CONCLUSIONS

1. The reaction of N-chloro-N-sodium-p-chlorobenzenesulfonamide with acrylonitrile in aqueous medium proceeds as cyanoethylation and leads mainly to the formation of N,N-di-(2-cyanoethyl)-p-chlorobenezenesulfonamide.

2. The reaction of allyl chloride with the same chloramine in aqueous medium proceeds through the steps of replacing the allylic chlorine and leads to the formation of N-chloro-N-(allyl)-p-chlorobenzenesulfonamide.

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OXIDATION OF CYCLOHEXENE WITH Ce (IV) SALTS

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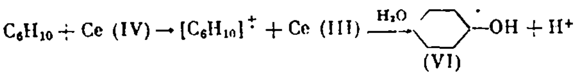
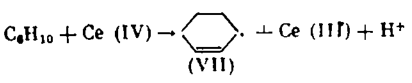
Cerium ammonium nitrate (CAN) is an efficient oxidizing agent for organic compounds. The unsaturated hydrocarbons that were studied in the reaction with CAN included cyclohexene. It is assumed that the 2-nitroxycyclohexyl and cyclohexenyl radicals are generated from cyclohexene in the initial oxidation step. In $CH_3 \cdot CN$ and DMSO, containing Ce(IV), these radicals are converted to cyclohexen-2-ol (I) and 1,2-cyclohexanediol [1].

In the present paper we studied the reaction of cyclohexene (containing ~1% of water) with CAN or cerium ammonium sulfate (CAS) in the absence of a solvent. Both oxidizing agents convert cyclohexene predominantly to (I) and cyclohexen-2-one (II). In addition, cyclohexanone (III) and bicyclohexen-2-yl (IV) are obtained with CAS, while cyclohexanol (V), 3-nitrocyclohexene, and (IV) are obtained with CAN. The obtained data differ from those given in [1], which gave reason to expand the concepts regarding the mechanism of this reaction.

The formation of the saturated products, (II) and (V), evidently serves as evidence that when cyclohexene reacts with Ce(IV) salts an electron can be transferred to the metal ion with the generation of the cation-radical $[C_6C_{10}]^{+\cdot}$, which is then solvated by water [reaction (1)]. The thus formed 2-hydroxycyclohexyl radical (VI) is converted along two directions: it cleaves hydrogen from the H donor (cyclohexene) [reaction (3)] and is oxidized by Ce(IV) [reaction (4)]:



(1)



(2)

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$$(VI) + C_6H_{10} \rightarrow (V) + (VII) \tag{3}$$

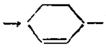
$$(VI) + Ce(IV) \rightarrow (III) + Ce(III) + H^+ \tag{4}$$

Probably only (III) is formed in this manner, in contrast to (V), whose precursor can also be the 2-nitroxycyclohexyl radical. The direct oxidation of (V) to (III) is practically nil under the reaction conditions. This follows from the results of experimentally determining the reactivity of (V) when reacted with CAN and CAS, which proved to be least in the series: (I) > (III), cyclohexene > (V).

The relative reactivity of the enumerated compounds was determined kinetically by the rate of the transition Ce(IV) → Ce(III). The residual amounts of CAN and CAS in the reaction system were established by titration (heterogeneous conditions), and also spectrometrically by the concentrations of Ce(IV) for a homogeneous solution of CAN and oxidized substance in aqueous CH_3CN [2, 3].

The unsaturated products, (I), (II), and 3-nitrocyclohexene, are obtained by the oxidation of (VII), and possibly (VI) [reactions (5)-(7)]. The recombination of two cyclohexyl radicals leads to (IV) [reaction (8)]:

$$(VI) \text{ or } (VII) + Ce(IV) \rightarrow (I) + Ce(III) + H^+ \tag{5}$$

$(VII) + Ce(NO_3)_6^{-2} \rightarrow$  $-NO_2 + Ce(III)$ (6)

$$(I) + 2Ce(IV) \rightarrow (II) + 2Ce(III) + 2H^+ \tag{7}$$

$$2(VII) \rightarrow (IV) \tag{8}$$

Compound (I) is partially dehydrated under the reaction conditions and is converted to bicyclohexen-2-yl ether. The total yield of all of the identified products when based on CAN is 70%, and 15% when based on CAS. The given scheme is in good agreement with the composition of the obtained compounds, and supplements the mechanism proposed in [1] for the oxidation of cyclohexene.

EXPERIMENTAL

The GLC analysis was run on an LKhM-8MD instrument equipped with a flame-ionization detector. The columns were: 1 m × 3 mm with 15% PEGS, both deposited on Chromosorb W (60-80 mesh); the carrier gas was nitrogen. The IR spectra were taken on a UR-20 spectrometer as a thin layer and in CCl_4 solution; the mass spectra were taken on Varian MAT CH-6 and Varian MAT 111 (GNOM) instruments; the NMR spectra were taken on a Bruker WP-60 instrument (internal standard = D_2O). In the kinetic experiments the spectrophotometric measurements of the CAN concentration were run on a Specord UV-VIS spectrophotometer in the 510 nm region at 25°C in 75% aqueous CH_3CN, using a layer thickness of 1 cm. When the reactivity was determined under heterogeneous conditions the Ce(IV) salt was back-titrated with 0.02N $FeSO_4$ solution in the presence of ferroin. The cp $(NH_4)_2Ce(NO_3)_6$ and $(NH_4)_2Ce(SO_4)_3 \cdot 2H_2O$ were used as such. The cyclohexene was distilled through a column and contained ~1% of water (determined by the Fischer method).

Oxidation of Cyclohexene with Cerium Ammonium Nitrate. A mixture of 200 mmoles of cyclohexene a and 20 mmoles of CAN was stirred in an argon atmosphere for 15 h at 70° until the orange color changed to light yellow. Then the mixture was extracted with ether (2 × 30 ml), the ether and unreacted cyclohexene were distilled off, and the amount of reaction products in the residue was determined by GLC using cyclohexanone as the internal standard. We obtained: 2 mmoles of (II), IR spectrum (ν, cm^{-1}): 1685 (C = C – C = O), 1620 (C = C – C = O), and mass spectrum (m/e): 96 (M^+), 68 ($M - C_2H_4$), 55 (CH_2CHCO^+); 0.22 mmole of (V), IR spectrum (ν, cm^{-1}): 3450 (OH), and mass spectrum (m/e): 100 (M^+), 82 ($M - H_2O$), 67 ($M - H_2O - CH_3$), 57 ($CH_2=CHCH=OH^+$); 1.5 mmoles of (I), IR spectrum (ν, cm^{-1}): 1650 (C = C), 3450 (OH), and mass spectrum (m/e): 98 (M^+), 80 ($M - H_2O$), 54 ($M - H_2O - C_2H_2$), 39 ($M - H_2O - C_2H_2 - CH_3$); 0.21 mmole of (IV), IR spectrum (ν, cm^{-1}): 1645 (C = C), and mass spectrum (m/e): 162 (M^+), 81 ($M - C_6H_9$), 53 ($M - C_6H_9 - C_2H_4$); 0.8 mmole of 3-nitrocyclohexene, IR spectrum (ν, cm^{-1}): 1345, 1527 (NO_2), 1650 (C = C), and mass spectrum (m/e): 127 (M^+), 97 ($M - NO$), 81 ($M - NO_2$), 53 ($M - NO_2 - C_2H_4$). NMR spectrum (δ, ppm): 1.8 and 2.5 m (CH_2), 3.7 t (CH), 7.2 m (CH = CH). The products were identified by comparing with the standards. The (IV) standard was prepared from 3-bromocyclohexene by the Grignard reaction (bp 229-230°). Bicyclohexyl was obtained by the hydrogenation of (IV), obtained by the oxidation of cyclohexene, on Ni bromide catalyst at 50° in methanol solution. Mass spectrum (m/e): 166 (M^+), 83 ($M - C_6H_{11}$), 55 ($M - C_6H_{11} - C_2H_4$).

Oxidation of Cyclohexene with Cerium Ammonium Sulfate. To 20 mmoles of CAS was added to 80 mmoles of cyclohexene and the mixture was stirred in an argon atmosphere for 45 h at 70°. The subsequent workup was the same as described above. The internal standard was cyclohexanol. We obtained: 0.45 mmole of (II), 0.3 mmole of (I), 0.15 mmole of (IV), and 0.15 mmole of (III), IR spectrum (ν, cm^{-1}): 1720 (C =O), and mas spectrum (m/e): 98 (M^+), 69 ($M - C_2H_5$), 55 ($CH_2CHC \equiv O^+$), 42 ($C_3H_6^+$).

Bicyclohexen-2-yl ether was identified in the products of oxidizing cyclohexene with CAN and CAS. Infrared spectrum (ν, cm^{-1}): 1080 (C – O – C), 1650 (C =C). NMR spectrum (δ, ppm): 1.8 (12H, CH_2), 3.8 (2H, CH), 5.5 (4H, CH =CH).

CONCLUSIONS

Together with the main products, namely cyclohexen-2-ol and cyclohexen-2-one, the oxidation of cyclohexene with cerium ammonium nitrate or cerium ammonium sulfate gives cyclohexanol and cyclohexanone, which are probably formed by the cation-radical mechanism.

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MONOTHIO-β-DIKETONES WITH A 1,1,2,2-TETRAFLUOROETHYL MOIETY AND THEIR METAL CHELATES

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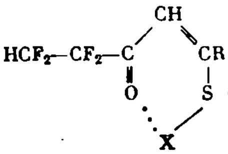
β-Diketones and their metal chelates have a number of valuable properties and find wide application [1]. Their closest structural analogs, the monothio-β-diketones, in which one CO group is replaced by the thiocarbonyl group, have received little study up to now, especially the monothio-β-diketones with polyfluoroalkyl substituents.

Monothio-β-diketones (I)-(IV), which contain the 1,1,2,2-tetrafluoroethyl moiety, and also their nickel chelates (V)-(VIII), were obtained in the present paper:



(I)—(VIII)

X = H (I)—(IV); Ni/2 (V)—(VIII). R = CH_3 (I), (V); n-C_4H_9 (II), (VI); $C(CH_3)_3$ (III), (VII); C_6H_5 (IV), (VIII)

All of the monothio-β-diketones were obtained by reacting the corresponding polyfluorinated β-diketones [2] with H_2S in abs. ethanol, saturated with HCl, at −50 to −70°C [3, 4], and were purified by fractional distillation in vacuo. On the basis of [4], the possibility of forming two structural isomers due to the symmetry of the starting β-diketones can be explained by the predominant replacement of the oxygen atom of the CO group attached to the unfluorinated substituent. The nickel chelates (Table 1) were obtained by treating alcohol solutions of the monothio-β-diketones with aqueous nickel acetate solution.

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