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MICHAEL ADDITION OF A 5-NITRO-1,3-DIOXANE *

ADDYCJA MICHAELA 5-NITRO-1,3-DIOKSANU

by Hanna PIOTROWSKA, Tadeusz URBAŃSKI, and Irena KMIOTEK

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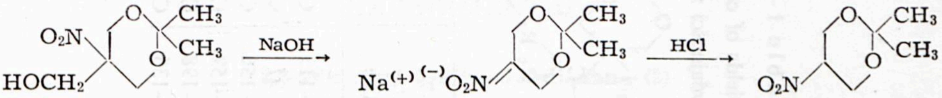
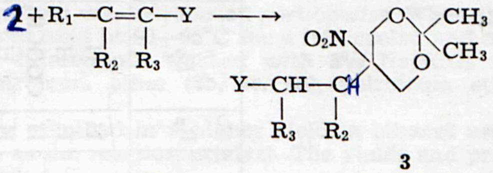
Continuing our research on 5-nitro-1,3-dioxane derivatives we prepared a new series of Michael adducts using 2,2-dimethyl-5-nitro-1,3-dioxane (**2**) as the active hydrogen donor. Compound **2** is easily accessible by cautious acidification of its sodium salt which is formed by treating 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane [1] (**1**) with 10% sodium hydroxide. This method gives much better results than the direct cyclization of 2-nitropropanediol-1,3 with acetone described by Linden and Gold [1].


1 **2**

Compound **2** was then subject to Michael reaction with acrylonitrile, methyl acrylate, methyl benzylidenemalonate, benzylideneacetone, ω-nitrostyrene and cinnamaldehyde. The reaction was carried out at 60—70°C in dioxane solution using in most cases Triton B as the catalyst. The reaction with ω-nitrostyrene was carried out in presence of diethylamine, and it was found that in the instance of cinnamaldehyde the highest yields were obtained when the addition was done in ethanolic sodium ethoxide medium.


3

3a: $R_1 = R_2 = R_3 = H$, $Y = CN$
3b: $R_1 = R_2 = R_3 = H$, $Y = COOCH_3$
3c: $R_1 = C_6H_5$, $R_2 = H$, $R_3 = Y = COOCH_3$
3d: $R_1 = C_6H_5$, $R_2 = R_3 = H$, $Y = COCH_3$
3e: $R_1 = C_6H_5$, $R_2 = R_3 = H$, $Y = NO_2$
3f: $R_1 = C_6H_5$, $R_2 = R_3 = H$, $Y = CHO$

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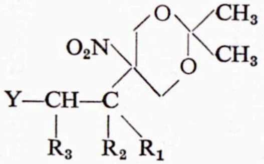
* Part CIX on Chemistry of Nitroparaffins. Part CVIII: Piotrowska H., Urbański T., Sienicki W., *Roczniki Chem.*, 47, 193 (1973).

Table 1 — Tablica 1

Properties and yields of compounds of general structure

Własności i wydajności związków o ogólnym wzorze



3

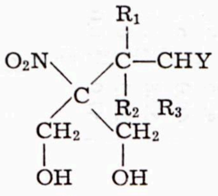
Compound No Nr związku	R_1	R_2	R_3	Y	Yield Wyd. %	M.p. t.t. °C	Empirical formula Wzór sumaryczny	Analysis — Analiza, %					
								Calcd. — obliczono			Found — otrzymano		
								C	H	N	C	H	N
3a	H	H	H	CN	91	112—113	$C_9H_{14}O_4N_2$	50.5	6.5	13.1	50.5	6.7	13.2
3b	H	H	H	$COOCH_3$	80	96—97	$C_{10}H_{17}O_{\cancel{5}6}N$	48.6	6.9	5.7	48.7	6.9	5.8
3c	C_6H_5	H	$COOCH_3$	$COOCH_3$	86	155—156	$C_{18}H_{23}O_8N$	56.7	6.1	3.6	56.9	6.2	3.8
3d	C_6H_5	H	H	$COCH_3$	76	158—159	$C_{10}H_{21}O_5N$	62.5	6.8	4.7	62.7	7.0	4.7
3e	C_6H_5	H	H	NO_2	24	196—198	$C_{14}H_{18}O_0N_2$	54.2	5.8	9.0	54.3	5.9	9.2
3f	C_6H_5	H	H	CHO	70	135—136	$C_{15}H_{19}O_5N$	61.4	6.5	4.8	61.6	6.6	4.9

All compounds **3** were crystalline solids of sharp melting points. The presence of two identical substituents in the position 2 of the dioxane ring excluded the possibility of *cis-trans* isomer formation.

Compound **3a** was also prepared directly from **1** by dissolving it in 10% sodium hydroxide solution and shaking with acrylonitrile. This method failed with other acceptors.

The yields and properties of compounds **3** are collected in Table 1.

Dioxanes **3** are readily subject to ring opening by heating with hydrochloric acid in aqueous methanol or aqueous dioxane solution to yield the corresponding 2 substituted 2-nitropropanediol-1,3-derivatives (**4**)



4

4a: $R_1 = R_2 = R_3 = H$, $Y = CN$

4b: $R_1 = R_2 = R_3 = H$, $Y = COOCH_3$

4c: $R_1 = C_6H_5$, $R_2 = H$, $R_3 = Y = COOCH_3$

4d: $R_1 = C_6H_5$, $R_2 = R_3 = H$, $Y = COCH_3$

4e: $R_1 = C_6H_5$, $R_2 = R_3 = H$, $Y = CHO$

The yields and properties of compounds **4** are collected in Table 2.

The structure of compounds **3** and **4** was confirmed by IR and NMR spectra.

EXPERIMENTAL

2,2-Dimethyl-5-nitro-1,3-dioxane (2)

5.73 g (0.03 mole) of 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane [1] (**1**) was dissolved in 10% sodium hydroxide (60—70 cm^3) and kept at 60°C for 1 hr. Then the solution was cooled to 5°C and at this temperature acidified with 15% acetic acid. The precipitated solid was filtered off, dried and crystallized from petroleum ether yielding 3.4 (70%) of **2**, m.p. 60—61°C.

Michael adducts 3

3.22 g (0.02 mole) of compound **2** was dissolved in 7 cm^3 of dioxane the catalyst added (0.2 cm^3 of 40% Triton B, except for the reaction with ω-nitrostyrene when 0.3 cm^3 of diethylamine was used), and the whole heated to 70°C. Then 0.02 mole of the unsaturated component was introduced portionwise. When the exothermic reaction ceased the mixture was kept at 90—95°C for 4 hrs, cooled and acidified with 5% HCl. The precipitate was filtered off, washed with 5% $NaHCO_3$ and water, dried and crystallized from petroleum ether (**3b**, **3c**, **3d**), petroleum ether — benzene (**3f**) or ethanol (**3a**, **3e**).

Compound **3f** was obtained in a higher yield in ethanol using equimolar amount of sodium ethoxylate as the reaction catalyst. The yields and properties of compounds **3** are collected in Table 1.

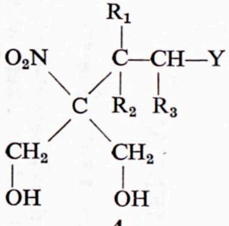
Preparation of 2,2-dimethyl-5-(2-cyanoethyl)-5-nitro-1,3-dioxane (3a) directly from 1 [1]

5.73 g (0.03 mole) of 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane (**1**) was dissolved in 100 cm^3 of 10% sodium hydroxide. 1.75 g (0.035 mole) of acrylonitrile was added and the flask shaken for a short time. After cooling the precipitate was filtered off, washed with water and crystallized from ethanol yielding 4.5 g (70%) of **3a**, m.p. 112—113°C.

T a b l e 2 — T a b l i c a 2

Properties and yields of compounds of general formula

Własności i wydajności związków o ogólnym wzorze



4

Compound No Nr związku	R_1	R_2	R_3	Y	Yield Wyd. %	M.p. T.t. °C	Empirical formula Wzór sumaryczny	Analysis — Analiza, %					
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4a	H	H	H	CN	54	102—104	$C_6H_{10}O_3N_2$	45.6	6.4	17.7	45.8	6.5	17.9
4b	H	H	H	$COOCH_3$	46	76—78	$C_7H_{13}O_5N$	44.0	6.9	7.3	44.2	7.1	7.3
4c	C_6H_5	H	$COOCH_3$	$COOCH_3$	78	143—144	$C_{15}H_{19}O_8N$	52.8	5.6	4.1	52.9	5.8	4.2
4d	C_6H_5	H	H	$COCH_3$	74	139—141	$C_{13}H_{17}O_5N$	58.5	6.4	5.2	58.7	6.5	5.4
4e	C_6H_5	H	H	CHO	68	121 – 123	$C_{12}H_{15}O_5N$	57.0	6.0	5.5	57.2	6.2	5.6

Acid hydrolysis of compounds 3

0.01 mole of compound **3** is refluxed with 20—30 cm^3 of 50% methanol or 1:1 dioxane — water mixture and 1 cm^3 of conc. HCl for 30 min — 1 hr. After cooling the product is either filtered off (**4c, 4d, 4e**) or the solution concentrated in vacuum and the residue left in a refrigerator to crystallize (**4a, 4b**). The yields and properties of compounds **4** are collected in Table 2.

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REFERENCES

1. Linden G. B., Gold M. H., *J. Org. Chem.*, **21**, 1175 (1956).

STRESZCZENIE

2,2-Dwumetylo-5-nitro-1,3-dioksan (**2**) otrzymano przez zakwaszenie roztworu soli sodowej **2** powstałej przez działanie 10%-owym NaOH na 2,2-dwumetylo-5-hydroksymetylo-5-nitro-1,3-dioksan[1] (**1**). Związek **2** poddano następnie reakcji Michaela z akrylonitrylem, akrylanem metylu, benzylidenomalonianem metylu, benzylidenoacetonem, ω-nitrostyrenem i aldehydem cynamonowym. Addycję prowadzono w dioksanie, używając Trytonu B lub dwuetyloaminy (reakcje z ω-nitrostyrenem) jako katalizatora. W przypadku reakcji z aldehydem cynamonowym największe wydajności otrzymano w środowisku etanolowego roztworu etoksylanu sodu. Związki **3** poddano następnie hydrolizie kwasowej w środowisku wodno-metanolowym lub wodno-dioksanowym, otrzymując pochodne 2-nitropropanodiolu-1,3 (**4**). Własności związków **3** i **4** zebrano w tablicach 1 i 2.

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