UDC 542.97:542.953:547.594.4:547.594.3

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4-Halomethyl-2,5-cyclohexadien-l-ones (I) in their reactions with carbanion derivatives display dual reactivity (see Scheme below), which may be explained in terms of perturbation theory [1]. Thus, despite the possible differences in the mechanisms of these reactions, it would appear that stabilized (i.e., more polarizable and less nucleophilic) carbanion species (including under conditions of the absence of electrophilic coordination of the positive counter-ion (NR₄⁺) at the oxygen atom of the carbonyl group (CG)) attack the more polarizable enone fragment of (I) in a Michael-type reaction [2] (pathway (A)), while non-stabilized (i.e., polar and highly nucleophilic) carbanions prefer (upon coordination of a metal at the oxygen atom of the CG) to attack the more polar reaction site, namely, the carbon atom of the CG (pathway (B)) by Reformatskii [3], Grignard [4], or Wittig reactions [5].



Type-B processes are commonly used for producing an exocyclic double bond in para-semiquinoid systems (II). This method has not been used, to our knowledge, for the construction of such systems by the condensation of ketones with compounds, possessing an activated methylene group, catalyzed by weak bases (Knoevenagel reaction) [6]. We have found that upon the use of EtoNa in EtoH or piperidine in $C_{5}H_{5}N$ (EtOH), dienone (III), which is readily available by the Zincke-Suhl reaction, is capable of condensing with dimedone (IV) to form a new trienedione (V) in 3-8% yield. Trienedione (V) is a bright yellow crystalline compound whose structure was demonstrated by elemental analysis data, PMR, IR, and UV spectroscopies, and mass spectrometry.*

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^{*}In the case of excess piperidine and heating the reaction mixture at reflux, piperidine hydrochloride was isolated in 71% yield, indicating possible nucleophilic aromatization of (V) with the loss (and subsequent dissociation) of the CCl₃ anion from the geminal carbon.

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The PMR spectrum of product (V), in comparison with starting dienone (III), shows marked deshielding of ring protons H^A and H^{A^*} located in positions of identical parity with the carbon atoms of the exocyclic CG ($\Delta\delta$ 1.45 (C_6D_6) and 0.44 ppm (CDCl₃)). Along with the pronounced shift of the UV maximum of (V) in comparison with (III) toward longer longer wavelengths (λ_{max} 330-340 nm, log ε 3.54), this is in good accord with the existence of two extended cross- π, π, π -conjugation of the double bonds of the semiquinoid ring with the two electron-withdrawing CG [7].

We should note that (V) is formed in much lower yield than the products of the Knoevenagel reaction [6]. This effect may be attributed to both the equilibrium nature of the formation of trienedione (V) (enhanced rate of its retrodissociation by the action of base) and the reduced reactivity of the CG of dienone (III) due to its conjugation with two π -bonds. In addition, we should take account that steric hindrance from the two substituents at C⁴ in (III) may suppress the theoretically more favorable nucleophilic attack of its ring at a C=C bond (see Scheme A in the Scheme), which requires the bulky and polarizable carbanionic dimedone derivative to attack the polar CG.



 $X = CI, OCH_3(VII).$

Since the simplest exo-alkylidene-2,5-cyclohexadienes (VI), containing a trichloromethyl derivative in the geminal unit, undergo the Auwers rearrangement even at 20°C with 1,5-migration of the CCl₃ radical to the benzyl position [8], we should note the high thermal stability of bicyclic semiquinoid trienedione (V) with mp 168°C. We may assume that the observed enhancement in the stability of semiquinoid form (V) in comparison to this homolytic rearrangement, apparently related to the greater polarity of the cross conjugation system in this case due to the introduction of two electron-withdrawing carbonyl groups in the 1,1'exo positions, is rather general in nature [9] and may be found in a broad range of semiquinoid compounds upon their exo-functionalization. We have recently observed an analogous increase in the stability of semiquinoid structures upon the introduction of electron-withdrawing Cl₂(O)P and (CH₃O)₂(O)P groups and one or two HgCl substituents into the exo-methylene position [10]. Thus, (VII) are thermally more stable than triene (VI) and undergo 1,5isomerization only under photolysis conditions [11].

EXPERIMENTAL

The PMR spectra were obtained on a Bruker WP-200SY spectrometer at 200 MHz using TMS as the internal standard. The UV spectra were taken on a Cary 219 spectrometer for a 0.005 M solution in chloroform. The IR spectra were taken on a UR-20 spectrometer for hexane solutions at 1500-1700 cm⁻¹. The mass spectra were taken on an AEI MS-30 spectrometer at 12 eV.

 $\frac{4-\text{Methyl}-4-\text{tricholoromethyl}-1-(4,4-\text{dimethyl}-2,6-\text{dioxocyclohexylidene})-2,5-\text{cyclohexadiene}}{\text{a}}$ (V). a) A solution of 16.1 g dienone (III) and 10 g dimedone (IV) in 300 ml abs. ethanol containing four drops of piperidine was heated at reflux for 24 h. The crystalline precipitate of (V) was separated by decantation, washed with ethanol, and dried in vacuum to give 0.68 g (2.8%), mp 168-169°C. R_f = 0.88 Silufol UV-254 plates using 3:1 benzene-ether as the eluent.* Found: C 55.37; H 4.90; Cl 30.39%. Calculated for C_{16H17}Cl₃O₂: C 55.27; H 4.89; Cl 30.61%. PMR spectrum in CDCl₃ (δ , ppm, J, Hz): 1.04 and 1.09 s (2CH₃ of the cyclohexane ring), 1.57 br. s (4H, CH₂), 2.64 s (3H, CH₃ of the cyclohexadiene ring), 6.75 and 7.55 AB quartet (4H, CH, J_{AB} = 10.5). Mass spectrum (m/z): 346-350 (M⁺). IR spectrum: 1665 cm⁻¹ (C=0).

After separation of the precipitated crystals, the reaction was continued by heating of the mother liquor for 6 h or maintenance for 7-10 days. The yield of the second portion of (V) was 0.5 g (2.3%). The total product yield after threefold separation was 1.4 g (7%).

b) A solution of 0.3 g (1.3 mmoles) dienone (III) and 0.186 g (1.3 mmoles) dimedone (IV) in 2.5 ml abs. ethanol containing 1.2 ml piperidine was heated at reflux for 8 h. The mixture turned cherry red. A voluminous white precipitate of piperidine hydrochloride formed upon maintainence of the mixture for 12 h at about 20°C. The precipitate was purified by reprecipitation from ethanol by the addition of ether with subsequent drying in vacuum to give 0.05 g (71%), mp 238°C [12].

CONCLUSIONS

1. The possibility was demonstrated for the base-catalyzed Knoevenagel condensation of 4-methyl-4-trichloromethyl-2,5-cyclohexadien-1-one with dimedone with the formation of 4-methyl-4-trichloromethyl-1-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2,5-cyclohexadiene.

2. An explanation was offerred for the thermal stability and spectral characteristics of the semiquinoid trienedione obtained assuming polarization of the product molecule due to the presence of two extended $(C=C)_2C=C(C=0)$ cross- π,π,π -conjugation chains.

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^{*}Product (V) has weak fluorescence and does not appear upon the irradiation of chromatographic plates with a UV indicator. Thus, it was developed by placing the plates in an iodine chamber.