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Abstract

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Interaction of Nitroolefins and Compounds with Active Methyl Groups

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Earlier, one of us showed that nitroolefins (nitrostyrene), in the presence of basic catalysts, readily condense with substances containing labile hydrogen atoms in methylene groups (malonic and acetoacetic esters, acetyl- and benzoylacetone) ([1]–[3]).

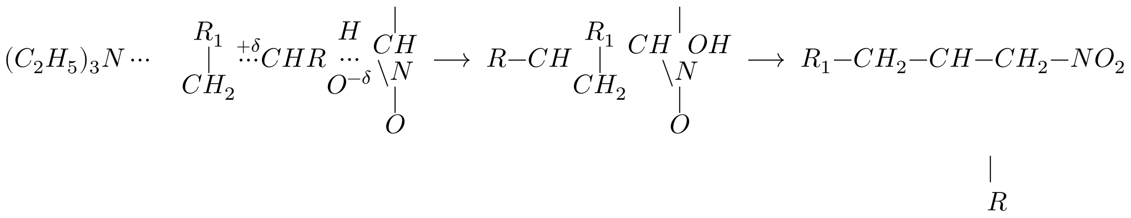
It seemed of interest to extend this reaction to compounds with labile hydrogen atoms in methyl groups. The interaction of these substances with cationoid reagents—aldehydes, nitroso and diazo compounds—has long been well studied, whereas reactions with nitroolefins have been described only very sparsely (,).

We have for the first time carried out the interaction of nitroolefins of the aliphatic, aromatic, and heterocyclic series (nitroisohexylene, nitrostyrene, and furyl-nitroethylene) with active methyl components: trinitrotoluene, mesomethylacridine, and the iodomethylates of quinaldine and methylbenzthiazole.

The synthesis proceeded on heating equimolecular quantities of the substances in organic solvents in the presence of basic catalysts; the best yields were usually obtained in the presence of triethylamine. In some cases the reaction occurred instantaneously upon addition of traces of catalyst to the melt of the components (condensation of nitrostyrene with trinitrotoluene, yield 70%). The reaction conditions and the analytical results for the synthesized substances are given in Tables 1–2.

On reduction and heating with hydrochloric acid, the condensation products were converted into the corresponding amines and carboxylic acids.

It may be assumed that the reaction mechanism consists in the formation of a reaction complex, which is converted into the final product as a result of addition of the methyl component at positions 1-4 of the nitroolefin. The methyl group of the methyl component is active owing to conjugation with electrophilic groups (π-, σ-conjugation), while the reactivity of the nitroolefin is increased by fixation of its electron deficiency by the catalyst.



$$(C_2H_5)_3N\cdots \underset{CH_2}{\overset{R_1}{|}} \overset{+\delta}{\cdots} CHR \overset{H}{\cdots} O^{-\delta}\ \overset{|}{CH}\backslash N \underset{O}{|} \longrightarrow R{-}CH\underset{CH_2}{\overset{R_1}{|}}\ \overset{|}{CH}\ OH\backslash N\underset{O}{|} \longrightarrow R_1{-}CH_2{-}\underset{R}{\underset{|}{CH}}{-}CH_2{-}NO_2$$

where R is alkyl, aryl, or heterocycle; R_1 is an electrophilic residue conjugated with the methyl group.

Table 1

Active methylene compound	Starting substances	No.	Final products	Solvent	Catalyst	Temperature, °C	Reaction duration, h	Yield, % of theory
Trinitrotoluene	Nitrostyrene	I	$R_2-CH-CH_2NO_2$ | CH_2 2,4,6-trinitrophenyl residue	methanol	TEA*	~ 50	7	70
Trinitrotoluene	Furyl nitroethylene	II	$R_3-CH-CH_2NO_2$ | CH_2 2,4,6-trinitrophenyl residue	benzene	TEA	20	24	63.4
Mesomethylacridine	Nitroisohexylene	III	$R_1-CH-CH_2NO_2$ | CH_2 acridine residue	methanol	TEA	boil.	5	53.5
Mesomethylacridine	Nitrostyrene	IV	$R_2-CH-CH_2NO_2$ | CH_2 acridine residue	benzene	pyridine	boil.	5	56.5
Mesomethylacridine	Furyl nitroethylene	V	$R_3-CH-CH_2NO_2$ | CH_2 acridine residue	benzene	TEA	boil.	8	69.5
Quinaldine methiodide	Nitroisohexylene	VI	quinolinium iodide derivative: [Quinoline$-N^+(CH_3)-CH_2-CH(R_1)-CH_2NO_2$] I^-	methanol	TEA	40	5	62.7
Quinaldine methiodide	Nitrostyrene	VII	quinolinium iodide derivative: [Quinoline$-N^+(CH_3)-CH_2-CH(R_2)-CH_2NO_2$] I^-	benzene	TEA	boil.	8	96

Active methylene compound	Starting substances	No.	Final products	Solvent	Catalyst	Temperature, °C	Reaction duration, h	Yield, % of theory
Quinaldine methiodide	Furyl nitroethylene	VIII	quinolinium iodide derivative: $[\mathrm{Quinoline{-}N^+(CH_3){-}CH_2{-}CH(R_3){-}CH_2NO_2}]\ \mathrm{I^-}$	benzene	TEA	boil.	1	84

Table 1 (continued)

Starting substances	No.	Final products	Solvent	Catalyst	Temperature, °C	Reaction duration, h	Yield, % of theory
Iodomethylbenzthiazole; nitroisohexylene	IX	$[\mathrm{2\text{-}(C{-}CH_2{-}CH(R_1){-}CH_2NO_2)\text{-}3\text{-}methylbenzthiazolium}]^+\ \mathrm{I^-}$	methanol	tea	b.p.	4	59.5
Iodomethylbenzthiazole; nitrostyrene	X	$[\mathrm{2\text{-}(C{-}CH_2{-}CH(R_2){-}CH_2NO_2)\text{-}3\text{-}methylbenzthiazolium}]^+\ \mathrm{I^-}$	methanol	tea	b.p.	4	52.3
Iodomethylbenzthiazole; furylnitroethylene	XI	$[\mathrm{2\text{-}(C{-}CH_2{-}CH(R_3){-}CH_2NO_2)\text{-}3\text{-}methylbenzthiazolium}]^+\ \mathrm{I^-}$	benzene	tea	b.p.	4	86.0

* tea —triethylamine.

Note. $R_1—CH_2—CH—(CH_3)_2$; $R_2—C_6H_5$; R_3— furyl.

Table 2

Substance	M.p., °C	Found, % C	Found, % H	Found, % N	Found, % S	Found, % I	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % S	Calculated, % I	Mol. wt., found	Mol. wt., calculated
I	162.5 (benzene)	47.67 47.38	3.38 3.29	14.79 15.00	—	—	47.90	3.21	14.89	—	—	388 371	376.1

Substance	M.p., °C	Found, % C	Found, % H	Found, % N	Found, % S	Found, % I	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % S	Calculated, % I	Mol. wt., found	Mol. wt., calculated
II	137 – 138(benzene)	43.06 [illegible]	[illegible]	[illegible] 15.09	–	–	42.91	2.75	15.3	–	–	399 [illegible]	366.2
III	148 – 149(ethanol)	74.39 [illegible]	[illegible]	[illegible] 8.69	–	–	74.57	6.87	8.68	–	–	328 [illegible]	322.41
IV	164.6 [illegible] (dichloroethane)	[illegible]	[illegible]	[illegible] 8.37	–	–	77.19	5.3	8.18	–	–	358 [illegible]	342.3
V	166 – 166.5(benzene)	72.11 [illegible]	[illegible]	[illegible] 8.38	–	–	72.27	4.88	8.42	–	–	338 [illegible]	332.4
VI	178(methanol)	[illegible]	[illegible]	[illegible] 6.47	–	30.68 [illegible]	[illegible]	5.59	6.75	–	30.64	–	–
VII	174.5 [illegible] (methanol)	[illegible]	[illegible]	[illegible] 6.66	–	29.15 [illegible]	[illegible]	4.41	6.49	–	29.23	–	–
VIII	161(ethanol)	48.06 [illegible]	[illegible]	[illegible] 6.54	–	–	48.14	4.04	6.60	–	29.92	–	–
IX	153(ethanol)	42.83 [illegible]	[illegible]	[illegible] 6.78	–	30.04 [illegible]	[illegible]	5.03	6.66	7.63	30.20	–	–
X	171(methanol)	46.25 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	4.12	6.36	7.26	28.83	–	–
XI	163(methanol)	41.79 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3.51	6.51	7.43	29.50	–	–

The reaction described is general in character and opens a route for introducing a nitroethyl group, linked to various alkyl, aryl, and heterocyclic residues, into compounds with active methyl groups. In the simplest case (in the interaction of active methyl components with a nitroethylene), this reaction may be characterized as a nitroethylation reaction.

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Note: Figure translations are in progress. See original paper for figures.