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MICHAEL ADDITION REACTION IN THE PRESENCE OF POTASSIUM AND RUBIDIUM FLUORIDES AS CATALYSTS*

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Abstract—Donors of the Michael reaction such as ethyl nitroacetate, nitroketones with a CH_2NO_2 group and *gem*-dinitroalkanes react with potassium fluoride to form double salts composed of KHF_2 and the nitro compound. The structure of these salts and the presence of KHF_2 in the molecule was proved by UV and IR spectra.

Upon reaction with acceptors, the salts decompose to yield normal Michael reaction products with an exception of the double salts of the nitroketones which give condensation products of acceptors with nitromethane, the latter being formed as the result of the solvolysis of nitroketones. Rubidium and caesium fluorides form similar double salts. They are not formed by lithium and sodium fluorides.

YASUDA *et al.*[1–4] and the present authors[5–7] have found that the Michael reaction can be catalyzed by potassium fluoride as well as by rubidium and caesium fluorides giving good yields of normal addition products.

In the case of ethyl nitroacetate and *gem*-dinitroalkanes, the reaction first produced double salts composed of potassium fluoride and the nitro compound. Upon further reaction with acceptors these salts decomposed to yield normal Michael reaction products.

Nitroketones with a nitromethyl group gave a similar but more complicated reaction: the salts with potassium fluoride on further reaction with acceptors yielded condensation products of acceptors with nitromethane and not with the original nitroketones. We suggest that the mechanism of nitromethane formation is via an intermediate carbanion initiated by potassium fluoride:

1. $O_2NCH_2COR + 2KF \rightarrow K^{\oplus\ominus}O_2N{=}CHCOR + KHF_2$
2. $K^{\oplus\ominus}O_2N{=}CHCOR + HOR' \rightarrow [K^{\oplus\ominus}O_2N{=}CH]^{\ominus} + RCOOR' + H^{\oplus}$
3. $[K^{\oplus\ominus}O_2N{=}CH]^{\ominus} + H^{\oplus} \rightarrow K^{\oplus\ominus}O_2N{=}CH_2$
4. $3CH_2{=}CHCOOMe + K^{\oplus\ominus}O_2N{=}CH_2 + KHF_2 \rightarrow O_2NC(CH_2CH_2COOMe)_3 + 2KF$

$R = Me, Et, Ph$
$R' = Me, Et$

Table 1 lists the salts all of which are new.

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* Paper VII, *Michael reaction* and Paper LXXXV, *Chemistry of Nitroparaffins*, read at the National Congress of the Polish Chemical Society, Wroclaw, June (1967).

TABLE 1

No.	Salts	Solvent		Analysis			
				Required		Found	
				N	K	N	K
0	1	2	3	4	5	6	7
1	$C_2H_5CO_2CHNO_2K + KHF_2$	acetonitryl	$C_4H_7NO_4K_2F_2$	5·62		5·66 5·54	
2	$CH_3COCHNO_2K + KHF_2$	methanol	$C_3H_5NO_3K_2F_2$	6·39	35·61	6·22 6·49	34·80 34·79
3	$C_6H_5COCHNO_2K + KHF_2$	methanol	$C_8H_7NO_3K_2F_2$	4·91	27·81	5·42	27·90 27·96
4	$CH_3C\|NO_2\|_2K + KHF_2$	methanol	$C_2H_4N_2O_4K_2F_2$		33·02		31·75 32·70
5	$CH_3CH_2C\|NO_2\|_2K + KHF_2$	methanol	$C_3H_6N_2O_4K_2F_2$		30·90		31·21
6	$2{,}4\|NO_2\|_2C_6H_3OK + KHF_2$	methanol	$C_6H_4N_2O_5K_2F_2$		26·02		34·16 35·26
7	$3\text{-}NO_2\text{—}C_6H_4CO_2K + KHF_2$	methanol	$C_7H_5NO_2K_2F_2$	4·86		4·50	
8	$C_6H_5\text{—}CH_2CO_2K + KHF_2$	benzene	$C_8H_8O_2K_2F_2$		30·95		31·88 33·62
9	$4\text{-}NO_2\text{—}C_6H_4CH_2CO_2K + KHF_2$	benzene + acetone	$C_8H_7O_4NK_2F_2$	4·71		4·20 4·28	
10	$HCO_2CH_2CH_2CO_2K + KHF_2$	benzene	$C_4H_6O_4K_2F_2$		33·32		32·12 34·75
11	$CF_3COCH\text{—}CO_2C_2H_5K + KHF_2$	methanol	$C_6H_7O_3K_2F_5$		26·01		25·11
12	$CH_3COCHNO_2Rb + RbHF_2$	methanol	$C_3H_5NO_3Rb_2F_2$	4·49	Rb	3·97 3·82	Rb
13	$C_6H_5COCHNO_2Rb + RbHF_2$	methanol	$C_8H_7NO_3Rb_2F_2$	3·86	45·82	3·74	42·51 42·98
14	$C_2H_5CO_2CHNO_2Cs + CsHF_2$	methanol	$C_4H_7NO_4Cs_2F_2$	3·20	Cs	3·01	Cs

Most of the salts have a ratio of nitro compound to potassium fluoride of 1:2. We also found that the potassium fluoride can form double salts with carboxylic acids and nitrophenols.

IR spectra, of the salts of potassium fluoride with aliphatic and aromatic nitro compounds, exhibit characteristic bands at frequencies of 2040, 1830, 1460 and 1230 $\pm$ 5 cm^{-1}, indicative of KHF_2 whose anion $[F...H...F]^{\ominus}$ is responsible for absorption bands at the above frequencies.[8] It is important to point out that the 1560 cm^{-1}

band attributable to asymmetric vibrations of the nitro group does not appear in the spectra of the nitro compounds.

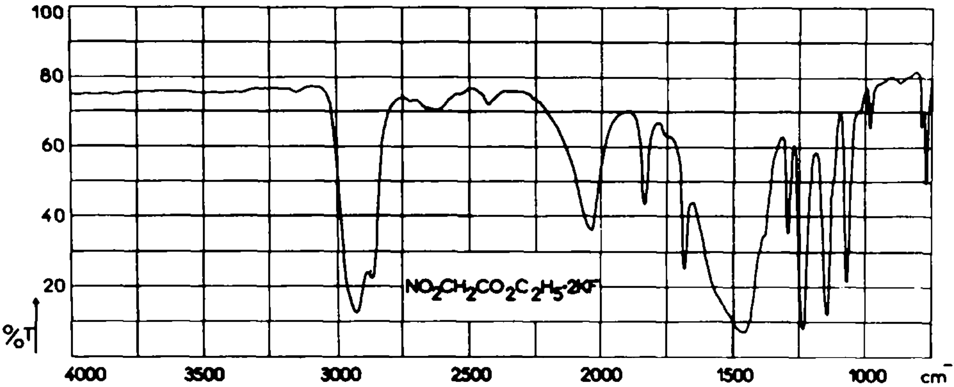


Fig. 1. Infrared spectrum of ethyl nitroacetate salt (Oil bands are omitted).

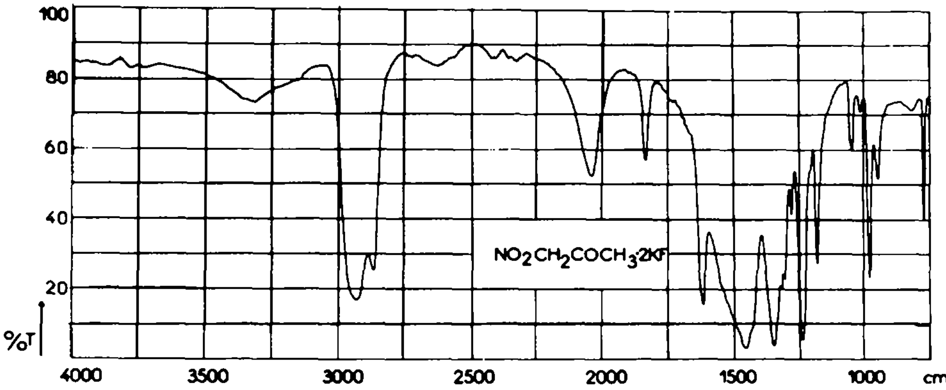


Fig. 2. Infrared spectrum of ethyl nitroacetone salt (Oil bands are omitted).

UV absorption spectra recorded for ethyl nitroacetate–potassium fluoride salt indicate that the species investigated are ethyl aci-nitroacetate and potassium hydrogen fluoride. Comparison of the UV spectra of the salt of potassium fluoride with ethyl nitroacetate and of the potassium salt of aci-nitroacetate show that the spectra are identical, except for a difference in the extinction at the wavelength $\lambda = 304$ mμ.

The low solubilities of the potassium salts and of acid potassium fluoride in organic solvents render separation of the salts by crystallization difficult. By using dimethylsulphoxide as solvent the potassium salt of aci-ω-nitroacetophenone could be separated from insoluble acid potassium fluoride. However, the potassium salt of ethyl nitroacetate could not be crystallized from this solvent because the salt decomposed on heating.

In water the potassium fluoride salts with nitro compounds undergo hydrolysis and the nitro compound can be isolated. In this manner ethyl nitroacetate and *gem*-dinitro-alkanes were recovered in 70–80 and 60–70% respectively.

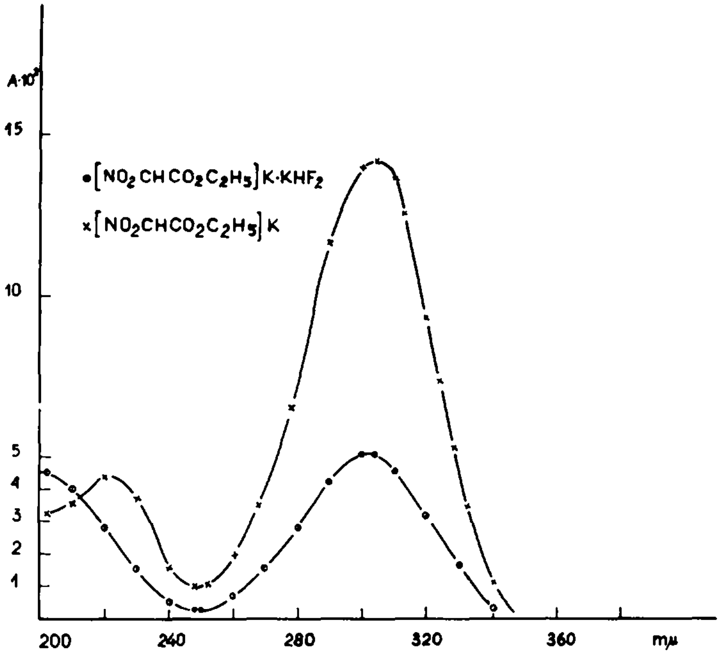


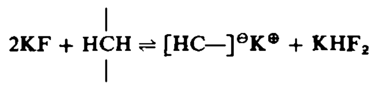
FIG. 3. Ultraviolet spectra of the salt of ethyl nitroacetate with potassium fluoride and of the potassium salt of aci-nitroacetate.

The pK_a values listed in Table 2 for the investigated compounds indicate that salt formation is related to the acid strength of the compound: the double potassium salts are formed by compounds with pK_a less than 7. For that reason no salts were isolated with acetylacetic ester ($pK_a = 10$) and nitroalkanes ($pK_a = 7$). In the presence of relatively strong acids, e.g. picric acid ($pK_a = 0{\cdot}80$), potassium fluoride undergoes decomposition to a potassium picrate with the accompanying liberation of hydrogen fluoride.

In order to elucidate whether aci-anion was formed by the nitro compounds and potassium fluoride we compared UV spectra of the nitro compounds (Fig. 4, curve A) in the presence of potassium fluoride (curve B) and in the presence of diethylamine (curve C), the latter being a typical curve of an aci-nitro anion.

Anion formation was also observed by Rand[9] in his studies on ethyl cyanoacetate in the presence of potassium fluoride at elevated temperature. As the temperature was reduced, the extinction diminished to zero. However, Rand failed to detect either free hydrogen fluoride or acid potassium fluoride.

The formation of the acid potassium fluoride and of the anion supports the assumption that the Michael reaction with alkali fluorides proceeds via formation of a carbanion, as is the case with any basic catalysts, according to the following diagram:



$$2KF + H\overset{|}{\underset{|}{C}}H \rightleftharpoons [HC—]^{\ominus}K^{\oplus} + KHF_2$$

TABLE 2

No.	Compounds	pK$_a$	t °C	Ref.	Salts with fluorides			
					Na	K	Rb	Cs
1	$CH_3{-}NO_2$	10·21	25	19		—		
2	$CH_3CH_2{-}NO_2$	8·60	25	19	—	—		
3	$CH_3CHCl{-}NO_2$	7·0	25	19		—		
4	$CH_3CH{-}\|NO_2\|_2$	5·21	20	19		+		
5	$CH_3{-}CH_2CH{-}\|NO_2\|_2$	5·53	20	19		+		
6	$CH_3CH_2CO_2CH_2{-}NO_2$	5·82	25	20	—	+		+
7	$CH_3COCH_2{-}NO_2$	5·09	25	20		+	+	
8	$C_6H_5COCH_2{-}NO_2$					+	+	
9	m-$NO_2{-}C_6H_5CO_2H$	3·49	25	21		+		
10	p-$NO_2{-}C_6H_5CH_2CO_2H$	3·85	25	21		+		
11	$HCO_2CH_2{-}CH_2CO_2H$	4·16 5·61	25	21		+		
12	$CF_3COCH_2CO_2{-}C_2H_5$					+		
13	$CH_3COCH_2CO_2{-}C_2H_5$	10·68	25	22		—		
14	$C_6H_5{-}OH$	9·89	25	21		—		
15	$2,4\|NO_2\|_2C_6H_5{-}OH$	3·96	25	21		+		
16	m-$NO_2{-}C_6H_5{-}OH$	8·28	25	21		—		
17	$C_6H_5{-}CH_2{-}CO_2H$	4·31	25	21		+		

In an alcoholic solution an equilibrium becomes established between the potassium salt of a nitro compound and acid potassium fluoride. The above mechanism is in agreement with the fact that potassium salts can be isolated when aci-nitro compounds have a pK_a lower than 7.

Berthelot[10] and Richards[11] were the first to indicate that certain organic acids react with potassium fluoride in an aqueous medium to yield salts and acid potassium fluoride, but they failed to isolate the salts. On heating, the potassium salts of carboxylic acids evolve carbon dioxide and produce a hydrocarbon and a ketone. This is the explanation of the alkaline catalyst activity of potassium fluoride in the reactions of decarboxylation and cyclization to ketones carried out by Nesmeyanov[12] and Rand.[13]

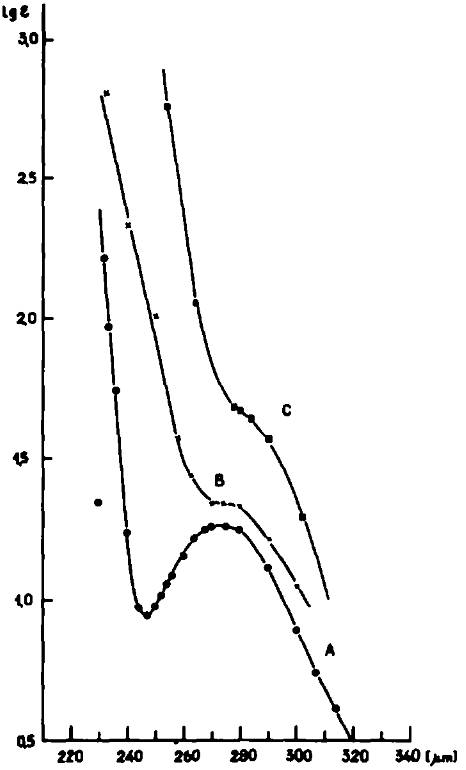


Fig. 4. Ultraviolet spectrum of the nitroethane. Curve A—nitroethane in methanol, curve B—nitroethane in methanol in the presence of potassium fluoride; curve C—nitroethane in methanol in the presence of diethylamine.

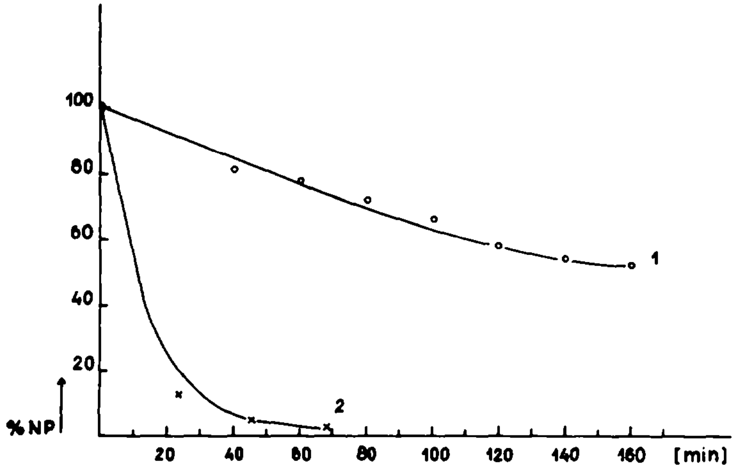


Fig. 5. Condensation of 2-nitropropane with methyl acrylate in the presence of (1) potassium fluoride and (2) rubidium fluoride.

Similarly, rubidium fluoride and caesium fluoride produce salts with ethyl nitroacetate, nitro ketones, carboxylic acids, etc. In contrast, lithium fluoride and sodium fluoride do not form salts. Apparently the catalytic properties of alkali metal fluorides increase in the order of increasing alkalinity of group one metals: Li < Na < K < Rb < Cs. Comparison of the condensation rates of 2-nitropropane with methyl acrylate in the presence of potassium fluoride and rubidium fluoride show the latter to be a stronger catalyst.

EXPERIMENTAL

Starting materials. Ethyl nitroacetate was obtained from ethyl acetylacetate according to Belikov.[14] Nitroketones were prepared by oxidation of carbinols.[15] *gem*-Dinitroalkanes were prepared from nitroalkanes by the Kaplan method.[16] Other donors and acceptors were analytical-grade reagents. They were purified by distillation or crystallization. The alkali metal fluorides were analytical grade reagent and dried before use at 150–180°.

IR and UV spectra. IR spectra were recorded on a Unicam Sp-200 and a Hilger H-800 spectrophotometer. Oil bands were not omitted in the spectra. UV spectra were recorded on a Unicam Sp-500 spectrophotometer.

Preparation of salts of alkali metal fluorides with various compounds (Table 1). Nitroalkane, carboxylic acid ester, or nitrophenol (0·15 mol) was added to KF, RbF or CsF (0·02 mol) dissolved in MeOH, benzene or acetonitrile. A white or yellow ppt formed after 15 min. The reaction mixture was allowed to stand for 12 hr at room temp. The ppt was washed with anhyd benzene and dried over KOH. The yield was over 95%. K or Rb content was determined with the aid of sodium tetraphenylborate. The salt of ω-nitroacetophenone and KF was separated by dissolving in DMSO. The potassium salt of aci-ω-nitroacetophenone was identified by comparison of its IR spectrum with the spectrum of a standard sample obtained from ω-nitroacetophenone and potassium alcoholate.

Condensation of ethyl nitroacetate with acrylonitrile compound I, Table 3. Ethyl nitroacetate (4 g, 0·033 mol), KF (2 g, 0·034 mol) and acrylonitrile (3·2 g, 0·06 mol) were mixed. A white ppt was formed immediately. The temp rose to 40°. The mixture was refluxed for 6 hr at 60–65° and cooled to room temp. Water was added to remove the KF. The organic layer was separated and the aqueous one was extracted with benzene. The combined organic layers were dried over $MgSO_4$ and distilled to yield 4·2 g (75%) of ethyl-3-cyano-1-nitropropanecarboxylate b.p. 126–128° (1 mm).[17]

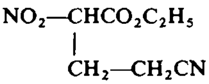
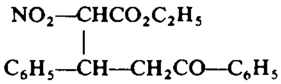
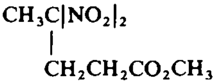
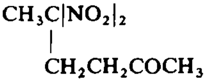
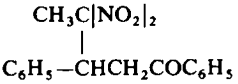
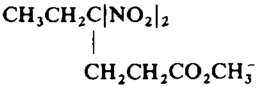
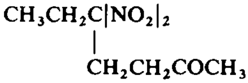
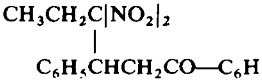
Condensation of ethyl-nitroacetate with chalcone compound II, Table 3. The mole ratios of nitroacetate (4 g, 0·33 mol) and chalcone (6·3 g, 0·033 mol) dissolved in 10 ml MeOH and KF were, together with the subsequent procedure, the same as for acrylonitrile. The reaction was not exothermic. The reaction mixture was cooled to −10°, the white ppt (yield 6·5 g) was washed with water and recrystallized from EtOH to yield ethyl 3-benzoyl-2-phenyl-1-nitropropane-carboxylate.

Decomposition of nitroacetone in methanol in the presence of potassium fluoride. Nitroacetone (0·51 g, 0·005 mol), anhydr KF (0·58 g, 0·01 mol) were added to MeOH (2 ml). A white ppt was formed after a few min and the mixture was refluxed at 60–65° for 30 min. The ppt became yellow and a part of it decomposed. The liquid phase was distilled off under atm press and the distillate was subjected to gas chromatography. 0·4–0·8 μ litre samples were withdrawn from the reaction vessel by a hypodermic syringe and were analysed on a Perkin–Elmer 452 gas chromatograph using ¼ in × 2 m long column packed with chromosorb N (60–80 mesh) coated with 10% polyphenyl ether. The retention times of AcOMe and nitromethane at column temp 50° and carrier gas (H_2 flow rate equal 48 ml/min) were respectively 3·5 and 7·3 min. It was found that over 90% of nitroacetone decomposed to yield nitromethane and methyl acetate.

The identical decomposition of nitroacetone in MeOH was obtained under action of diethylamine (0·1 g for 0·51 g of nitroacetone) instead of KF.

Condensation of nitroketones with methyl acrylate. Nitroacetone (3·3 g, 0·031 mol), methyl acrylate (5 g, 0·05 mol) dissolved in MeOH (10 ml) and anhyd KF (1·8 g, 0·03 mol) were mixed. A white ppt was immediately formed. The mixture was heated for 1 hr at 50–55° to decompose the salt, and after further 4 hr heating, cooled and water (100 ml) was added. The organic layer was separated. The aqueous one was extracted with ether. The combined organic layers were dried over $MgSO_4$. The presence of AcOMe and nitromethane was established by gas chromatography. Finally, 4·1 g (61·2%) of a yellow oil of nitro-tri(propiomethyl)methane, b.p. 184–187°/0·15 mm was obtained; n_D^{20} 1·4693. (Found: C, 48·74; H, 6·90; N, 4·76. $C_{13}H_{21}O_8N$ requires: C, 48·90; H, 6·63; N, 4·39%).

TABLE 3. COMPOUNDS OBTAINED IN THE CONDENSATION OF ETHYL NITROACETATE

No.	Donor	Acceptor	Product	yield %
I	$NO_2{-}CH_2{-}CO_2C_2H_5$	$CH_2{=}CHCN$	 $\begin{array}{l} NO_2{-}CHCO_2C_2H_5 \\ \quad\vert \\ CH_2{-}CH_2CN \end{array}$	75
II	$NO_2{-}CH_2{-}CO_2C_2H_5$	$C_6H_5{-}CH{=}CHCO{-}C_6H_5$	 $\begin{array}{l} NO_2{-}CHCO_2C_2H_5 \\ \quad\vert \\ C_6H_5{-}CH{-}CH_2CO{-}C_6H_5 \end{array}$	63
III	$CH_3CH\vert NO_2\vert_2$	$CH_2{=}CHCO_2CH_3$	 $\begin{array}{l} CH_3C\vert NO_2\vert_2 \\ \quad\vert \\ CH_2CH_2CO_2CH_3 \end{array}$	79
IV	$CH_3CH\vert NO_2\vert_2$	$CH_2{=}CHCOCH_3$	 $\begin{array}{l} CH_3C\vert NO_2\vert_2 \\ \quad\vert \\ CH_2CH_2COCH_3 \end{array}$	66
V	$CH_3CH\vert NO_2\vert_2$	$C_6H_5{-}CH_2{=}CHCO{-}C_6H_5$	 $\begin{array}{l} CH_3C\vert NO_2\vert_2 \\ \quad\vert \\ C_6H_5{-}CHCH_2COC_6H_5 \end{array}$	67
VI	$CH_3CH_2CH\vert NO_2\vert_2$	$CH_2{=}CHCO_2CH_3$	 $\begin{array}{l} CH_3CH_2C\vert NO_2\vert_2 \\ \quad\vert \\ CH_2CH_2CO_2CH_3 \end{array}$	88
VII	$CH_3CH_2CH\vert NO_2\vert_2$	$CH_2{=}CHCO{-}CH_3$	 $\begin{array}{l} CH_3CH_2C\vert NO_2\vert_2 \\ \quad\vert \\ CH_2CH_2COCH_3 \end{array}$	74
VIII	$CH_3CH_2CH\vert NO_2\vert_2$	$C_6H_5CH{=}CH{-}CO{-}C_6H_5$	 $\begin{array}{l} CH_3CH_2C\vert NO_2\vert_2 \\ \quad\vert \\ C_6H_5CHCH_2CO{-}C_6H_5 \end{array}$	29

Condensation of nitroketones with chalcone. Nitroacetone, chalcone (0·02 mol each, 2·9 g and 4·16 g respectively) dissolved in 10 ml MeOH and KF were mixed together in equimolecular amounts and the procedure was the same as for acrylonitryl. It was washed with water to remove the KF and then the syrupy sediment was recrystallized from MeOH and toluene to yield 1 g (33%) of white crystalline 1,5-dibenzoyl-2,4-diphenyl-3-nitropentane, b.p. 218–221°.[18] AcOMe and nitromethane were identified by gas chromatography. The same product was obtained on condensation of chalcone with ω-nitroacetophenone. It gave no m.p. depression on mixing with the product obtained from ω-nitroacetophenone. Methyl benzoate and nitromethane were identified by gas chromatography.

Condensation of gem-*dinitroethane* (DNE) *and* gem-*dinitropropane* (DPN) *with methyl acrylate* (*compound* III, VI). Equimolecular amounts (0·02 mol) of DNE and methyl acrylate (2·4 g and 1·7 g respectively) were mixed with 0·015–0·020 mole (0·9 g and 1·2 g) of anhyd KF in 10 ml MeOH. After a few min a yellow ppt was obtained. The mixture was further processed as described for the condensation of nitroketones. It yielded ethyl n-3.3-dinitrovalerate and methyl 3.3-dinitrocapronate (Table 3).

ITROALKANES IN THE PRESENCE OF POTASSIUM FLUORIDES

b.p.	n_D^{20}		Analysis					
			Required			Found		
			C	H	N	C	H	N
126–128/1	—	$C_7H_{10}O_4N_2$			15·05			14·90[17]
7	—	$C_{19}H_{19}O_5N$	66·05	5·61	4·10	66·61	5·77	4·04
95–97/0·7	1·4556	$C_6H_{10}N_2O_6$			13·59			13·68[23]
118–120/0·5	1·4621	$C_6H_{10}N_2O_5$			14·73			14·50[23]
159	—	$C_{17}H_{16}N_2O_5$	62·19	4·91	8·53	62·64	4·59	8·91
120–122/1·3	1·4572	$C_7H_{12}N_2O_6$	38·18	5·49	12·72	38·85	5·41	12·53
120–122/0·4	1·4625	$C_7H_{12}N_2O_5$	41·17	5·92	13·72	41·27	5·80	14·14
27	—	$C_{18}H_{18}N_2O_5$	63·15	5·30	8·18	63·01	5·17	8·02

Condensation with methyl vinyl ketone (IV, VII Table 3). Processed as described for the condensation with methyl-acrylate.

Condensation with chalcone (V, VIII, Table 3). Processed as above. The product twice recrystallized from MeOH afforded white thread-shaped crystals of 4-benzoyl-3-phenyl-2,2-dinitrobutane and 5-benzoyl-4-phenyl-3.3-dinitropentane.

Reaction rate. 2-Nitropropane and methyl acrylate were made to react in the presence of RCF and KF. 2-Nitropropane, 0·9 ml (0·01 mol), and 0·9 ml (0·01 mol) methyl acrylate, 0·5 ml isobutanol and 3 ml MeOH were mixed with 1·0 g (0·01 mol) anhyd RbF (Measurement II) in a 10-ml flask and the flask was tightly stoppered with a serum cap. The flask was thermostated at 50° ± 0·2°. Samples were withdrawn (3–5 μlitres at 18–22 min intervals by a hypodermic syringe. They were analysed on a Carlo Erbs Model R chromatograph in the following conditions: column 2 m long packed with polyethylene glycol (20%) impregnated on chromosorb W 60/10, vapour temp 75°, detector current 110 mA, and N_2 gas flow rate 45 ml/min. Isobutanol was used as internal standard. The amounts of passing nitro compounds, methyl

TABLE 4

Measurement I			Measurement II		
No.	Time, min.	2-nitropropane, %	No.	Time, min.	2-nitropropane, %
1	0	100·0	1	0	100·0
2	23	15·0	2	20	83·0
3	45	5·8	3	40	81·0
4	68	3·5	4	60	77·5
			5	80	71·2
			6	100	66·4
			7	120	58·0
			8	140	54·2
			9	160	52·0

acrylate and MeOH were estimated by planimetering their peak areas and evaluating by reference to the isobutanol peak areas. Under experimental conditions the product of condensation did not pass through the column.

Measurement I was carried out with KF (1·16 g, 0·08 mole) under strictly similar conditions. The results are listed in Table 4 and presented in Fig. 5.

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