17-keto group, etc. were detected in small amounts. A complete analysis of the reaction mixture will be given in subsequent communications.

The fact that the results of the catalytic ionic hydrogenation are similar to the hydrogenation results obtained with the $Et_3SiH-CF_3COOH$ system confirm the ionic mechanism of the catalytic hydrogenation of the studied systems in CF_3COOH. The catalytic ionic hydrogenation of 8(9),14(15)-bisdehydroestrone in CF_3COOH as the medium, in the presence of $H_3Ir(Ph_3P)_3$, is a convenient method for the synthesis of 8α,9α,14β-estrone, whose yield under these conditions exceeds 80%.

EXPERIMENTAL

A glass test tube, containing 10-40 mg of catalyst, 100-1000 mg of the bisdehydroestrone, and 1-5 ml of CF_3COOH, was placed in a steel autoclave and hydrogenated at an H_2 pressure of 50-100 at for 15-40 h at 50-70°. The CF_3COOH was removed in vacuo, the product was extracted with ether, and the catalyst was separated. The reaction products were analyzed by GLC.

When using PtO_2 the catalyst was first reduced in CF_3COOH, the hydrogenation was run at ~20° and atmospheric H_2 pressure for 1-5 h, and the reaction was stopped when the calculated amount of H_2 had been absorbed. The catalyst was filtered, and the products were analyzed as described above. Hydrogenation in the presence of the silane was run using a substrate:silane:acid mole ratio = 1:2:20, at 25°, for 4 h.

CONCLUSIONS

$(Ph_3P)_2PtCl_2$, $Ru(OCOCF_3)_3$ and $(Ph_3P)_3IrH_3$ in CF_3COOH as the medium catalyze the ionic hydrogenation of bisdehydroestranes.

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PREPARATION OF TRINITROETHYL-SUBSTITUTED SECONDARY AMIDES OF CARBOXYLIC, CARBONIC, AND SULFONIC ACIDS

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The N-trinitroethyl derivatives of the primary amides of carboxylic and carbonic acids were obtained by the condensation of the methylol derivatives of the primary amides with trinitromethane (TNM) [1-4], of unsubstituted amides with trinitroethyl alcohol [5], or by the reaction of TNM salts with N-chloromethyl-substituted primary amides [6].

We proposed two methods for synthesizing the N-trinitroethyl derivatives of secondary amides. The first consists in treating N-chloromethylalkylamides with TNM salts. The reaction with the triethylamine salt of TNM proceeds easily in MeCN or Et_2O and leads in good yields to the N-trinitroethyl-substituted secondary

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TABLE 1. Yields of N-Alkyl-N-trinitroethylamides

Starting compound	(II)		Yield of (II) when based on reaction (I), %	Yield of (II) when based on reaction (2), %
	R	X		
(Ia)	Me	p-$MeC_6H_4SO_2$	71	–
(Ib), (IIIb)	Me	$MeCO_2$	74	50
(Ic), (IIIc)	Me	MeCO	53	57
(Id)	*i*-Pr	$MeSO_2$	75	–
(IIIe)	Me	$MeSO_2$	–	71

TABLE 2. Yield of N-Methyl-N-trinitroethylacetamide (IIc) as a Function of the Solvent and Reaction Time

Solvent	Reaction time at 20°, h	Yield of (IIc), %	Solvent	Reaction time at 20°, h	Yield of (IIc), %
H_2O	2,0	45	H_2O	4,0	28
H_2O	2,5	57	MeOH	2,5	38
H_2O	3,0	36	AcOEt	2,5	68

amides of carboxylic, carbonic, and sulfonic acids.

$$\underset{(Ia\text{-}d)}{XN(R)CH_2Cl} + Et_3N\cdot HC(NO_2)_3 \rightarrow \underset{(IIa\text{-}d)}{XN(R)CH_2C(NO_2)_3} + Et_3N\cdot HCl \qquad (1)$$

$$R = Me,\ X = p\text{-}MeC_6H_4SO_2\ (a),\ MeCO_2\ (b),\ MeCO\ (c);\ R = i\text{-}Pr,\ X = MeSO_2\ (d).$$

The conclusion as to the structure of the obtained compounds was made on the basis of the elemental analysis and the IR and PMR spectral data. The synthesized compounds are either solids or liquids. In contrast to the urethane and sulfamide derivatives, the trinitroethyl derivative of acetamide decomposes when stored under ordinary conditions.

It should be mentioned that, in contrast to the primary amides, the N-chloromethyl-substituted secondary amides do not form the corresponding N-(2,2-dinitroalkyl)amides with the salts of dinitro compounds. Apparently, this is explained by the fact that unstable alkylation products at the oxygen atoms of the nitro groups are obtained.

The second method for synthesizing the N-trinitroethyl derivatives of alkylamides consists in the reaction of TNM with methoxymethylalkylamides.

$$\underset{(III\ b\text{—}e)}{XN(Me)CH_2OMe} + HC(NO_2)_3 \rightarrow \underset{(IIb\ \text{—}e)}{XN(Me)CH_2C(NO_2)_3} + MeOH \qquad (2)$$

$$R = Me,\ X = MeSO_2\ (e).$$

In both methods the yields of the amidomethylation products using TNM are 50-75% (Table 1).

The reaction of TNM with the methoxymethyl derivatives of secondary amides can be run in water, alcohols, or nonhydroxyl solvents. The yields of the condensation products are quite dependent on the reaction time, in which connection the relation bears an extremal character (Table 2).

EXPERIMENTAL

N-Methyl-N-trinitroethyl-p-toluenesulfamide (IIa). To a solution of 1.51 g (0.01 mole) of $HC(NO_2)_3$ in 15 ml of abs. MeCN was first added 1.01 g (0.01 mole) of Et_3N, and then 2.33 g (0.01 mole) of (Ia). The mixture was stirred for 2 h at ~ 20°C. The precipitate was filtered and the solvent was evaporated in vacuo. The solid residue was dissolved in acetone and the product was precipitated with water. We obtained 2.5 g (71%) of (IIa), mp 127.5-128.5° (from $EtOH-C_6H_6$). PMR spectrum (acetone-d_6, δ, ppm): 2.40 s ($Me-C_6H_4$), 2.75 s (MeN), 4.73 s (CH_2), 7.45 q (aromatic H). IR spectrum (ν, cm^{-1}): 1615, 1307, 810 ($C(NO_2)_3$); 1350, 1165 (S = O). Found: C 34.40; H 3.34%. $C_{10}H_{12}N_4SO_8$. Calculated: C 34.50; H 3.45%.

N-Methyl-N-trinitroethylmethanesulfamide (IIe). To 0.76 g (0.005 mole) of $HC(NO_2)_3$ in 10 ml of AcOEt was added 0.77 g (0.005 mole) of (IIIe) and the mixture was stirred for 2 h at ~20°. The white precipitate (0.13 g) was filtered, mp 178-179° (from dioxane). The IR and PMR spectra were identical with those of $MeSO_2N(Me)CH_2N(Me)SO_2Me$. The solution was washed with water, dried over Na_2SO_4, and the solvent was evaporated to give 0.97 g of (IIe) (71%), mp 102-103.5° (from $CHCl_3$). PMR spectrum (in acetone-d_6, δ, ppm): 2.97 s ($Me-SO_2$, MeN); 5.17 s (CH_2). IR spectrum (ν, cm^{-1}): 1625, 1310, 825 ($C(NO_2)_3$); 1350, 1170 (S–O).

N-Isopropyl-N-trinitroethylmethanesulfamide (IId). With stirring and cooling with water, to 1 g (0.0067 mole) of $HC(NO_2)_3$ in 10 ml of abs. MeCN was first added in drops a solution of 0.67 g (0.0067 mole) of Et_3N in 5 ml of MeCN, and then 1.68 g (0.0067 mole) of (Id), the mixture was stirred for 2 h at ~ 20°, 30 ml of abs. Et_2O was added, the white precipitate was filtered, and the solvent was evaporated in vacuo. The residual semicrystalline mass was treated with water and the white solid was filtered and dried in the air to give 1.5 g (75%) of (IId), mp 108.5-109.5° (from CCl_4). PMR spectrum (in acetone-d_6, δ, ppm): 1.21 d (2 Me–CH), 3.05 s (Me−SO$_2$), 4.03 m (CH−N), 5.13 c (CH$_2$). IR spectrum (ν, cm^{-1}):1625, 1312, 815 (C(NO$_2$)$_3$); 1345, 1165 (S=O). Found: C 24.22; H 3.90; S 10.69; N 18.15%. $C_6H_{12}O_8N_4S$. Calculated: C 24.00; H 4.03; S 10.66; N 18.65%.

N-Methyl-N-trinitroethylmethylurethane (IIb). a) With stirring and cooling with ice water, to 1 g (0.0067 mole) of HC(NO$_2$)$_3$ in 10 ml of abs. Et$_2$O was added in drops a solution of 0.67 g (0.0067 mole) of Et$_3$N in 5 ml of abs. Et$_2$O. The mixture was stirred for 5 min until a yellow precipitate appeared, after which a solution of 0.91 g (0.0067 mole) of (Ib) in 5 ml of abs. Et$_2$O was added and the mixture was stirred for 5 h at ~20°. The precipitate was filtered, the solvent was evaporated, and the residual pale yellow oil was distilled to give 1.86 g (74%) of (IIb), bp 66-68° (1 mm), n_D^{20} 1.4680.

b) To 1.33 g (0.01 mole) of (IIIb) in 10 ml of H$_2$O was added 1.65 g (0.011 mole) of HC(NO$_2$)$_3$ and the mixture was stirred for 2.5 h. The obtained oil was separated, dissolved in 50 ml of CH$_2$Cl$_2$, and the solution was washed well with water and dried over Na$_2$SO$_4$. The solvent was evaporated and the residual pale yellow oil was distilled to give 1.27 g (50%) of (IIb), bp 102-103° (2 mm), u_D^{22} 1.4673. PMR spectrum (in acetone-d$_6$, δ, ppm): 2.78 s (Me−N), 3.60 s (Me−CO$_2$), 4.77 s (CH$_2$). IR spectrum (ν, cm^{-1}): 1730 (C=O); 1620, 1320, 820 (C(NO$_2$)$_3$). Found: C 24.82; H 3.26; N 22.80%. $C_5H_8O_8N_4$. Calculated: C 24.82; H 3.18; N 22.20%.

N-Methyl-N-trinitroethylacetamide (IIc). a) With stirring and cooling with ice water, to 1 g (0.0067 mole) of HC(NO$_2$)$_3$ in 10 ml of abs. Et$_2$O was first added in drops a solution of 0.67 g (0.0067 mole) of Et$_3$N in 5 ml of abs. Et$_2$O, and then 0.8 g (0.0067 mole) of (Ic). The mixture was stirred for 5 h at ~ 20°, the precipitate was filtered, and the ether solution was evaporated to give 0.82 g (53%) of (IIc), mp 58-60° (decompn.) (from Et$_2$O).

b) With stirring, to 1.51 g (0.01 mole) of HC(NO$_2$)$_3$ in 8 ml of H$_2$O was added in drops 1.2 g (0.01 mole) of (IIIc), the mixture was stirred for 2.5 h, extracted with CH$_2$Cl$_2$ (4 × 10 ml), washed with NaHCO$_3$ solution, dried over Na$_2$SO$_4$, and the solvent was evaporated in vacuo to give 1.33 g (57%) of (IIc), mp 58-60° (decompn.) (from Et$_2$O). PMR spectrum (in CDCl$_3$, δ, ppm): 2.08 s (Me−CO), 3.08 s (Me−N), 5.10 c (CH$_2$). IR spectrum (ν, cm^{-1}): 1675 (C=O); 1610, 1315, 820 (C(NO$_2$)$_3$). Found: C 25.50; H 3.16; N 23.20%. $C_5H_8O_7N_4$. Calculated: C 25.41; H 3.39; N 23.70%.

CONCLUSIONS

Methods were proposed for the synthesis of the previously unknown N-trinitroethyl derivatives of the secondary amides of carboxylic, carbonic, and sulfonic acids by reacting the N-chloromethyl derivatives of the secondary amides with either trinitromethane salts or the methoxymethyl derivatives of the secondary amides with trinitromethane.

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