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SYNTHESIS OF ALIPHATIC α-IODONITRO COMPOUNDS, N-IODO-N-NITROAMINES, AND N-IODOIMIDES OF OF CARBOXYLIC ACIDS

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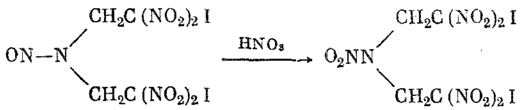
Aliphatic α-iodonitro compounds are difficult to synthesize. They are usually synthesized in low yields by reacting Ag, K, or Na salts of nitro derivatives with iodine [1-4]. The synthesis of iodonitrodimedone by iodination of the potassium salt of nitrodimedone by the complex of ICl with dioxane has been described [5]. α-Iodopolynitroalkanes and their functional derivatives have scarcely been known until now. N-Iodo-N-nitroamines have not been described in the series of N-halo-N-nitroamines. Nevertheless, such compounds are of interest for the study of their properties and physiological activity owing to the presence in them of a positively polarized halogen on a C or N atom. Therefore, the development of convenient methods for the synthesis of α-iodonitro compounds remains a timely problem in the chemistry of nitro derivatives [6].

We found that the potassium salts of polynitroalkanes and their functional derivatives readily react with ICl to form the corresponding α-iodopolynitroalkanes with good yields. The reaction proceeds under mild conditions in a medium of inert solvents or in water. The direction of the reaction is due to the positive polarization of iodine in ICl [7].

$$RC(NO_2)_2K + ICl \rightarrow RC(NO_2)_2I + KCl$$
$$R = NO_2\ (I);\ CH_3(II);\ CH_3OCOCH_2CH_2(III);\ C_2H_5OCOCH_2OCOCH_2CH_2(IV);\ C_2H_5OCOCH_2OCOCH(CH_3)CH_2(V);\ O_2NOCH_2CH_2N(NO_2)CH_2(VI);\ IC(NO_2)_2CH_2OCH_2OCH_2(VII);\ CH_2OCOCH_2N(NO_2)CH_2(XI)$$

The possibility of replacing a mobile hydrogen by iodine has been demonstrated in the case of nitroform. Unlike the case of the potassium salt of nitroform, this reaction results in a small yield of iodotrinitromethane when the reactants are boiled in CCl_4. As the reaction time is increased from 10 to 30 min, the yield of iodotrinitromethane increases from 5 to 36%.

The iododinitromethyl group was found to be stable in concentrated HNO_3. This made it possible to carry out the synthesis of bis(2-iodo-2,2-dinitroethyl)-N-nitroamine (IX) from bis(2-iodo-2,2-dinitroethyl)-N-nitrosoamine (VIII)



$$ON{-}N(CH_2C(NO_2)_2I)_2 \xrightarrow{HNO_3} O_2NN(CH_2C(NO_2)_2I)_2$$

(VIII) (IX)

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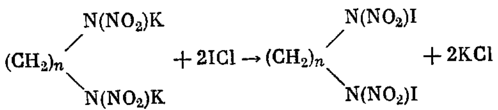
TABLE 1. α-Iodonitro Compounds

Compound	α-Iodo derivative	Yield, %	mp, °C (solvent)	Empirical formula	Found/calculated, %	
					I	N
(I)	Iodotrinitromethane	71	55–56 (n-hexane)	CIN_3O_6	45,64 45,84	15,23 15,16
(II)	2-Iodo-2, 2-dinitroethane	85	–2,5÷–2 (n-hexane)	$C_2H_3IN_2O_4$	51,94 51,70	11,52 11,38
(III)	Methyl 4-iodo-4, 4-dinitrobutyrate	76	59–60 (ethanol)	$C_5H_7IN_2O_6$	40,23 39,93	9,02 8,80
(IV)	Ethyl 4-iodo-4, 4-dinitrobutyrylhydroxyacetate	64	57–58 (methanol –H_2O)	$C_7H_{11}IN_2O_8$	32,73 32,56	7,36 7,17
(V)	Ethyl 2-methyl-4-iodo-4, 4-dinitrobutyrylacetate	60	39–41 (methanol –H_2O)	$C_8H_{13}IN_2O_8$	31,61 31,43	7,16 6,93
(VI)	2-Iodo-2, 2-dinitroethylethanol-N-nitroamine nitrate	68	79–80 (CCl_4)	$C_4H_6IN_5O_9$	32,34 32,15	17,99 17,72
(VII)	Bis(2-iodo-2, 2-dinitroethyl)formal	84	52–53 (HNO_3–H_2O)	$C_5H_6I_2N_4O_{10}$	47,64 47,38	10,71 10,44
(VIII)	Bis(2-iodo-2, 2-dinitroethyl)-N-nitrosoamine	75	87–88 (HNO_3–H_2O)	$C_4H_4I_2N_6O_9$	47,86 47,56	15,92 15,73
(IX)	Bis(2-iodo-2, 2-dinitroethyl)-N-nitroamine	87	137–138 (HNO_3)	$C_4H_4I_2N_6O_{10}$	46,20 46,18	15,35 15,27
(X)	Bis(2-iodo-2, 2-dinitroethyl)ethylene-N,N'-dinitrodiamine	91	161–162 (HNO_3)	$C_6H_2I_2N_8O_{12}$	40,15 39,81	13,43 13,15
(XI)	Methyl 2-iodo-2, 2-dinitroethyl-N-nitroaminoacetate	80	90–91 (CCl_4)	$C_5H_7IN_4O_8$	33,46 33,59	15,02 14,81
(XII)	N,N'-Diiodo-N,N'-dinitroethylenediamine	20	136–137 (acetone–CCl_4)	$C_2H_4I_2N_4O_4$	63,11 63,18	13,81 13,93
(XIII)	N,N'-Diiodo-N,N'-dinitrohexamethylenediamine	19	80–81 (acetone–CCl_4)	$C_6H_{12}I_2N_4O_4$	55,24 55,45	12,45 12,22

The synthesis of nitramine IX by another method is difficult, since in a number of cases 2,2,2-trinitroethyl-N-nitroamines, particularly, bis(2,2,2-trinitroethyl)-N-nitroamine, undergo destruction upon reduction by KI unlike 2,2,2-trinitroethyl-N-nitrosoamines.

The α-iodonitro compounds obtained (Table 1) are white or light yellow crystalline compounds with a weakly expressed tear-exciting activity. The compounds are stable during storage in a cold dark place.

We were also able to involve the potassium salts of N-nitroamines in the reaction with ICl, i.e.,



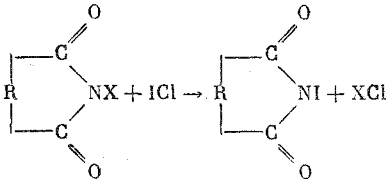
$$(CH_2)_n\begin{cases}N(NO_2)K\\N(NO_2)K\end{cases} + 2ICl \rightarrow (CH_2)_n\begin{cases}N(NO_2)I\\N(NO_2)I\end{cases} + 2KCl$$

$n = 2$ (XII); 6 (XIII) (XII), (XIII)

Unlike the α-iodopolynitroalkanes, the N-iodo-N-nitroamines prepared in this manner are unstable and are readily hydrolyzed by the moisture in the air to form primary nitroamines.

The α-iododinitro derivatives and the N-iodo-N-nitroamines rapidly and quantitatively oxidize KI and undergo reductive hydroxymethylation [8].

The method involving iodination by ICl proved to be suitable for the synthesis of the hard to synthesize N-iodoimides of carboxylic acids, which are sources of "positive" iodine and serve as effective iodinating agents [7], according to the scheme



(XIV), (XV)

R=CH_2CH_2 (XIV); C_6H_4 (XV); X=K, Na

Thus, the reaction involving the replacement of alkali metals in organic compounds by iodine with the aid of ICl is clearly a general reaction. This method of iodination is exceptionally simple and, unlike the other methods, permits more complete utilization of the iodine introduced into the reaction system for the synthesis of the iodo derivative. The last fact may be of great importance in the development of technical methods for the synthesis of iodo derivatives.

EXPERIMENTAL

The potassium salts of the nitro compounds were prepared by the reduction of the respective trinitromethyl derivatives by KI according to the method in [9-12]. The potassium salts of the N-nitroamines were obtained by the iodoalkalinization of the nitroamines by KOH in methanol.

Methyl 4-Iodo-4,4-dinitrobutyrate (III). a. A 0.7-g portion of ICl in 20 ml of CCl_4 was added to a suspension of 1.0 g of the potassium salt of methyl 4,4-dinitrobutyrate [9] in 10 ml of CCl_4 at 10-15°C. The mixture was stirred for 20 to 30 min, and the KCl precipitate was filtered. After the evaporation of the mother liquid and the unreacted ICl, 1.0 g (76%) of III was obtained with mp 59-60°C.

Compounds I, II, IV, V, and VII were obtained in an analogous manner. In the case of the synthesis of VI, VIII, X, and XI, the reaction mixture was heated to boiling for 1 to 2 min.

b. A 1.4-g portion of a freshly prepared solution of ICl in 10 ml of methanol was added with stirring at 5-10°C to a suspension of 2.0 g of the potassium salt of methyl 4,4-dinitrobutyrate in 50 ml of water. A yellow (sometimes dark) precipitate instantly appeared. The latter was separated, washed with water, dried, and reprecipitated by water from a methanolic solution. The yield of III was 2.4 g (88%), mp 59-60°C. The compound did not cause any melting-point depression when mixed with the compound obtained according to method a.

Compounds VIII (82% yield) and X (88% yield) were synthesized in an analogous manner.

Bis(2-iodo-2,2-dinitroethyl)-N-nitroamine (IX). A 0.5-g portion of nitrosoamine VIII was added with stirring at 18-20°C to 15 ml of fuming HNO_3, and the mixture was held at that temperature for 30 to 35 min. The precipitate formed was recrystallized from the reaction mixture, filtered, washed with water, and dried. The yield of IX was 0.45 g (87%), mp 137-138°C.

Iodotrinitromethane (I). A solution of 5.0 g of nitroform and 5.4 g of ICl in 50 ml CCl_4 was boiled for 90 min. Evaporation of the solvent and the unreacted nitroform and ICl yielded 1.0 g (10.9%) of compound I, which did not cause any melting point depression in a mixed sample with a known specimen [1].

N,N'-Diiodo-N,N'-dinitroethylenediamine (XII). An equimolar portion of ICl in 20 ml of CCl_4 was added to 5.0 g of the dipotassium salt of N,N'-dinitroethylenediamine in 40 ml of CCl_4. The mixture was stirred for 2 h at ~25°C, and the precipitate was separated and dried. The material obtained was treated with 50 ml of dry acetone, and XII was precipitated out from the acetone extract by an addition of CCl_4. The yield of XII was 1.8 g.

Derivative XIII was obtained in an analogous manner.

N-Iodophthalimide (XV). A 5.0-g portion of ICl in 15 ml of $CHCl_3$ was added to a suspension of 5.0 g of the sodium salt of phthalimide in 30 ml of $CHCl_3$. The temperature then increased from 20 to 30°C. The mixture was thoroughly stirred with thorough grinding of the lumps, brought up to boiling, and again stirred for 1 h at ~20°C. The precipitate was filtered, washed with $CHCl_3$, dried, and recrystallized from dry CH_3CN or precipitated out from an acetonitrile solution by ethyl ether (prolonged heating in CH_3CN results in decomposition of the product). Evaporation of the chloroform mother liquids yielded an additional amount of N-iodophthalimide. The total yield of XV was 8.8 g (89%), mp 209-212°C. Found: I 45.8%. Calculated for $C_8H_4INO_2$: I 45.6%.

N-Iodosuccinimide (XIV) was synthesized in an analogous manner with a 95% yield, mp 187-190°C. Found: I 55.9%. Calculated for $C_4H_4INO_2$: I 56.6%.

All the compounds were analyzed for the relative concentration of active iodine in them according to the method in [13]. The relative concentration of active iodine in the N-iodo-N-nitroamines and N-iodoimides gradually decreases during storage; therefore, it is recommended that these compounds be used for 1 to 3 days after being synthesized.

CONCLUSIONS

1. The reaction of the potassium salts of polynitroalkanes, their functional derivatives, nitroamines, and imides of carboxylic acids with ICl in a medium of inert solvents or in water results in the formation of the corresponding α-iodonitro derivatives, N-iodo-N-nitroamines, and N-iodoimides of the carboxylic acids.

2. The possibility of the replacement of a mobile hydrogen by iodine when nitroform is reacted with iodine monochloride has been demonstrated.

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THE REACTION OF FLUORINE-CONTAINING β-ALKOXYVINYL KETONES AND β-DIKETONES WITH ISOCYANIDES

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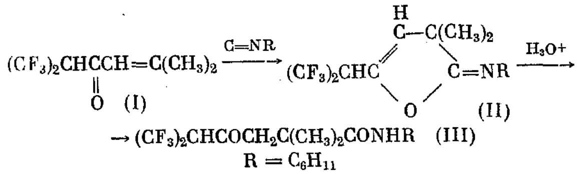
Trifluoromethyl β,β-dimethylvinyl ketone reacts with isocyanides to form 1,4-cycloaddition products [1]. Hexafluoroisopropyl β,β-dimethylvinyl ketone (I) reacts with isocyanides in the same way



Attempted addition of isocyanide to trifluoromethyl β,β-diethoxyvinyl ketone resulted in isomerization of the ketone to the ester as a result of 1,5-alkyl shift from the enolic oxygen to the carbonyl oxygen [2]

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