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STUDIES ON MONO AND POLY NITROALKANES—II*

THE MICHAEL REACTION WITH SUBSTITUTED β-NITROSTYRENES

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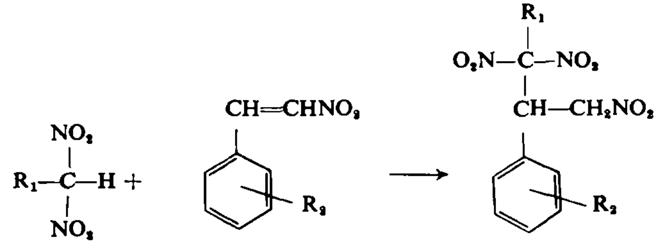
Abstract—The Michael additions of 2-nitropropane, *gem*-dinitroalkanes and nitroform to a number of nuclear substituted β-nitrostyrenes are described. The influence of different substituents and different substituted positions on the reactivity of the β-nitrostyrenes has been studied.

SUBSTITUTED β-nitrostyrenes have been used as acceptors in the addition reaction with a variety of amines or hydrazines,[1-7] and with methylene compounds activated by carbonyl or carboxyl groups (Michael reaction).[8-11]

Worrall and Benington[2] found a correlation between nature and position of the substituents and the capability of the substituted β-nitrostyrenes to give addition reactions with amines and hydrazines. In continuation of our study with mono and poly nitroalkanes,[12] we are reporting our findings with substituted β-nitrostyrenes as acceptors in Michael reactions.

gem-Dinitroalkanes add to β-nitrostyrene and its Bz-chloro and nitro derivatives without external catalyst according to the equation:



where $R_1 = CH_3$ or C_2H_5
$R_2 = H$, Cl or NO_2

There were no great differences in reactivity between the above compounds although the acceptor:donor ratio and the time of reaction had an influence on the yields (Table 1).

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* Part I: *Israel J. Chem.* **3**, 63 (1965).

[1] D. E. Worrall, *J. Amer. Chem. Soc.* **49**, 1598 (1927).

[2] D. E. Worrall and F. Benington, *J. Amer. Chem. Soc.* **60**, 2844 (1938).

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[5] D. E. Worrall and F. Benington, *J. Amer. Chem. Soc.* **62**, 493 (1940).

[6] D. E. Worrall and H. T. Wolosinski, *J. Amer. Chem. Soc.* **62**, 2449 (1940).

[7] T'ung-Yiin Yii and Yiin I Chia, *Hua Hsueh Hsueh Pao* **25**, 417 (1959).

[8] V. V. Perekalin and A. S. Sopova, *Zh. Obsh. Khim.* **24**, 513 (1954).

[9] A. S. Sopova and A. A. Temp, *Zh. Obsh. Khim.* **31**, 1532 (1961).

[10] M. M. Zobacheva and V. V. Perekalin, *Nauk Dokl. Vysshei̮ Shkoly, Khim i Khim. Tekhnol.* 740 (1958).

[11] M. J. Kamlet, *J. Amer. Chem. Soc.* **77**, 4896 (1955).

[12] A. Solomonovici and S. Blumberg, *Israel J. Chem.* **3**, 63 (1965).

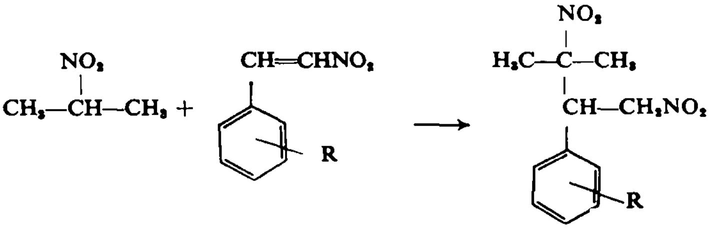
As β-nitrostyrene and its Bz-chloro and -nitro derivatives polymerize in the presence of alkali, we could not obtain adducts from these compounds and 2-nitropropane which did not add without an external catalyst, i.e. in the absence of a base.

TABLE 1. 1,1-DINITROETHANE AND SUBSTITUTED β-NITROSTYRENES

-β-Nitrostyrene	Molar ratio acceptor:donor	Time of reaction (hr)	Yield (%)
o-Chloro-	1:1	6	43
	1:3	10	86
m-Chloro	1:1	5	40
	1:3	10	66
p-Chloro-	1:2	5	56
	1:3	10	73
o-Nitro-	1:3	6	51
	1:3	10	70
m-Nitro-	1:1	3	38
	1:3	10	83
p-Nitro-	1:3	4	70
	1:3	10	83

gem-Dinitroalkanes did not add to methoxy and dimethoxy β-nitrostyrenes without external catalyst if the same conditions were employed as for the chloro and nitro derivatives. The *m*-methoxy compound can be induced to react with 1,1-dinitroethane even without external catalyst under drastic conditions (acceptor:donor ratio 1:3; time of reaction 30 hr, yield 78%). In all other cases, a base was needed as catalyst. Under these conditions, the Michael addition and polymerization proceeded together. To obtain the adduct, it was necessary to use an excess of the donor; otherwise polymerization predominated. Thus *p*-methoxy-β-nitrostyrene gave with 1–3 moles 1,1-dinitropropane only the polymer, while with 10 moles 1,1-dinitropropane the product was the expected adduct. In some cases (2-nitropropane with *m*-methoxy and 3,4-dimethoxy β-nitrostyrene) even with 20 moles of donor only the polymer was isolated. The increase of the ratio donor:acceptor and of the time of reaction improved the yields, as can be seen from Table 2.

2-Nitropropane added to methoxy and dimethoxy β-nitrostyrenes in the presence of basic catalysts, giving normal adducts according to the equation:



where R = OCH_3.

As expected, nitroform added to all substituted β-nitrostyrenes used, without external catalyst; however in some cases the isolation of the pure adduct was difficult.

TABLE 3. GEM-DINITROALKANES AND NITROFORM WITH β-NITROSTYRENE, CHLORO-β-NITROSTYRENES AND β-DINITROSTYRENES.

-β-Nitro-styrene	Donor	Molar ratio acceptor: donor	Time of reaction (hr)	Yield (%)	Formula of adduct	M.p.[a]	Solvent	Calc.				Found			
								%C	%H	%N	%Cl	%C	%H	%N	%Cl
	1,1-Dinitro-ethane	1:1	5	61	$C_{10}H_{11}N_3O_6$	104–105°	cyclohexane	44·6	4·1	15·6		44·8	4·5	15·6	
	1,1-Dinitro-propane	1:3	15	27	$C_{11}H_{13}N_3O_6$	50–51°	hexane	46·6	4·6	14·8		46·9	5·5	14·8	
	Nitroform	1:1	2½	40	$C_9H_8N_4O_8$[b]	84–85°	hexane	36·0	2·7	18·6		36·0	3·0	18·2	
o-Chloro-	1,1-Dinitro-ethane	1:1	6	43	$C_{10}H_{10}N_3O_6Cl$	70–71·5°	ethanol	39·6	3·3	13·9	11·5	39·7	3·8	13·8	11·4
	1,1-Dinitro-propane	1:1	6	60	$C_{11}H_{12}N_3O_6Cl$	87–88°	cyclohexane	41·6	3·8	13·2	11·0	41·8	4·5	12·6	11·6
	Nitroform	1:2	3	58	$C_9H_7N_4O_8Cl$	68–69°	cyclohexane	32·3	2·1	16·8	10·5	32·6	2·9	16·5	10·9
m-Chloro-	1,1-Dinitro-ethane	1:1	5	40	$C_{10}H_{10}N_3O_6Cl$	88–89°	hexane	39·6	3·3	13·9	11·5	39·7	3·8	12·9	11·9
	1,1-Dinitro-propane	1:3	7	32	$C_{11}H_{12}N_3O_6Cl$	55–56°	hexane	41·6	3·8	13·2	11·0	41·6	4·8	12·6	11·1
	Nitroform	1:2	3	30	$C_9H_7N_4O_8Cl$	101–102°	hexane	32·3	2·1	16·8	10·5	31·9	2·8	15·9	11·1
p-Chloro-	1,1-Dinitro-ethane	1:2	5	56	$C_{10}H_{10}N_3O_6Cl$	83–84°	cyclohexane	39·6	3·3	13·9	11·5	39·2	4·6	13·2	11·8
	1,1-Dinitro-propane	1:2	5	38	$C_{11}H_{12}N_3O_6Cl$	66–67°	cyclohexane	41·6	3·8	13·2	11·0	41·7	4·8	12·6	11·4
	Nitroform	1:5	3	40	$C_9H_7N_4O_8Cl$	122–123°	cyclohexane	32·3	2·1	16·8	10·5	32·1	2·8	15·8	11·2
o-Nitro-	1,1-Dinitro-ethane	1:3	6	51	$C_{10}H_{10}N_4O_8$	98–99°	ethanol	38·2	3·2	17·8		38·3	3·5	17·3	
	1,1-Dinitro-propane	1:5	3	36	$C_{11}H_{12}N_4O_8$	88·5–90°	ethanol	40·2	3·7	17·1		40·1	4·1	17·0	
m-Nitro-	1,1-Dinitro-ethane	1:1	3	38	$C_{10}H_{10}N_4O_8$	99–100°	isopropyl alcohol	38·2	3·2	17·8		38·0	3·6	17·5	
	1,1-Dinitro-propane	1:2	6	45	$C_{11}H_{12}N_4O_8$	86–88°	ethanol	40·2	3·7	17·1		40·6	3·7	16·7	
	Nitroform	1:6	3	30	$C_9H_7N_5O_{10}$	111–112°	cyclohexane	31·3	2·0	20·3		32·3	2·0	19·5	
p-Nitro-	1,1-Dinitro-ethane	1:3	4	70	$C_{10}H_{10}N_4O_8$	94–95°	ethanol	38·2	3·2	17·8		38·3	4·2	17·3	
	1,1-Dinitro-propane	1:3	4	36	$C_{11}H_{12}N_4O_8$	83–84°	ethanol	40·2	3·7	17·1		40·1	4·0	16·8	

[a] The m.ps in all Tables are uncorrected.

[b] The compound (m.p. 87–88°) was obtained by a similar method by J. Hine and L. A. Kaplan, *J. Amer. Chem. Soc.* **82**, 2915 (1960), and by M. H. Gold and H. Plaut, U.S. Patent 3,094,566 (1963).

TABLE 4. 2-NITROPROPANE, *gem*-DINITROALKANES AND NITROFORM WITH MONO AND DIMETHOXY-β-NITROSTYRENES

-β-Nitro-styrene	Donor	Molar ratio acceptor: donor	Time of reaction (hr)	Yield	Formula of adduct	M.p.	Solvent	Calc.			Found		
								%C	%H	%N	%C	%H	%N
o-Methoxy-	2-Nitropropane	1:3	5	52	$C_{12}H_{16}N_2O_5$	80–81°	cyclohexane	53·7	6·0	10·5	53·5	6·9	10·6
	1,1-Dinitroethane	1:3	2	53	$C_{11}H_{13}N_3O_7$	87–88°	cyclohexane	44·1	4·4	14·0	44·1	4·7	13·8
	1,1-Dinitropropane	1:3	4	77	$C_{12}H_{15}N_3O_7$	88·5–90°	cyclohexane	46·0	4·8	13·1	45·4	5·3	12·9
	Nitroform	1:2	3	66	$C_{10}H_{10}N_4O_9$	54–55°	cyclohexane	36·4	3·0	17·0	36·8	3·2	16·7
m-Methoxy-	1,1-Dinitroethane	1:3	3	70	$C_{11}H_{13}N_3O_7$	111–112°	hexane	44·1	4·4	14·0	43·9	4·7	13·7
	1,1-Dinitropropane	1:3	3	64	$C_{12}H_{15}N_3O_7$	86–87°	hexane	46·0	4·8	13·1	46·2	5·3	13·4
p-Methoxy-	2-Nitropropane	1:10	5	45	$C_{12}H_{16}N_2O_5$	105–106°	cyclohexane	53·7	6·0	10·5	54·0	6·3	10·5
	1,1-Dinitroethane	1:1	5	66	$C_{11}H_{13}N_3O_7$	88·5–89·5°	cyclohexane	44·1	4·4	14·0	44·0	4·8	13·9
	1,1-Dinitropropane	1:10	3	58	$C_{12}H_{15}N_3O_7$	85–86°	cyclohexane	46·0	4·8	13·1	46·5	5·4	12·6
	Nitroform	1:2	3	55	$C_{10}H_{10}N_4O_9$	32–33°	cyclohexane	36·4	3·0	17·0	36·8	3·9	16·8
2,4-Dimethoxy-	2-Nitropropane	1:6	4	80	$C_{13}H_{18}N_2O_6$	83–84°	cyclohexane	52·4	6·0	9·4	52·4	5·8	9·5
	1,1-Dinitroethane	1:1	3	61	$C_{12}H_{15}N_3O_8$	84–85°	cyclohexane	43·8	4·6	12·8	43·5	5·8	12·2
	1,1-Dinitropropane	1:3	3	64	$C_{13}H_{17}N_3O_8$	88–89°	cyclohexane	45·6	5·0	45·4	12·2	4·6	12·2
	Nitroform	1:10	3	50	$C_{11}H_{12}N_4O_{10}$	55–56°	cyclehexane	36·7	3·3	15·5	37·0	4·8	14·7
2,5-Dimethoxy-	2-Nitropropane	1:3	4	60	$C_{13}H_{18}N_2O_6$	97–98°	cyclohexane	52·4	6·0	9·4	52·5	7·0	9·1
	1,1-Dinitroethane	1:3	3	97	$C_{12}H_{15}N_3O_8$	93·5–95°	cyclohexane	43·8	4·6	12·8	43·9	4·8	12·5
	1,1-Dinitropropane	1:3	6	82	$C_{13}H_{17}N_3O_8$	83–85°	cyclohexane	45·6	5·0	12·2	45·7	5·2	12·0
3,4-Dimethoxy-	1,1-Dinitroethane	1:5	3	55	$C_{12}H_{15}N_3O_8$	108–109°	hexane	43·8	4·6	12·8	44·6	5·1	12·9
	1,1-Dinitropropane	1:10	3	70	$C_{13}H_{17}N_3O_8$	104–105°	cyclohexane	45·6	5·0	12·2	45·8	5·7	12·5
	Nitroform	1:10	3	55	$C_{11}H_{12}N_4O_{10}$	83–84°	hexane	36·7	3·3	15·5	37·1	3·9	15·0

TABLE 2. 1,1-DINITROETHANE AND METHOXY β-NITROSTYRENES

-β-Nitrostyrene	Molar ratio acceptor:donor	Time of reaction (hr)	Yield (%)
o-Methoxy-	1:3	3	53
	1:3	10	87
m-Methoxy-	1:3	3	70
	1:3	10	87
p-Methoxy-	1:1	5	66
	1:3	10	67

The adducts with 2-nitropropane showed the nitro band at 1550–1565 cm^{-1}, those with *gem*-dinitroalkanes the *gem*-dinitro band at 1585–1600 cm^{-1}, and those with nitroform the trinitromethyl band at 1590–1615 cm^{-1}.

An alkyl group in the side chain of Bz-substituted β-nitrostyrenes blocked both the addition and the polymerization. We tried in vain to induce the reaction of *gem* dinitroalkanes and nitroform with β-methyl- β-nitrostyrene, with β-methyl- and β-ethyl-β,*m*-dinitrostyrene and with β-methyl-2,5-dimethoxy-β-nitrostyrene by refluxing the reactants in ethanol or dioxane with piperidine, Triton B, or without catalyst. β,*m*-Dinitrostyrene in the presence of piperidine polymerized quickly, while under the same conditions, β-methyl- and β-ethyl- β,*m*-dinitrostyrene did not polymerize. These facts are in agreement with Worrall's findings regarding the reaction between *amines* and substituted β-nitrostyrenes.[4]

EXPERIMENTAL

Materials. The preparation of *gem*-dinitroalkanes and nitroform has been described;[11] commercial 2-nitropropane and β-nitrostyrene were used. The substituted β-nitrostyrenes were prepared by minor modifications of the method of Fieser and Daudt[12]: To a solution of 0·08 mole of nitroalkane and 0·05 mole of the corresponding benzaldehyde, 8 drops of Et_3N was added and the solution kept 24 hr at room temp. Then 45 ml Ac_2O and 2·5 g molten AcONa were added and the solution refluxed until it became dark red. The mixture was poured into 500 ml ice water with separation of the crude product as a solid or an oil which solidified after some hr.

The following products were prepared (recrystallization solvents and m.ps in brackets): *o*-Chloro-β-nitrostyrene (EtOH, 42–43°), *m*-chloro-β-nitrostyrene, (EtOH, 42–43°), *p*-chloro-β-nitrostyrene (EtOH, 109–110°), β,*o*-dinitrostyrene (EtOH, 101–102°), β,*m*-dinitrostyrene (EtOH, 122–123°), β,*p*-dinitrostyrene (dioxan, 199–201°), *o*-methoxy-β-nitrostyrene (EtOH, 41–42°), *m*-methoxy-β-nitrostyrene (EtOH, 89–91°), *p*-methoxy-β-nitrostyrene (EtOH, 83–84°), 2,4-dimethoxy-β-nitrostyrene (EtOH, 100–101°), 2,5-dimethoxy-β-nitrostyrene (EtOH, 118–119°), 3,4-dimethoxy-β-nitrostyrene (EtOH, 139–140°), β-methyl-β-nitrostyrene (EtOH, 58°), β-methyl-β,*m*-dinitrostyrene (EtOH, 55°), β-ethyl-β,*m*-dinitrostyrene (EtOH, 80°), β-methyl-2,5-dimethoxy-β-nitrostyrene (EtOH, 70°).

General procedures

Addition of gem-*dinitroalkanes and nitroform to β-nitrostyrene and its Bz-chloro and -nitro derivatives.* The addition was carried out by refluxing the reactants in EtOH for 2½–15 hr (Table 3). The solid addition products were isolated by cooling at 0° or in a dry ice-acetone bath with stirring.

Addition of 2-nitropropane, gem-*dinitroalkanes and nitroform to methoxy- and dimethoxy-β-nitrostyrenes.* The nitro-compound and 5 drops of piperidine were added to an alcoholic solution of the substituted β-nitrostyrene (0·01 mole), and the reaction mixture refluxed for 2–6 hr (Table 4). The solid reaction products separated when the mixtures were cooled with stirring at 0° or in a dry ice-acetone bath.

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[12] L. F. Fieser and W. H. Daudt, *J. Amer. Chem. Soc.* **68**, 2248 (1946).