the cycle voltamperograms of 0.005 M (I) correspond to the one-electron reversible reduction of (I) to the RA. At rates from 0.1 to 10 V/sec, an oxidation peak (O_2) is observed at −1.23 V (Fig. 1). By analogy with the data of Koppang [2] and Oturan [3], this peak corresponds to oxidation of the dianion. The dependence of the heights of the O_2 and O_1 peaks on the potential scan rate is qualitatively identical to that described for 9-cyanoanthracene [3]. The characteristic change of the cyclic voltamperograms upon an increase in the concentration of (I), consisting in a decrease in the $I_a^{O}1/I_c^{R}1$ ratio and increase in the current of the O_2 peak [2], also indicate the reversible dimerization of the RA of (I).

EXPERIMENTAL

The cyclic voltamperograms were taken on an Lp-7e polarograph using a three-electrode cell. The working electrode is a platinum disk with a 0.07-mm^2 area. The auxiliary electrode is a platinum coil, and a saturated aqueous calomel reference electrode was used.

A sample of DMF was distilled over CaH_2. A benzonitrile sample was purified by distillation.

CONCLUSIONS

Cyclic voltamperometric data indicated that the benzonitrile anion-radical undergoes reversible dimerization in DMF containing tetraethylammonium perchlorate.

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DICHLOROACETAMIDES IN THE DARZENS REACTION

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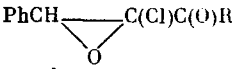
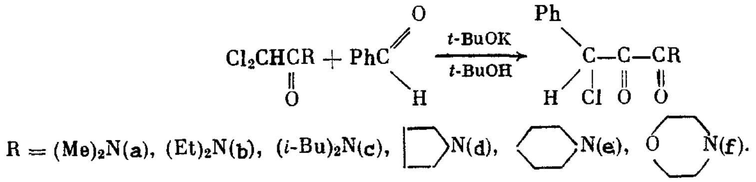
α-Halonitriles [1], diazoketone derivatives [2], α-halothioesters [3], and α-halolactones [4] react with ketones and aromatic aldehydes under the conditions of the Darzens reaction with the formation of the corresponding substituted epoxides. The behavior of dialkylamides of dichloroacetic acid under these conditions has virtually not been studied. In this communication, results are given for the study of the reaction of substituted dichloroacetamides (I) with benzaldehyde in the presence of potassium tert-butylate. The products of this reaction are amides of 3-phenyl-3-chloro-2-ketopropionic acid (II). The structures and purity of (IIa)-(IIf) were confirmed by spectral data and elemental analysis. The formation of amides (II) may be attributed to the isomerization of the intermediate chloroepoxides 



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to more stable products (IIa)-(IIf). We should note that dichloroacetate esters under the conditions of the Darzens reaction similarly give esters of 3-phenyl-3-chloro-2-ketopropionic acid [5].

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.

N,N-Diethylamide of 3-phenyl-3-chloro-2-ketopropionic acid (IIb). A solution of t-BuOK obtained by dissolving 3.5 g (0.09 mole) potassium in 100 ml t-BuOH was added to a mixture of 17.3 g (0.09 mole) (Ib) and 9.54 g (0.09 mole) benzaldehyde at 10-12°C in an argon atmosphere over 1.5 h. The mixture was stirred for 3.5 h and left overnight at about 20°C. After evaporation of t-BuOH on a rotary evaporator, the residue was treated with ether and aqueous NaCl and thrice extracted with ether. The extract was dried sodium sulfate. After the removal of ether, the residue was distilled in vacuum to give 18.0 g (79%) (IIb), bp 126-128°C (0.1 mm), n_D^{20} 1.5278. Found: C 61.40; H 6.18; N 5.48; Cl 14.65%. Calculated for $C_{13}H_{16}NClO_2$: C, 61.55; H 6.30; N 5.55; Cl 14.39%. IR spectrum (ν, cm^{-1}): 1650 (C=O), 1760 (RC=O). PMR spectrum in CCl_4 (δ, ppm): 1.00 t (CH_3), 3.10 q (CH_2), 6.10 s (CHCl), 7.30 s (Ph).

Other amides (II) were obtained analogously.

N,N-Dimethylamide of 3-phenyl-3-chloro-2-ketopropionic acid (IIa) was obtained in 74% yield, bp 112-114°C (0.015 mm), n_D^{20} 1.5385. Found: C 58.43; H 5.07; N 6.27; Cl 15.68%. Calculated for $C_{11}H_{12}NClO_2$: C 58.56; H 5.31; N 6.20; Cl 15.73%. IR spectrum (ν, cm^{-1}): 1660 (C=O), 1730 (RC=O). PMR spectrum (CCl_4, δ, ppm): 2.80 and 2.86 s ($(CH_3)_2N$), 6.10 s (CHCl), 7.26 s (Ph).

N,N-Diisobutylamide of 3-phenyl-3-chloro-2-ketopropionic acid (IIc) was obtained in 70% yield, bp 130-132°C (0.01 mm), n_D^{20} 1.5120. Found: C 65.55; H 7.43; N 4.61; Cl 11.83%. Calculated for $C_{17}H_{24}NClO_2$: C 65.93; H 7.75;; N 4.52; Cl 11.14%. IR spectrum (ν, cm^{-1}): 1660 (C=O), 1740 (RC=O), PMR spectrum in CCl_4 (δ, ppm): 0.73 d, 0.86 d ($(CH_3)_2CH$), 1.36-2.23 m (CH), 2.90, 3.04 (2d) (CH_2), 6.06 s (CHCl), 7.22 s (Ph).

N-Pyrrolidide of 3-phenyl-3-chloro-2-ketopropionic acid (IId) was obtained in 73% yield, bp 160-163°C (0.015 mm) as an oil which crystallizes upon standing, mp 60-62°C (from hexane). Found: C 61.91; H 5.43; N 5.47; Cl 14.31%. Calculated for $C_{13}H_{14}NClO_2$: C 62.04; H 5.56; N 5.56; Cl 14.10%. IR spectrum (ν, cm^{-1}): 1650 (C=O), 1720 (RC=O). PMR spectrum in CCl_4 (δ, ppm): 1.43-2.06 m ($N(CH_2)_2$), 3.00-3.66 m (CH_2CH_2), 6.30 s (CHCl), 7.06-7.53 m (Ph).

N-Piperidide of 3-phenyl-3-chloro-2-ketopropionic acid (IIe) was obtained in 69% yield, bp 146-148°C (0.01 mm), n_D^{20} 1.5505 as an oil which crystallizes upon standing, mp 66-67°C. Found: C 63.12; H 6.00; N 5.31; Cl 13.75%. Calculated for $C_{14}H_{16}NClO_2$: C 63.29; H 6.02; N 5.27; Cl 13.36%. IR spectrum (ν, cm^{-1}): 1675 (C=O), 1750 (RC=O). PMR spectrum in CCl_4 (δ, ppm): 1.23-1.70 m ($N(CH_2)$), 2.96-3.60 m ($CH_2CH_2CH_2$), 6.16 s (CHCl), 7.33 s (Ph).

N-Morpholide of 3-phenyl-3-chloro-2-ketopropionic acid (IIf) was obtained in 72% yield, bp 154-155°C (0.01 mm), n_D^{20} 1.5531. Found: C 58.14; H 5.07; N 5.29; Cl 13.41%. Calculated for $C_{13}H_{14}NClO_3$: C 58.33; H 5.23; N 5.23; Cl 13.26%. IR spectrum (ν, cm^{-1}): 1650 (C=O), 1730 (RC=O). PMR spectrum in CCl_4 (δ, ppm): 2.73-3.33 m (CH_2NCH_2), 3.33-3.76 m (CH_2OCH_2), 6.10 s (CHCl), 7.30 s (Ph).

CONCLUSIONS

The reaction of substituted dichloroacetamides with benzaldehyde in the presence of potassium tert-butylate gave amides of 3-phenyl-3-chloro-2-ketopropionic acid.

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