$CH_2Br \xrightarrow{-Br} cyclo-C_6H_{11}NHC = \dot{N}_ \begin{array}{c} \text{cyclo-C}_{6}\text{H}_{1}\text{NHCN}\\ \text{(XI)} 0 \\ \end{array} \\ N=0 \\$ -cyclo-C₆H₁₁NCO -H+ $\xrightarrow{\text{H}_2\text{O}} \text{HO}(\text{CH}_2)_2\text{N} = \text{NOH} \xrightarrow{-N_2} \text{HO}(\text{CH}_2)_2\text{OH}$

EXPERIMENTAL

The synthesis of NAU is described in [4]. The buffer solutions were obtained according to [5]. The pH was monitored by using a Radelkis OP-208/1 digital pH meter. The change in the NAU concentration was followed spectrophotometrically on a SF-26 apparatus with a ShCh-1312 digital voltmeter at wavelengths corresponding to the λ_{max} of the compounds in the visible region.

CONCLUSIONS

1. The dependence of the rate of decomposition in aqueous solutions of dialkyl substituted nitrosoureas based on monoquaternary alkylammonium salts on pH conforms to the ElcB mechanism of decomposition.

2. A new compound of the chloroethylnitrosourea class has been discovered. Its rate of decomposition in neutral and weakly alkaline media is independent of pH.

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REPLACEMENT OF HALOGEN IN α -HALONITRO-COMPOUNDS OF THE ALIPHATIC SERIES.

3.* PREPARATION AND PROPERTIES OF SODIUM SALTS OF ESTERS OF

NITROSULFOACETIC ACID

- A. I. Yurtanov, A. V. Yarkov,
- T. I. Ignat'eva, V. O. Zavel'skii,
- B. K. Beznosko, O. V. Novikova,
- V. N. Semyonova, and I. V. Martynov

Substitution of halogen atoms in chloronitro- and bromonitroacetic acid (CNA, BNA) by other radicals is a practical problem the solution of which opens up a route to the synthesis of many types of compound including α -aminoacid precursors. There is little information on the properties of the C-Hal bond in these compounds; only the replacement of halogen by hydrogen using catalytic hydrogenation [1], and the action of triphenylphosphine [3] and sodium dithionite [2] are known. Alkyl esters of CNA and BNA do not take part in a Grignard reaction with alkyl bromides nor in a Friedel-Crafts reaction with benzene or toluene in the presence of AlCl3. This is evidence of the inadequate polarization of the C-Hal bond in esters of CNA and BNA.

*For previous communications, see [1, 2].

Institute for Physiologically Active Substances, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2549-2556, November, 1988. Original article submitted April 28, 1987.

UDC 542.91:547.465.1'26-38

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(IIIa)	CH3	32,8	107 - 108	15,03	2,22	5,75	$C_3H_4NNaO_5S$	15,07	2,53	5,87
(q[11])	C2115 *	29,1	120-121	19,70	3,60	5,66	C ₄ H ₆ NNaO ₅ S	18,99	3,19	5,54
(IIIc)	C ₃ II ₇	29,4	123-124	22,28	3,50	5,02	C ₅ II ₈ NNaO ₅ S	22,47	3,77	5,24
(1114)	$C_3II_{7}-i$	36,7	105-107	22,19	3,27	5,34	C ₅ II ₈ NNaO ₅ S	22,47	3,77	5,24
(IIIe)	C,H, *	26,2	121-122	25,67	4,30	5,28	C ₆ II ₁₀ NNaO ₅ S	25,62	4,30	4,08
(II JE)	C ₅ H ₁₁ +	21,0	98-100	30,26	4,41	5,25	C7H12NNaO5S	30,32	4,36	5,05
(IIIg.)	C ₈ H ₁₇	24,3	106-107	35,20	5,60	4,32	C ₉ H ₁₈ NNaO ₅ S	35,60	5,98	4,15
(4(11)	C12H25	16,6	16-91	42,99	6,9%	3,87	C ₁₃ II ₂₆ NNaO ₅ S	42,73	71,7	3,56
(1111)	cyclo-C ₆ II ₁₁	33,7	118-120	30,67	1,20	5,02	G ₇ II ₁₂ NNaO ₅ S	31,27	4,59	4,56
([111])	CH ₂ C ₆ H ₅	29,0	170	33,51	3,19	4,08	C ₈ H ₈ NNaO ₅ S	34,27	3,20	4,44
		_			-			-	-	

*Found, S: for (IIIb) 12.49%, (IIIe) 11.78%. Calculated 12.67, 11.40%, respectively. tAnhydrous product.

TABLE 2. Reaction of (Ia-e) with Na₂SO₃ and NaHSO₃

Reaction	Reaction products, yield, %	Reaction	Reaction prod- ucts, yield, %
(Ib)+NaHSO3	(IIIb). 29, (Ib). 25 (IVb) 33	(Id) +NaHSO ₃ +NaHCO ₃ (Id) (Br) +NaHSO ₂ +NaHCO ₃	(IIId), 17 (IIId), 19
$(Ic) + NaHSO_3$	(III c), 13, (Ic), 42, (IVc), 6	$(Ib) + Na_2SO_3$	(IIIb), 18.5, (Ib), 14,
(Ic) (Br) +NaHSO ₃	(IIIc), 17. (Ic), 32. (IVc), 18	(Id) +Na ₂ SO ₃	(IVb).7 (IIId).13.(Id),
(Id)+NaHSO3	(IIId). 16.(Id), 7.(IVd). 34	$(Id) (Br) + Na_2SO_3$	24. (IVd). 5 (IIId), 16,5,
$(Ia) + NaHSO_3 + NaHCO_2$ $(Ib) + NaHSO_3 + NaHCO_2$ $(Ic) + NaHSO_3 + NaHCO_2$	(III a), 18.4 (III b), 29 (III c), 16.5	$(Ie) + Na_2SO_3$	(Id). 21 (IIIe), 15, (Ie), 24.5

RESULTS AND DISCUSSION

In a previous communication [2] we described the reactions of CNA and BNA (I) with sodium dithionitrite (II) which lead to the formation of previously unknown sodium salts of esters of nitrosulfoacetic acid (III) together with esters of nitroacetic acid (IV) [1].

$$\begin{array}{c} O_2 \text{NCHXCOOR} + \text{Na}_2 S_2 O_4 \xrightarrow{\text{Aqueous ethanol}} & \rightarrow O_2 \text{NCH}(\text{SO}_3 \text{Na}) \text{COOR} + O_2 \text{NCH}_2 \text{COOR} \\ (\text{III} a - j) & (\text{IV} a - j) \end{array}$$

X = C1, Br.

The formation of compounds (IIIa-j) (Table 1) formally takes place through the replacement of a chlorine or bromine atom in (I) by a sodium sulfo-group. Among the products of the reaction NaCl, SO₂ (7-9 mole %), and CO₃ (3-5 mole %) were observed. The pH of the reaction mixture was close to neutral. The presence of CO₂ among the reaction products is evidence of decarboxylation of the starting material and possibly of the reaction products. It is well known [4] that CNA, for example, readily undergoes decarboxylation. Compounds (IIIa-j) were stable, white, crystalline solids. The earlier members of the series were freely soluble in water but less soluble in alcohol. With increasing complexity of the ester radicals, the later members of the series (IIIg-j) dissolved less readily in water.

The sodium salts are also formed by reaction of (I) with sodium sulfite or bisulfite

$$(I) + Na_2SO_3(NaHSO_3) \xrightarrow{Aqueous ethanol} (III) + (IV)$$

The yield of (III) in these reactions is, on the whole, somewhat lower than when using (II) (Tables 1, 2). In addition, the use of Na_2SO_3 results in contaminated (III). All three reactions take place with evolution of heat (up to 40-60°C) and the reaction mixture acquires a yellow color. However, when Na_2SO_3 and $NaHSO_3$ are used no gaseous products separate.

With the object of studying the reactivity of (I) in the form of sodium salts, the same reactions were carried out in the presence of $NaHCO_3$. The reaction of (I) with sodium sulfite in the presence of a double quantity of $NaHCO_3$ led only to the formation of the sodium salts of the CNA esters (V). Reducing the amount of $NaHCO_3$ made it difficult to isolate the pure products

$$(Ia, b, j) + Na_2SO_3 + 2NaHCO_3 \xrightarrow{Aqueous ethano1} Na^{\dagger}[O_2NCXCO_2R]^{-} (Va, b, j)$$

In the reaction of (I) with NaHSO₃ in the presence of an equimolar quantity of NaHCO₃, (II) is formed (Table 2). Evidently, the reaction first yields Na_2SO_3 which then enters into a sulfonato-dehalogenation reaction. The use of a double and triple excess of NaHCO₃, as in the previous case, leads to (V).

The reaction of (I) with (II) in the presence of an equimolar quantity of $NaHCO_3$ proceeds with splitting off of the nitro-group, which is difficult to explain, and replacement of the halogen by SO_3Na , the reaction product being the sodium salt of an ester of sulfoacetic acid (VIb, d).

$$(\mathrm{lb},\mathrm{d})+\mathrm{Na}_{2}\mathrm{S}_{2}\mathrm{O}_{4}+\mathrm{Na}\mathrm{HCO}_{3}\xrightarrow{\mathrm{Aqueous}}-\xrightarrow{\mathrm{ethanol}}\mathrm{NaO}_{3}\mathrm{SCH}_{2}\mathrm{CO}_{2}\mathrm{R}\quad(\mathrm{VIb},\mathrm{d})$$

The mechanism of the nucleophilic oxidation-reduction replacement of halogen by a sulfogroup apparently comprises attack of the line pair of electrons of the S(IV) atom on the electron-deficient central C atom with the formation of a C-S bond and conjugate oxidation of S(IV) to S(VI) and elimination of a halogen anion

Group	(IIIa)	(IIIb)	NaO ₃ SCH ₂ CO ₂ Et (VIb)	NaO ₃ SCH ₂ NO ₂ (VIII)
vH₂O δH₂O	3530 s 3493 s, 1646av (IR)	3603 s , 3570 s , 1628 av (IR)	_	
vCH	2990 av (Raman)	2990 av (IR)	_	3052 av, 2978av (IR)
vC=0	1760 s (IR, Raman)	1750 s (IR,Raman)	1733 s (IR)	-
vasNO2	1575.1560 s(IR). w (Raman)	1573. 1559 s (IR). w (Raman)	-	1586 s, 1551 s (IR)
vsNO2	1373 s <u>(R</u> aman)	1350 s (Raman)	-	1395 av, 1384 av (Raman)
vasSO3	1290. 1260 v.s. (IR). w (Raman)	1300.1255 v.s. (IR), w (Raman)	1270 v.s.(IR)	1268 v.s. 1254 v.s 1233 v.s. (IR)
vasCOC	1230 s (IR), w (Raman)	1230 s(IR),w (Raman)	1230 s (IR)	-
v _s SO ₃	1070 av (IR),s (Raman)	1065 av(IR), s (Raman)	1065 av 1044 av (IR)	1070 av 1063 av, (IR)
vsCOC	1015 av (IR, Raman)	1020 av(IR, Raman)	1044-1030 sh (IR)	-
vCN	890 s (Raman)	877 s (Raman)	-	l. –

TABLE 3. Vibrational Spectra of Compounds (III), (VI), (VIII) (v, cm⁻¹)

 $2Na^{+} O \xrightarrow{- S: + CH \rightarrow NO_{2}} X \xrightarrow{- NaX} O \xrightarrow{- S - CH} O \xrightarrow{- S - CH} O \xrightarrow{- NaX} O \xrightarrow{- NaX} O \xrightarrow{- No_{2}} O \xrightarrow{-$

Replacement of halogen atoms in alkyl halides by Na and K sulfites would seem to take place by a similar mechanism (the Strecker reaction [5]), as also does the reaction of sodium sulfite with α -chloronitroethane [6]. The salts (V), because of the increase in the electron density on the central carbon atom in comparison with (I), are capable of entering into a sulfonato-dehalogenation reaction under these conditions. The nitroesters (IV) evidently are products of the hydrolysis of the concurrently formed anhydrides Na⁺[0₃SON(0)CHCO₂R]⁻.

As aliphatic nitrocompounds containing a mobile H atom in the α -position, (I) are converted by NaOH into salts of esters of nitrosulfoacetic acid (VII)

 $O_2NCH(SO_3Na)COOR \xrightarrow{NaOH} Na^+[O_2NC(SO_3Na)COOR]^-$ (VII)

Reaction of (VII) with HCl in dry ether leads again to (III). In spite of an excess of HCl, over a period of one day no acidification of the SO_3Na group to SO_3H takes place.

The chief bands in the vibrational spectra of compounds (III), (VI), and (VIII) are in agreement with their structures (Table 3). Assignment of the δ HOH peak in (I) was effected by replacing H₂O by D₂O (recrystallization from D₂O). The absorption bands for C=O in (III) and (VI) and for the nitro group in (III) and the Na salt of nitrosulfomethane (VIII) [2] appeared in characteristic regions of the spectrum [7, 8]. Thus, replacement of the α -methyl proton by the SO₃Na group does not result in a shift of the vibrational frequency of the ester carbonyl which is characteristic for (VIIb, d) and the salts of the chloronitroacetic esters [9]. The shift of the C=O bands of (VIIb, d) by 60-80 cm⁻¹ into a longer-wave region in comparison with (Ib, d) is evidence of a shift of electron density in the direction of the ester group of its more uniform distribution in the anion of (VII), and of the planarity of the latter.

The doublet nature of the vibrational bands $v_{as}NO_2$, v_sNO_2 , $v_{as}SO_3$, and several other bands in the spectra of crystalline samples of (II) and (VIII) is associated with the effect of packing in the crystal cell which leads to nonequivalence in the molecule. This is demonstrated by the disappearance of the doublets in aqueous (D₂O) solution, the bands acquiring a regular, uniform contour.

Three broad absorption bands are observed in the UV spectra of aqueous solutions of (IIIa-h): weak, ~400 nm; more intense, ~280 nm; and most intense, ~200 nm (Table 4). According

TABLE 4. UV Spectra (λ , nm), Extinction Coefficients [(2-5) · 10⁻⁴ M] and CH-Acidity (μ = 0.1, 25°C) of Compounds (III), (VI), (VIII) in Water

Compound	$\lambda_1(\epsilon_1)$	$\lambda_2(\varepsilon_1)$	$\lambda_{-3}(\epsilon_2)$	pKa
(IIIa) (IIIb) (IIIc) (IIId) (IIIe) (IIIf) (IIIf) (IIIf) (VIb) (VIb) (VIb)	$\begin{array}{c} 396 (13) \\ 400 (20) \\ 398 (17) \\ 398 (27) \\ 398 (27) \\ 398 (16) \\ 399 (24) \\ 400 (7,5) \\ 396 (11) \\ 398 (15) \\ 399 (13) \\ 398 (20) \end{array}$	284 (220) 281 (200) 280 (190) 279 (190) 280 (180) 282 (190) 279 (130) 284 (220) 	203 (5510) 202 (5860) 202 (5090) 202 (5500) 202 (5290) 200 (5390) 206 (12520) 213 (sh) (160), 190 (560) 206 (sh) (490), 190 (890) 202 (7420)	$\begin{array}{c} 6.102{\pm}0.005\\ 6.257{\pm}0.004\\ 6.330{\pm}0.005\\ 6.381{\pm}0.005\\ 6.347{\pm}0.006\\ 6.339{\pm}0.007\\ 6.394{\pm}0.004\\ 6.084{\pm}0.008\\ 12.24{\pm}0.03\\ 11.56{\pm}0.03\\ 8.82{\pm}0.04 \end{array}$

TABLE 5. Chemical Shifts (δ , ppm) in Proton and Carbon-13 NMR Spectra of Compounds (III), (VI), (VIII)

Com- pound	'Η	٦٤
(IIIb)	6.35(CH), 4.235(CH ₂), 1,235(CH ₃), (DMSO - d_{6} , TMS)	161.33(C=O). 97.78(CH), 63.02(CH ₂), 14.16(CH ₃) (DMSO- d_6 , TMS)
(III b)	6.44(CH), 4.42(CH ₂), 1,35(CH ₃), (CD ₂ OD, TMS .)	<pre>161.06(C=O), 96,5(CH). 65,28(CH₂), 13.17(CH₃) (D₂O, TMS in coaxial capillary)</pre>
(IIIe)	6,31(CH), 4.17(1-CH ₂), 1,57(2-CH ₂), 1.35(3-CH ₂), 0,88(CH ₃), DMSO-d ₆ , TMS)	160.9 (C=O), 97,48 (CH), 65,77, 29.9 (2-CH ₂), 18.31 (3-CH ₂), 13,43 (CH ₃) (DMSO- d_6 , TMS)
(VI b)	4.23(CH ₂), 3.96(CH ₂ CH ₃), 1,13(CH ₃), (DMSO-d ₆ , TMS)	167.81(C=O). 65,04(SCH ₂). 65.37(CH ₂ CH ₃), 13.19(CH ₃) (D ₂ O, TMS in coaxial capillary)
(VIII)	5,35 (DMSO-d ₆ , TMS)	87,19 (D ₂ O, TMS in coaxial capillary)

to [10], the absorption of the carbonyl groups in (VIa, b) give characteristic absorption bands at $\lambda_{max} \sim 210$ and 190 nm, corresponding to $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions and the nitro group absorptions in (VIII) appear at λ_{max} 278 and 202 nm.

Comparing the absorption spectra of compounds (IIIa-h) and (VIa, b) and (VIII), one can assign the bands with λ_{max} 202 nm in the spectra of (IIIa-h) both to C=O absorptions and to the absorptions of the nitro groups. In accordance with [10], the bands with λ_{max} ~280 nm are also assigned to nitro group absorptions and those at ~400 nm to absorptions of the SO₃²⁻ group.

The chemical shifts in proton and carbon-13 NMR of (III), (VI), and (VIII) in different solvents are set out in Table 5. Increase in the number of electron-acceptor substituents in this series leads to a down-field shift of the α -CH proton signal and this is corroborated by the PMR spectra of other related compounds [6, 7, 11, 12]. The chemical shift of the carbonyl C atom of (IIIb, e) is situated at the upfield boundary of the range established for esters which is evidence of an increased electron density thereon in comparison with, for example, (VIb).

The pK_a values of (IIIa-h) (Table 4) are close to those given for ethyl nitroacetate and its analogs [13]. Compound (VIII) is a weaker CH acid than (III) but stronger than nitromethane for which $pK_a = 10.21$ [13].

According to the classification of [14], compounds (IIIa-h) are classed as practically nontoxic substances since their $LD_{50} > 2000 \text{ mg/kg}$ on intraperitoneal ingestion. Thus, replacement of a chlorine atom in esters of chloronitroacetic acid with an SO₃Na group is accompanied by a reduction in toxicity (LD_{50} for esters of chloronitroacetic acid on intragastric ingestion is 830-2300 mg/kg [15]).

EXPERIMENTAL

Infrared spectra of solid samples were run, as mulls in mineral oil, on a Perkin-Elmer PE-283B instrument with a resolution of 4 cm⁻¹. Spectra of solutions in D_2O were recorded on a Bruker IFS-113 V Fourier spectrometer. Raman spectra were run on a Ramanor HG-25 with a 5145 Å Ar laser and a resolution of 4 cm⁻¹. A Bruker CXP-200 Fourier impulse spectrometer was used for the NMR spectra, at 200 MHz for PMR and 50.3 MHz for carbon-13. The conditions are noted in Table 5. Electronic absorption spectra of aqueous solutions of the CH-acids in the visible and UV regions were recorded on a Perkin-Elmer M-551 spectrophotometer in 1 cm quartz cells. Potentiometric titrations were carried out on a Radiometer PHM-82 autotitrator (0.1 M KCl) in an atmosphere of argon free of impurities. The concentration of the CH acids was (2-5) $\cdot 10^{-3}$ M. Carbonate-free KOH was prepared by the method of [16]. Calculation of the acidity values was effected with the program of [17] run on a Nord-10 computer.

The acute toxicity was studied on nonpedigree albino male mice of 20-24 g body weight. Aqueous solutions of the substances under investigation were introduced intraperitoneally. The period of observation was 14 days.

Product yields were calculated, in the majority of cases, from the results of 1-2 experiments and expressed as a percentage on the amount of (I) taken initially. Melting points are uncorrected. Identity of products with known compounds was established on the basis of melting points and infrared spectra. The composition of esters (I) and (IV) as percentages of a two-component mixture was evaluated according to the ratio of the absorption bands in the IR spectra in the 1590-1550 cm⁻¹ (NO_{2as}) and 1765-1740 cm⁻¹ (C=O) regions, the variation of the refractive index of a mixture with the concentration of one of the components, and by liquid chromatography [1]. The error in the determination of the different methods did not exceed 5-7%. The composition of the gases evolved was determined by GLC-mass spectrometry using a Finnigan-4021 instrument with direct introduction of the samples. The Na₂SO₃ and NaHCO3 used were "chemically pure" grade, the Na2S2O5 was "for processing x-ray film," and the Na2S204 and AlCl3 were from Fluka. Solvents were not further purified before use, except for those described as "absolute" which were distilled over Na immediately before use. The esters of CNA and BNA were prepared by the methods of [4, 15, 18]. Determination of C, H, and N was carried out by a gas chromatographic method with a thermal conductivity detector, using an added combustion catalyst. Halogen and sulfur were determined by a titrimetric method in an aqueous-organic medium.

<u>1. Reaction of (Ia-j) with (II).</u> To a mixture of 50 mmoles (II), 50 mmoles (I), and 10 ml 96% ethanol, 5 ml water was added with stirring. The reaction mixture reached 50-60°C and 10-14 mole % of a gas mixture containing SO_2 and CO_2 in the ratio ~2:1 by volume was evolved. If the reaction became too vigorous, the mixture was cooled to 30-40°C. After 15-20 min the mixture was diluted with ethanol to 100 ml, the deposit removed, and the solution evaporated to dryness and ether added to the residue. The solidified residue was recrystallized from alcohol. Results are set out in Table 1. From esters of BNA were obtained: (IIIb) 32%, (IIIc) 27%, (IIId) 32.6%. Where necessary, the samples for analysis were further recrystallized. The ether extracts were evaporated and (I) and (IV) determined.*

<u>2. Reaction of (Ib-d) with NaHSO₁</u>. To a mixture of 25 mmoles (I), 15 mmoles $Na_2S_2O_5$ and 5-10 ml alcohol, 5-8 ml water was added with stirring. The mixture was heated at bp for 15 min. Crystals were deposited from the solution. The reaction mixture was diluted with alcohol and further treatment was as in method 1 (Table 2).

<u>3. Reaction of (Ib, c, e) with Na_2SO_3 .</u> Equimolar quantities of the reagents were mixed and on carrying out the experiment as in method 2, the salts (IIIb, c, e) were obtained (Table 2).

<u>4. Reaction of (Ia-d) with NaHSO₃ in Presence of NaHCO₃</u>. Using method 2, 25 mmoles (I), 25 mmoles NaHCO₃, 15 mmoles Na₂S₂O₅, 5-10 ml alcohol, and 8-12 ml water were mixed. The reaction yielded (IIIa-d) (Table 2).

5. Reaction of (Ib, d) with (II) in Presence of NaHCO₃. Reaction of 25 mmoles (I), 25 mmoles NaHCO₃, and 30 mmoles (II) in alcohol and water by the method of 2 yielded a viscous oil which crystallized after 2-3 h. Two recrystallizations resulted in analytically and spectroscopically pure Na-salts of esters of sulphoacetic acid. NaO₃SCH₂COOC₂H₅ (VIb), yield 2.04 g (43%), mp 250°C (decomp.). Found (%): C 24.6, H 3.33, S 17.9. Calculated for

"The amounts of (I) and (IV) were close to those noted in [1].

C₄H₇NaO₅S (%): C 25.26, H 3.68, S 16.86. NaO₃SCH₂COOC₃H₇-i (VId), yield 2.0 g (35%), mp 212°C (decomp.). Found (%): C 26.31, H 5.68, S 13.84. Calculated for C₅H₉NaO₅S·1.5H₂O (%): C 25.97, H 5.23, S 13.87.

<u>6. Reaction of (Ia, b, j) with Na₂SO₃ in Presence of NaHCO₃.</u> Reaction of 25 mmoles (I), 30 mmoles Na₂SO₃, 7-10 ml alcohol, and 15-20 ml water* by the method of 2 provided readily crystallizable Na-salts of esters of chloronitroacetic acid Na⁺[O₂NCC1COOR]⁻·H₂O: (Va) 41%, (Vb) 53%, (Vj) 28%, identified according to the IR spectra of known samples [9].

7. Preparation of (VII). Concentrated aqueous solutions of 0.253 g (1 mmole) (Ib) and 0.04 g (1 mmole) NaOH were mixed. The solution so obtained was diluted with ethanol over a period of 5-10 min until a sediment readily formed. The resulting crystals were separated and washed with ethanol and ether to yield 0.21 g (82%) (VIIb), mp 241°C (decomp.). A sample was recrystallized from aqueous ethanol for analysis. Found (%): C 19.00, H 1.56, N 5.41. Calculated for $C_4H_5NNa_2O_7S$ (%): C 18.68, H 1.95, N 5.44. A similar method was used to prepare (VIId), yield 0.24 g (88%), mp 274°C (decomp.). Found (%): C 21.91, H 2.08, N 4.91. Calculated for $C_5H_7NNa_2O_7S$ (%): C 22.14, H 2.58, N 5.17.

<u>8. Reaction of (Ib) with Grignard Reagent.</u> The reagent was prepared from equimolar quantities of Mg and isopropyl bromide (on a 0.2 mole scale) in 75 ml absolute ether. It was cooled to 10°C and a solution of 0.1 mole (Ib) in 40 ml absolute ether added dropwise over 30 min. The mixture was stirred for 2 h, heated to bp for 30 min, cooled, and 100 ml 20% H_2SO_4 added dropwise at 20°C. The organic layer was separated, the aqueous layer extracted with ether (3 × 100 ml), and the combined extract dried over Na₂SO₄; the ether was evaporated off and the residue distilled in vacuum. Yield 16.1 g (96%), bp 82-85°C/10 mm, n_D²⁰ 1.4358. The IR spectrum was identical with that of the initial (Ib).

Similar results were obtained when the reaction was carried out in absolute THF or dioxane, and when the ethyl ester of BNA was reacted with ethyl bromide in absolute ether.

<u>9. Reaction of (Ib) with Benzene in the Presence of AlCl₃.</u> A suspension of 0.1 mole AlCl₃ in absolute benzene was stirred, excluding moist air, and a solution of 0.1 mole (Ib) in 20 ml absolute benzene added dropwise at 10-15°C. The mixture was stirred for 2 h at 20°C and 2 h at 30°C; copious evolution of HCl was observed. The resulting mixture was poured onto 150 g crushed ice and after melting the organic layer was separated and the aqueous layer further extracted with 3×50 ml ether. The combined extracts were dried over CaCl₂, evaporated, and distilled in vacuum. The yield was 11.75 g (70%) of a product identical with (Ib) in terms of its IR spectrum, bp 58-60°C/2 mm. A similar result was obtained when the reaction was carried out in toluene.

The authors are grateful to V. I. Kozlovskii for running the chromatography-mass spectrometry analyses of the gas mixtures.

CONCLUSIONS

1. The reaction of esters of chloro- and bromonitroacetic acids (1) with $NaHSO_3$, Na_2SO_3 , and $Na_2S_2O_4$ has resulted in the formation of Na-salts of esters of nitrosulfoacetic acid.

2. In the reaction of (I) with Na_2SO_3 and a double quantity of $NaHCO_3$, Na-salts of esters of halonitroacetic acid are formed, and the reaction of (I) with $Na_2S_2O_4$ and $NaHCO_3$ leads to Na-salts of esters of sulfoacetic acid.

3. Physicochemical methods have been used to determine the spectroscopic characteristics and pK_a of sodium salts of esters of nitrosulfoacetic acids and their low toxicity has been established.

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*The quantity of NaHCO₃ is not stated in the original - Translator.

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CHARACTERISTIC FEATURES OF REACTIONS OF PHENOLATE IONS WITH POLYFLUOROCARBONYL COMPOUNDS

V. I. Dyachenko, A. F. Kolomiets, UDC 542.91:547.562.4'133-128:547.446.5'161 and A. V. Fokin

It has been shown previously [1, 2] that hexafluoroacetone (I) and methyl trifluoropyruvate (II) C-alkylate sodium phenolate, alkyl-, and dialkylphenolates in nonpolar solvents under much milder conditions than with free phenols, which conforms with the increase in the C-nucleopholicity on transition from phenol to phenolate systems. The characteristic feature of these reactions is their regiospecificity, manifesting itself in the exclusive formation of o-alkylation products and in the absence of ortho- and meta-substituents, in the formation also of ortho-ortho-dialkylation products. In the present work, we discuss the influence of the structure of the ambidentate phenolate ion on the conditions and direction of its reactions with (I) and (II), and also give the preliminary results of study of the influence of a counterion and aprotic solvents on these transformations.

Mono-substituted sodium phenolates with electron-acceptor substituents at the o-, m-, and p-positions also react with ketone (I) in Freon-113 under fairly mild conditions exclusively giving the o-alkylation products (III)-(VII) in a 72-96% yield



A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2557-2561, November, 1988. Original article submitted July 31, 1987.