

## $\alpha$ -MONONITROALKYL DERIVATIVES OF INDIUM

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(Received February 17th, 1972)

### SUMMARY

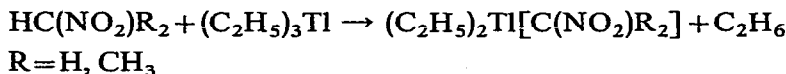
Dealkylation of trialkylindium by  $\alpha$ -mononitroalkane leads to the formation of the previously unknown  $\alpha$ -nitroalkyl derivatives of indium. An investigation of the chemical properties and of the  $^{115}\text{In}$  nuclear quadrupole resonance spectra of these compounds has been undertaken. An analysis of the data obtained from these investigations suggests the existence of intramolecular  $\text{O} \rightarrow \text{In}$  coordination in the  $\alpha$ -nitroalkyl derivatives of indium.

### INTRODUCTION

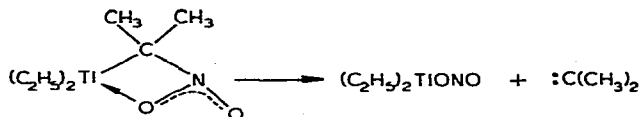
It has been shown earlier<sup>1</sup> that nitromethyl derivatives of mercury are unstable and undergo rearrangement at the instant of formation to give organomercuric fulminates:



Metal derivatives of mononitroalkanes (nitromethane and 2-nitropropane) were obtained only from their reaction with triethylthallium<sup>2</sup>:



Diethyl(2-nitropropyl)thallium was shown to be converted into diethylthallium nitrite under heating. This suggested that the cleavage of dimethylcarbene occurred during this reaction:



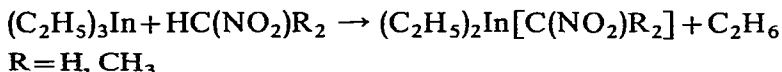
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Other  $\alpha$ -nitroalkane derivatives of diethylthallium decompose to yield the nitrite<sup>3</sup>.

As an extension of this work it was interesting to study the formation and conversion of the  $\alpha$ -nitroalkyl derivatives of indium. These compounds are described for the first time in this paper.

## RESULTS AND DISCUSSION

We have found that the action of nitromethane and 2-nitropropane on triethylindium (in ether and pentane) leads to diethylindium derivatives of these nitroalkanes in good yield:



Trimethylindium etherate also reacts readily with nitromethane. The resulting compounds are solids which hydrolyse readily in air and decompose when heated. The derivatives of 2-nitropropane may be stored unchanged whereas the colourless compounds dimethyl- and diethyl-(nitromethyl)indium become yellow in colour and exhibit some change in their IR spectra. A pure sample of diethyl(nitromethyl)indium decomposed explosively at 100° to give large amounts of a gas (3 moles of gas for the decomposition of each mole of compound) and a black inorganic residue. The gas consisted of a mixture of methane together with some carbon monoxide and dioxide. Rapid decomposition of the yellow samples of dimethyl- and diethyl-(nitromethyl)indium resulted in the formation of the corresponding fulminates.

An analysis of the decomposition products of the diethyl(1-methyl-1-nitroethyl)indium indicated the formation of tetramethylethylene. This result confirms the prediction<sup>2</sup> that carbenes are formed as a result of the decomposition of such compounds. According to this hypothesis such decomposition is the result of the intramolecular interaction of the metal atom with the oxygen atom of the nitro group:



The resulting diethylindium nitrite is apparently very unstable and decomposes readily. Attempts to prepare it directly lead to the formation of a complex mixture of products.

In order to examine the suggestion in the above hypothesis that intramolecular O→In coordination occurs in nitroalkylindium compounds, we have studied the <sup>115</sup>In NQR spectra of these compounds. The <sup>115</sup>In NQR spectra obtained are listed in Table 1. Since the spin of the <sup>115</sup>In nucleus is 9/2 (*I* = 9/2) four transition frequencies occur in the spectra: ( $\pm 1/2 \leftrightarrow \pm 3/2$ ), ( $\pm 3/2 \leftrightarrow \pm 5/2$ ), ( $\pm 5/2 \leftrightarrow \pm 7/2$ ) and ( $\pm 7/2 \leftrightarrow \pm 9/2$ ). The spectra of most of the compounds investigated consist of a single line (for each transition), indicating that one crystallographically independent molecule exists in the elementary cell. A small crystallographic splitting of the lines in the (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>In and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>In[C(CH<sub>3</sub>)<sub>2</sub>NO<sub>2</sub>] spectra has been observed.

TABLE 1

NUCLEAR QUADRUPOLE INTERACTION FREQUENCIES OF THE  $^{115}\text{In}$  AND  $^{69}\text{Ga}$  ISOTOPES IN SOME INDIUM AND GALLIUM DERIVATIVES (at 77°K)

Compound	NQR frequencies $\nu$ (MHz) (accuracy $\pm 0.01$ )				$e \cdot Q \cdot q_{zz}$	$\eta$ (%)
	$1/2 \leftrightarrow 3/2$	$3/2 \leftrightarrow 5/2$	$5/2 \leftrightarrow 7/2$	$7/2 \leftrightarrow 9/2$		
$\text{Me}_3\text{In}$	53.90	90.90	138.91		1115.1	14.0
	50.93 <sup>a</sup>	90.39	137.35		$1101.7 \pm 1.0$	$11.3 \pm 0.1$
$\text{Et}_3\text{In}$	51.44	93.06	141.40	188.50	1135.2	10.7
	52.12	95.53	143.16	193.16	1159.6	9.6
$\text{Et}_3\text{In} \cdot \text{OEt}_2$	43.00	84.94	127.61		1024.0	3.9
$\text{Et}_2\text{InCl}$	57.90	92.45	142.13		$1142.7 \pm 2.0$	$16.4 \pm 0.1$
$\text{Et}_2\text{InBr}^b$	54.30	94.73	144.25	192.64	$1158.0 \pm 1.3$	$12.2 \pm 0.1$
$\text{Et}_2\text{InCMe}_2\text{NO}_2$	72.36	74.25	117.00	158.60	$962.6 \pm 1.0$	
	72.36	74.25	117.00	158.60	$962.6 \pm 1.0$	$36.7 \pm 0.1$
	73.19	74.87	118.04	159.90	$970.4 \pm 1.0$	
$\text{Et}_2\text{InCH}_2\text{NO}_2$		75.09	118.50		$970.0 \pm 1.0$	$34.0 \pm 0.5$
$\text{Me}_2\text{InCH}_2\text{NO}_2$		73.07	115.28		$945 \pm 2$	$34.8 \pm 1.5$
$\text{Me}_3\text{Ga}^{c,d}$	80.99					
	80.35					
	81.01					
	81.17					
	81.47					
$(\text{InI}_3)_2^e$	36.718	26.864	37.420		327.2	65.04

<sup>a</sup> Temperature 296°K. <sup>b</sup>  $\nu(^{79}\text{Br}) = 74.73$  MHz. <sup>c</sup> Since the spin of  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$  is 3/2, only one line is observed in the NQR spectra which may be attributed to the ( $\pm 1/2 \leftrightarrow \pm 3/2$ ) transition. In the case of trimethylgallium a two phase spectrum was observed, one phase consisting of one (80.99 MHz) and the other of four crystallographically independent molecules. <sup>d</sup>  $\nu(^{71}\text{Ga}) = 51.06$  MHz. <sup>e</sup> Spectrum reported by H. Brooker and T. Scott (ref. 9).

The trimethylindium molecule is known to have a planar configuration<sup>4</sup>. Since the quadrupole constants  $e \cdot Q \cdot q_{zz}$   $^{115}\text{In}$  of trimethyl- and triethyl-indium<sup>8</sup> are rather close to each other, it is not unreasonable to expect that the triethylindium structure is similar to that of trimethylindium. The  $p_z$ -orbital of the indium atom is essentially unoccupied in these compounds, so that the change in the hybridization of the valence orbitals of the indium atom during complexing and the partial occupation of its hybrid  $p_z$ -orbital at the expense of the donor atom in the triethylindium-ether complex leads to a 10% reduction in the observed quadrupole constant and also to some reduction in the asymmetry parameter ( $\eta$ ).

In the nitroalkyl derivatives of indium the quadrupole constants were found

to be some 16% less in comparison with those of triethylindium, indicating an increase in the coordination number up to 4 (giving a tetrahedral configuration for the indium atom). However, a simultaneous large increase in the asymmetry parameter indicates that some deviation from the correct tetrahedral configuration occurs.

Such a sharp change cannot be due to unsymmetrical substitution of the indium atom because, unlike the nitroalkylindium derivatives, the quadrupole constant  $e \cdot Q \cdot q_{zz}$  for diethylindium chloride was found to be practically the same as that for triethylindium, but the increase in the asymmetry parameter for diethylindium chloride is nowhere near as large as that for the nitroalkylindium derivatives. Furthermore, the additional coordination interaction M-X is known to lead to a sharp increase in the asymmetry parameter of the metal atom and, as a rule, to a decrease in the quadrupole constant [see, for example, the NQR spectra of the dimeric molecules  $(\text{InI}_3)_2$  and  $(\text{InBr}_3)_2^{5-7}$ ].

One can only conclude, therefore, from this data that In-O coordination occurs in nitroalkyl derivatives of indium. Cleavage of dimethylcarbene ( $:\text{CMe}_2$ ) from the 1-methyl-1-nitroethyl derivatives of indium provides further evidence in favour of the intramolecular character of this coordination.

## EXPERIMENTAL

### *(Nitromethyl)diethylindium\**

Triethylindium (4.1 g; 0.02 mole) was added to a solution of 1.23 g (0.02 mole) of nitromethane in 20 ml of pentane which was cooled with ice and stirred. On slow heating up to room temperature a white precipitate was formed. After filtering and drying in a vacuum 1.16 g (25%) of (nitromethyl)diethylindium were obtained. (Found: C, 25.73; H, 5.20; N, 6.16; In, 49.50.  $\text{C}_5\text{H}_{12}\text{O}_2\text{NIn}$  calcd.: C, 25.75; H, 5.15; N, 6.01; In, 49.36%.)

Storage of the mother liquor at room temperature led to the formation of a yellow precipitate. Its IR spectrum exhibited bands characteristic of (nitromethyl)diethylindium together with broad bands at 1180 and  $650\text{ cm}^{-1}$ . The total amount of the precipitated material was 4.1 g (87%). The presence of the nitromethyl group was demonstrated by hydrolysis followed by the identification of nitromethane. At  $90-91^\circ$  the white sample became yellow. Tests using sulphanilic acid and  $\beta$ -naphthol indicated the presence of the nitrite ion.

The (nitromethyl)diethylindium (0.35 g; 0.0015 mole) was decomposed at  $100^\circ$  in an autoclave over a period of 6 h. The solid residue obtained consisted mainly of diethylindium fulminate which was identified by its IR spectrum (a band at  $2200\text{ cm}^{-1}$ ).

(Nitromethyl)dimethylindium was prepared in a similar manner. Its IR spectrum was identical with that of (nitromethyl)diethylthallium<sup>1</sup>. (Found: N, 6.74.  $\text{C}_3\text{H}_8\text{O}_2\text{NIn}$  calcd.: N, 6.83%.)

### *(1-Methyl-1-nitroethyl)diethylindium*

In a similar manner, 1.96 g (75%) of (1-methyl-1-nitroethyl)diethylindium (m.p.  $123-125^\circ$ ) was obtained from 2-nitropropane (0.89 g, 0.01 mole) in 7 ml of dry

\* All indium compounds prepared are oxidized in air.

ether and triethylindium (2.02 g, 0.01 mole). (Found: C, 32.13; H, 6.12; N, 5.58; In, 44.3.  $C_7H_{16}O_2NIn$  calcd.: C, 32.20; H, 6.13; N, 5.36; In, 44.06%.)

(1-Methyl-1-nitroethyl)diethylindium (1 g; 0.0038 mole) was decomposed by heating in boiling isopropylbenzene (30 ml) at 152°. Gas-liquid chromatographic analysis of the solution showed the presence of tetramethylethylene which was identical to a specially synthesized sample.

The NQR spectra were measured by means of an impulse spectrometer-relaxometer ISS-1 at 77°K.

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