

Substitution Reaction of Diphenylcyclopropenone with Ammonia to give α -Amino- β -phenylcinnamic Aldehyde

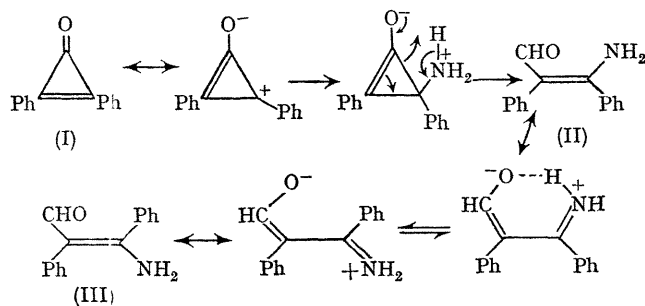
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ALTHOUGH addition of water,¹ phenylmagnesium bromide,¹ or amine² to the carbonyl group, and of hydroxylamine¹, diazomethane,^{1,3} or enamine⁴ to the double-bond of diphenylcyclopropenone (I) have been reported, substitution reactions of the parent system have not.

We report now the substitution reaction of liquid ammonia on (I) (in Et₂O) to give the title compound (II) [89%: m.p. 127°; λ_{\max} (EtOH) 232 (ϵ 12, 200), 254sh (9700), 307sh (8700), and 340 nm. (9500); n.m.r. (CDCl₃) τ 0.69 (s, CHO, 1H), 2.80 (m, Ph 10H) and 4.45 (b, NH₂, 2H); ν_{\max} (KBr)

3430, 3300, 3150 (NH), 2750, 2830 (CHO), 1610 (C=O), and 1560 cm^{-1} (C=C); M , Calc.: 223, Found (benzene): 225]. A possible mechanism is:



A solution of compound (II) in hydrochloric acid on being heated gave deoxybenzoin. Addition of water to an aqueous KOH-EtOH solution of (II), gave the geometrical isomer (III): [m.p. 120° : ν_{max} (KBr) 3450, 3300, 3150(NH), 2750, 2830(CHO), 1605(C=O) and 1535 cm^{-1} (C=C)]. The *trans*-isomer (III) isomerised easily into (II) (*cis*) in CHCl_3 or CCl_4 solution (Scheme). Stabilisation by intramolecular hydrogen-bonding may cause the *cis*-form to predominate in solution. In alkaline media, however, the *trans*-isomer (III) is formed by rotation about the central carbon-carbon bond. This is the first isolation of such a pair of isomers, although some analogous compounds in solution were shown⁵⁻⁷ to be an equilibrium mixture of *cis*- and *trans*-isomers.

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