.1	-3.4	6.0
5	—	57.9	+3.3	5.9
6	Cu ₂ Cl ₂	62.6	-3.6	6.3
7	CdCl ₂	50.2	+4.6	8.1
8	HgCl ₂	44.7	+2.5	4.4
9	Hg ₂ Cl ₂	38.3	+3.7	6.5
10	AgCl	31.5	+2.9	5.1
11	PtCl ₄	40.8	+2.5	4.4
12	PdCl ₂	42.6	+3.6	6.4
13	Cu ₂ Cl ₂ ^d	7.7	+0.87	1.5
14	CuCl ₂	44.5	-3.6	6.3

^a) 3 mole % catalyst used.

^b) Solvent: benzene.

^c) Calculated on -57° of the optically pure enantiomer (H. Rupe, *Ann.*, **369**, 335 (1909)).

^d) Inverse addition i.e. addition of phenylmagnesium bromide to (-)-methyl crotonate solution containing cuprous chloride.

This shows that the steric course of the reaction was altered by the presence of copper chlorides. In contrast to copper chlorides, other double-bond complexing agents such as Hg, Ag, Pt, Pd and Cd chlorides did not alter the stereoselectivity of this reaction and, even with cuprous chloride, when this reaction was carried out in an inverse manner, no catalyst effect was observed, the *S*-(+)-acid being the product.

Syntheses of 1-Phenyl-2-thiobarbituric Acid Derivatives and their Analgesic Activity

Jutaro OKADA, Hajime FUJIMURA and Yoshiko UEDA

*Yakugaku Zasshi (Journal of the Pharmaceutical
Society of Japan)* **82**, 976 (1962)

5-Alkylamino-2-thiobarbituric acid derivatives containing a *p*-substituted phenyl group in the nitrogen were synthesized in order to examine the presence of analgesic action in a compound by the introduction of two kinds of two kinds