CONCLUSIONS

Alkylthiochloroacetylenes and arylthiochloroacetylenes react with hydrazine to give 3,6bis(organylthiomethyl)-2,5-dihydro-1,2,4,5-tetrazines (II) and/or 3,5-bis(organylthiomethyl)-4-amino-1,2,4-triazoles depending on the nature of the substituent.

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REACTIONS OF ESTERS OF 3-PHENYL-3-CHLORO-2-KETOPROPIONIC ACID

WITH SODIUM ALCOHOLATES

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Epoxyesters formed as a result of the nucleophilic addition of an alcoholate to the carbonyl group [1] and hydroxyketals or hydroketones formed upon the subsequent decomposition of the epoxyesters [2] are frequently encountered side products of the Favorskii rearrangement. Bordwell et al. [3] has shown that the presence of a phenyl group in the α -position favors the formation of epoxide derivatives. In previous work [4], we reported that the methyl ester of 3-phenyl-3-chloro-2-ketopropionic acid (Ia) reacts with sodium methylate, depending on the conditions, to give the product of the reaction of two molecules, the dimethyl ester of 2,5-diketo-3,4-diphenyl-3-methoxyhexanedioic acid (IIa) and the product of the replacement of the chlorine atom by a methoxy group, namely, the methyl ester of 3-phenyl-3-methoxy-2-ketopropionic acid (IIIa).

In the present work, the behavior of the methyl (Ia) and ethyl esters (Ib) of 3-phenyl-3-chloro-2-ketopropionic acid under Favorskii rearrangement conditions was studied in greater detail and the physicochemical indices of the compounds obtained are given.

Independently of the ester used, (Ia) or (Ib) in methanol with MeONa at reflux gives (IIa), (IIIa), and methyl 2-phenyl-2-methoxyacetate (IVa). The use of EtONa in ethanol instead of MeONa in methanol leads to the formation of the diethyl ester of 2,5-diketo-3,4-diphenyl-3-ethoxyhexanedioic acid (IIb) and the ethyl ester of 3-phenyl-3-ethoxy-2-ketopropionic acid (IIIb). The ethyl ester of 2-phenyl-3-ethoxyacetic acid could not be isolated.



The reactions of (Ia) and (Ib) with the corresponding alcoholates in dilute alcohol solutions at 0°C give (IIIa) and (IIIb) in quantitative yield.

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The structures and purity of (II)-(IV) were indicated by IR and PMR spectroscopy and the elemental analysis. The structures and compositions of (IIa) and (IIb) were also indicated by mass spectrometry. The chemical ionization (CI) mass spectrum of (IIb) has peaks with m/z 427 and 381, corresponding to $[MH]^+$ and $[MH - C_2H_5OH]^+$. Analogous dissociative proton capture processes occur in (IIa) and (IIb): the $[MH]^+$ ion decomposes with the loss of methanol and ethanol, respectively. The loss of the alcohol molecule from the $[MH]^+$ ion is energetically favorable since a conjugated bond system containing both aromatic rings is formed.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer. The PMR spectra were taken on a Varian T-60 spectrometer with TMS as the internal standard. The chemical ionization mass spectra were obtained on a Finnigan MAT-212 mass spectrometer by direct inlet of the samples into the ion source. The injector temperature was varied from room temperature to 40°C. Iso-butane served as the reagent gas.

Dimethyl Ester of 2,5-Diketo-3,4-diphenyl-3-methoxyhexanedioic Acid (IIa). A solution of 0.029 mole (Ia) or (Ib) in 5 ml methanol was added from a dropping funnel into a solution of MeONa in methanol (0.032 mole Na in 25 ml methanol) at reflux. Stirring was continued for an additional 1.5 h. Water was added to the reaction mixture. The crystalline precipitate was filtered off and recrystallized from methanol to give 2.8 g (46%) (IIa), mp 158.5-160°C. IR spectrum in vaseline mull (ν , cm⁻¹): 1650, 1700, 1710, 1750 (4 C= 0). PMR spectrum (δ , ppm, (CD₃)₂SO): 3.06, 3.23 and 3.53 s (3CH₃O), 5.23 s (HC), 7.33 and 7.46 s (2C₂H₅). Chemical ionization (CI) mass spectrum (relative intensity, %): 385 (25), 353 (100). Found: C, 65.58; H, 5.29%. Calculated for C₂₁H₂₀O₇: C, 65.64; 5.20%.

The aqueous layer was extracted with two 40 ml portions of ether and one 50 ml portion of hexane. The organic layers were combined and dried over MgSO₄. Double vacuum distillation gave 0.7 g (11%) (IIIa) and 0.5 g (8%) (IVa). (IIIa), bp 88°C (0.025 mm), $n_D^{2^\circ}$ 1.5150. IR spectrum (v, cm⁻¹, neat): 1700, 1740 (2 C=0). PMR spectrum (δ , ppm, CCl₄): 3.43 and 3.70 s (2CH₃0), 4.20 s (HC), 7.23 s (C₆H₅). Found: C, 63.18; H, 5.57%. Calculated for C₁₁H₁₂O₄: C, 63.48; H, 5.76%. (IV), bp 101-102°C (9 mm), $n_D^{2^\circ}$ 1.5045 [5]. IR spectrum (v, cm⁻¹, neat): 1730 (C=0). PMR spectrum (δ , ppm, CCl₄): 3.26 and 3.66 s (2CH₃0), 5.13 s (HC), 7.16 s (C₆H₅). Found: C, 66.40; H, 6.47%. Calculated for C₁₀H₁₂O₃: C, 66.66; H, 6.66%.

Diethyl Ester of 2,5-Diketo-3,4-diphenyl-3-ethoxyhexanedioic Acid (IIb). The reaction was carried out by analogy with the same reagent ratio. After the cessation of stirring, the solvent was evaporated and the residue was recrystallized from hexane to give 2.4 g (37%) (IIb) mp 128.5-130°C. IR spectrum (ν , cm⁻¹, vaseline mull): 1640, 1690, 1710, 1740 (4 C=O). PMR spectrum (δ , ppm, CDCl₃): 0.76, 0.96, and 1.16 t (3CH₃), 3.06-4.20 m (3CH₂), 4.83 s (HC), 7.06-7.56 m (2C₆H₃). CI mass spectrum: 427 (100), 381 (30). Found: C, 67.57; H, 6.22%. Calculated for C₂₄H₂₆O₇: C, 67.62; H, 6.09%.

Hexane was removed from the mother liquor and the residue was distilled to give 0.8 g (12%) (IIIb), bp 99-100°C (0.03 mm). $n_D^{2°}$ 1.4990. IR spectrum (ν , cm⁻¹, neat): 1750 br (C=O), PMR spectrum (δ , ppm, CCl₄): 1.10 and 1.30 t (2CH₃), 3.73 and 4.16 q (2CH₂), 4.13 s (HC), 7.30 s (C₆H₅). Found: C, 66.34; H, 7.06%. Calculated for C₁₃H₁₆O₄: C, 66.12; H, 6.77%.

Methyl Ester of 3-Phenyl-3-methoxy-2-ketopropionic Acid (IIIa) and Ethyl Ester of 3-Phenyl-3-ethoxy-2-ketopropionic Acid (IIIb). A sample of 0.009 mole (Ia) was added rapidly to a solution of MeONa in methanol obtained from 0.075 mole sodium in 200 ml methanol at 0°C. After 2 h stirring, the solution was neutralized by the addition of acetic acid. Methanol was removed and the residue was washed with water. The aqueous layer was extracted twice by ether and once by hexane. The organic layer and the extracts were combined and dried over MgSO₄. The solvents were evaporated and the residue was distilled in vacuum to give 5.7 g (90%) (IIIa). An analogous procedure gave 6.1 g (92%) (IIIb).

CONCLUSIONS

1. The reaction of esters of 3-phenyl-3-chloro-2-ketopropionic acid with sodium alcoholates in alcohol (methanol or ethanol) at reflux leads to the formation of an ester of 2,5-diketo-3,4-diphenyl-3-methoxyhexanedioic or 2,5-diketo-3,4-diphenyl-3-ethoxyhexanedioic acid.

2. The reactions of esters of 3-phenyl-3-chloro-2-ketopropionic acid with the corresponding sodium alcoholates in dilute solution at 0°C give the product of the substitution of chlorine by an alkoxy group in quantitative yield.

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REACTION OF FLUOROCHLORONITROMETHANE WITH ALDEHYDES

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Nitroalcohols [1, 2] and their derivatives have a broad spectrum of useful properties [3]. The most general method for the synthesis of β -nitroalcohols is the condensation of nitro compounds with aldehydes and ketones [4]. In order to search for biologically active compounds and study the chemical behavior of aliphatic and aromatic alcohols having a fluoro-nitromethyl group, we carried out the reaction of aliphatic and aromatic aldehydes with fluoro-chloronitromethane in the presence of a basic catalyst.

The condensation with the aldehydes was carried out in water at $80-90^{\circ}$ C. The structures of nitroalcohols (II)-(V) were established by IR, PMR and ¹⁹F NMR spectroscopy. Products (I)-(V) are formed as diastereomer mixtures as seen in a doubling of the signals in the ¹H and ¹⁹F NMR spectra. The IR spectra of these products have bands at 1590 and 1330 cm⁻¹, corresponding to symmetrical and asymmetrical vibrations of the nitro group and a broad band at 3420 cm⁻¹, indicating the presence of an OH group.

Nitroalcohols (I)-(V) are capable of entering various chemical reactions involving the OH group. Thus, fluorochloronitroethanol (I) in the presence of H_2SO_4 reacts with formaldehyde to give formal (VI).

$$(I) + CH_2O + H_2SO_4 \rightarrow (O_2NCFClCH_2O)_2CH_2$$
(VI)

The reaction of (I)-(V) with acid chlorides, dialkyl chlorophosphates, or trimethylchlorosilane gives the corresponding esters (VII)-(XII), phosphates (XIII)-(XIV) and trimethylsilyl esters (XV).

The spectral indices of nitroalcohols (I)-(V) and their derivatives (VI)-(XV) are given in Table 1, while their physicochemical indices, yields, and elemental analysis data are given in Table 2.

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