IRON PENTACARBONYL HALOGEN INITIATED REACTION OF ETHYL ACETOACETATE AND ACETYLACETONE WITH ACRYLIC MONOMERS

R. A. Amriev, F. K. Velichko,
Z. A. Abdulkina, and R. Kh. Freidlina

UDC 542.955:541.128:547.484.34:
547.442.3:547.391

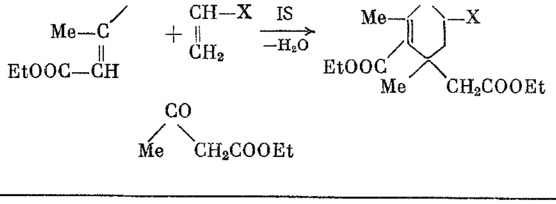
Iron pentacarbonyl in conjunction with bromine or iodine initiates the reaction of diethyl malonate with acrylic monomers [1]. We have found that ethyl acetoacetate (EAA) and acetylacetone add to the double bond of acrylic monomers in the presence of the initiating system $Fe(CO)_5 + Br_2$ (IS).

$$CH_3COCH_2R + CH_2{=}CR'X \xrightarrow[120-130°]{IS} CH_3COCHRCH_2CHR'X \quad \text{(Ia-c), (II), 27–56\%}$$

$$R = COOEt,\ R' = H,\ X = COOMe\ (Ia);\ R = COOEt,\ R' = H,$$
$$X = CN\ (Ib);\ R = COOEt,\ R' = Me,\ X = COOMe\ (Ic);$$
$$R = COMe,\ R' = H,\ X = COOMe\ (II).$$

The addition reaction described herein by us differs from the classical Michael reaction in that base is not required, and diadducts of the type $CH_3COCR(CH_2CHR'X)_2$, characteristic of the Michael reaction [2], are not formed. Also, in contrast to the Michael reaction, the addition reaction in the presence of IS does not occur with addends in which one of the H atoms in the activating CH_2 group is replaced with another group, as for example in $CH_3COCH(Et)CO_2Et$ or $CHCl(CO_2Et)_2$. Thus, as seen in Table 1, the addition of EAA to methyl acrylate may be carried out in ethyl α-ethylacetoacetate as solvent (experiment 5). Ethyl α-ethylacetoacetate also does not react with acrylonitrile in the presence of IS. In contrast, ethyl α-methylacetoacetate is easily cyanoethylated in the presence of sodium ethoxide [3]. IS also does not initiate the addition of chloroform to acrylonitrile, although the cyanoethylation of chloroform in the presence of base is well known [4]. The cyanoethylation of alcohols (i-PrOH, t-BuOH), which occurs readily with basic reagents [5], also does not occur with IS. These negative results concerning the lack of reactivity of ethyl α-ethylacetoacetate, chloroform, and alcohols indicate that in the addition reactions initiated by $Fe(CO)_5$ + halogen (bromine or iodine) the acidity of the activating CH_2 group is not as important as in the Michael reaction [6]. These features of the $Fe(CO)_5$–halogen-initiated addition preclude a purely ionic mechanism for the reaction. On the other hand, the amount of halogen present greatly influences the activity of the $Fe(CO)_5$–halogen-initiating system. The introduction of excess halogen relative to the amount of $Fe(CO)_5$ inhibits the addition reaction (cf. experiments 2 and 3, Table 1, and [1]). The sensitivity of the initiating system IS to various other additives is demonstrated in the reaction of EAA with methyl acrylate; the effectiveness of IS declines in the presence of hexane, $CHCl_3$, and DMF (see Table 1, experiments 4, 6, and 7). These two characteristics of the reaction suggest that in our system metal-complex-promoted initiation may occur via free radical intermediates.

In the reaction of EAA with methyl acrylate, in addition to the adduct Ia, the compound 3-carboethoxy-6-carbomethoxy-4-(carboethoxymethyl)-2,4-dimethyl-5,6-dihydropyran (III) is formed in up to 17% yield. The analogous product IV is obtained in the reaction of EAA with acrylonitrile. The structures of III and IV were ascertained by comparison of their PMR, ^{13}C-NMR, IR, and mass spectra with those of similar compounds [7-13] (see Experimental and Table 3).



X = COOMe (III), CN (IV).

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2550-2555, November, 1984. Original article submitted July 27, 1983.

TABLE 1. Addition of Ethyl Acetoacetate (EAA) to Methyl Acrylate (MA) Initiated by the System $Fe(CO)_5 + Br_2$ (125°, 2 h, EAA : MA : $Fe(Co)_5$: solvent = 1 : 1 : 0.05 : 1)

Expt. No.	Initiator and mole ratio of its components	Solvent	Yield of adduct (Ia), % (GLC)
1	$Fe(CO)_5$	No solvent	3
2	$Fe(CO)_5+Br_2$	»	56
3	$Fe(CO)_5+3Br_2$	»	0
4	$Fe(CO)_5+Br_2+$ DMF	»	25
5	$Fe(CO)_5+Br_2$	$CH_3COCHEtCOOEt$	40
6	$Fe(CO)_5+Br_2$	C_6H_{14}	10
7	$Fe(CO)_5+Br_2$	$CHCl_3$	4
8	$Fe(CO)_5+$ DMF	No solvent	0

TABLE 2. PMR and ^{13}C-NMR Spectra of Adducts

Adduct[a]	^1H-PMR[b]				
	CH_3 in R triplet	CH_3CO singlet	CHR (R″) triplet	OCH_3 singlet	CH_2 in R quartet
1 2 3 4 5 6 7 $CH_3COCHR-CH_2CH_2-COOCH_3$ (Ia)	1,23	2,18	3,57	3,57	4,13
$CH_3COCHR-CH_2CH_2-CN$ (Ib)	1,30	2,26	3,64	–	4,17
$CH_3COCHR-CH_2CHR'COOCH_3$[d, e] (Ic)	1,24	2,16	3,55	3,55	4,10
$CH_3COCHR''CH_2CH_2-COOCH_3$[f] (IIa)	–	2,20	3,62	3,62	–

Adduct[a]	^{13}C-NMR[c]						
	C^1	C^2	C^3	C^4	C^5	C^6	C^7
1 2 3 4 5 6 7 $CH_3COCHR-CH_2CH_2-COOCH_3$ (Ia)	27,9	201,0	57,4	22,1	30,2	171,7	50,4
$CH_3COCHR-CH_2CH_2-CN$ (Ib)	28,2	200,5	56,6	22,5	20,1	118,2	–
$CH_3COCHR-CH_2CHR'COOCH_3$[d, e] (Ic)	28,2	200,9	56,1	30,6	36,4	174,6	50,6
$CH_3COCHR''CH_2CH_2-COOCH_3$[f] (IIa)	28,2	197,2	65,4	21,8	39,2	171,9	50,3

---

[a] R = COOEt, R' = Me, R″ = COMe.

[b] CH_2CH_2 and CH_2CHR' multiplets: (Ia-c) 1.82-2.60 δ; (IIa) 1.60-2.89 δ.

[c] ^{13}C signals for the group $COOCH_2CH_3$ are as follows (ppm): (Ia) 168.2, 60.4, 13.1; (Ib) 167.5, 60.7, 13.9; (Ic) 168.4, 60.3, 13.1.

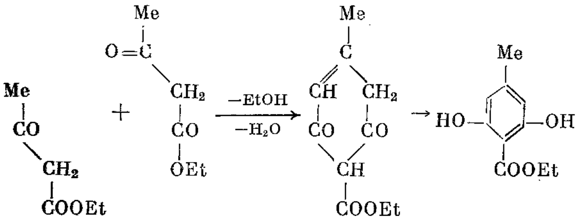
[d] For R' = Me (ppm): ^1H 1.12 δ, ^{13}C 16.1 t.

[e] Given for the diastereomer A (predominant in the mixture).

[f] The ^{13}C signals for R″ coincide with those for C^1 and C^2 in the structure.

The compounds III and IV are not formed in the Michael reactions of EAA.

Ethyl acetoacetate adds to methyl methacrylate with substantially more difficulty than to methyl acrylate or acrylonitrile under the same conditions, and the yield of adduct does not exceed 12%. The adduct of EAA with methyl methacrylate (Ic) occurs as a 1:1 mixture of 2 diastereomers, which can be separated into the individual components. A side product, ethyl 2,6-dihydroxy-4-methylbenzoate (V) is also formed, apparently as a result of a Claisen type condensation of EAA in the presence of $Fe(CO)_5$.



In comparison with EAA, acetylacetone proved to be much less active in the addition reactions under investigation. Of the three monomers mentioned above, only methyl acrylate formed an adduct with acetylacetone. Secondary condensations were also not detected in the case of acetylacetone. From a correlation of the data in [1] with the present study it follows that the acetyl group does not activate a neighboring CH_2

TABLE 3. IR Spectrum of 3-Carboethoxy-6-carbomethoxy-4-(carboethoxymethyl)-2,4-dimethyl-5,6-dihydropyran (III)

Structural fragment (III)	Vibrational type	Frequency, cm^{-1}	Reference
C=C–O	C–O str	1240 vs	[14]
C=C–C=O	C–C str	1635 s	[11]
$C{-}CH_3$	C–H de	1375 s, 1447 m	[14]
C=C–COOR	C–O str	1170 s, 1270 s	[12]
C=O	C–O str	1715 s, 1731 s	[14]
=C–O–C– (cyclic ether)	C–O str	1080 s	[14]
CH	C–H def	1340 w	[14]
CH_2COOR	C–H def	1410 m	[13]

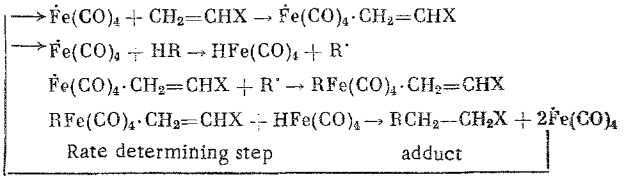
group as much as an ester group does in the addition reactions with acrylic monomers upon treatment with IS. Alkenes such as ethylene and 1-hexene do not react with EAA in the presence of IS.

With respect to the mechanism of the addition of active CH_2 reagents to the double bond of acrylic monomers in the presence of IS, the following steps constitute the most probable process: 1) formation of a coordinatively unsaturated Fe-containing moiety, for instance $Fe(CO)_4$, as a result of the reaction of $Fe(CO)_5$ with Br_2, in analogy with [15]; 2) coordination of the intermediate Fe complex with the acrylic compound, inasmuch as the active acrylic compound, as shown in [16, 17], is probably a complex of the type $CH_2{=}CHX \cdot Fe(CO)_4$; 3) participation by the coordinatively unsaturated Fe component in the dissociation of an H atom from the addend and transfer of the addend to the monomer (in the absence of halogen the coordinatively saturated $Fe(CO)_5$ either does not initiate the reaction or does so at an almost imperceptible rate (experiments 1 and 8, Table 1)).

The mechanism depicted below incorporates all of these features of the reaction. The symbol HR denotes an addend which contains an active hydrogen atom.

$$Fe(CO)_5 + Br_2 \rightarrow Fe(CO)_5^+ + Br^{\cdot} + Br^-$$

$$Fe(CO)_5^+ + Br^- \rightarrow \dot{F}e(CO)_4 + Br^{\cdot} + CO$$



$$\dot{F}e(CO)_4 + CH_2{=}CHX \rightarrow \dot{F}e(CO)_4 \cdot CH_2{=}CHX$$

$$\dot{F}e(CO)_4 + HR \rightarrow HFe(CO)_4 + R^{\cdot}$$

$$\dot{F}e(CO)_4 \cdot CH_2{=}CHX + R^{\cdot} \rightarrow RFe(CO)_4 \cdot CH_2{=}CHX$$

$$RFe(CO)_4 \cdot CH_2{=}CHX + HFe(CO)_4 \rightarrow RCH_2{-}CH_2X + 2\dot{F}e(CO)_4$$

Rate determining step

adduct

$$2Br^{\cdot} \rightarrow Br_2$$

EXPERIMENTAL

GLC analyses were performed on an LKhM-8MD-M5 chromatograph (katharometer) on 1000 × 3 mm stainless steel columns containing 5% SE-30 on N-AW-HMDS chromaton (0.16-0.20 mm); the carrier gas was He (1.5-2 liters/h). Preparative GLC was carried out on a Tsvet-1 chromatograph on 500 × 5 mm stainless steel columns containing 15% SE-30 on N-AW-DMCS chromaton (0.20-0.25 mm). PMR spectra were recorded on a Perkin-Elmer R-12 (60 MHz) spectrophotometer on 50-70% solutions in CCl_4. ^{13}C-NMR spectra were taken on a Bruker-Physik HX-90 spectrophotometer at 22.635 MHz with $CHCl_3$ as internal standard (chemical shifts are reported relative to TMS). Mass spectra were obtained on a MS-30 spectrometer at 70 eV electron energy. IR spectra were taken on a UR-20 spectrophotometer.

Addition Reaction of Ethyl Acetoacetate (EAA) with Methyl Acrylate. To a mixture of 65 g (0.5 mole) EAA, 43 g (0.5 mole) methyl acrylate, and 4.9 g (25 mmole) of $Fe(CO)_5$ under a stream of N_2 was added 4.0 g (25 mmole) Br_2 over 15 min with stirring. The mixture was stirred 2 h at 125°C, cooled, diluted with $CHCl_3$, washed with 10% HCl, and dried over $MgSO_4$. Fractional distillation afforded 39.6 g (37%) of methyl γ-carboethoxy-γ-acetylbutyrate (Ia), bp 98.5°C (1 mm), n_D^{20} 1.4415, d_4^{20} 1.1041. Found: C 55.64; H 7.34%. $C_{10}H_{16}O_5$. Calculated: C 55.55; H 7.46. Mass spectrum, m/e (relative intensity, %): M^+ 216 (0.6), M − CH_3CO + H 174 (47.3), M − $COOC_2H_5$ 143 (11.8), 138 (60.7), 128 (52.5), 114 (29.0), 101 (35.7), 100 (66.3), 73 (29.3), $COOCH_3$ 59 (18.4), 55 (55.7), CH_3CO 43 (100), C_2H_5 29 (34.5). PMR and ^{13}C-NMR spectra are given in Table 2. Higher fractions afforded 3-carboethoxy-6-carbomethoxy-4-(carboethoxymethyl)-2,4-dimethyl-5,6-dihydropyran (III), yield 11.2 g (14%), bp 154-156°C (1 mm), n_D^{20} 1.4800, d_4^{20} 1.1593. Found: C 58.35; H 7.23%. MR 79.33. $C_{16}H_{24}O_7$. Calculated: C 58.53; H 7.36%. MR 80.03. Mass spectrum: M^+ 328. PMR: 1.24 t ($C\underline{H}_3CH_2$), 1.29 t ($C\underline{H}_3CH_2$), 2.20 s ($CH_3C{=}$), 2.73 t (CH), 1.49 s ($CH_3{-}C_{quat}$), 3.73 s ($COOCH_3$), 4.16 q (OCH_2). ^{13}C-NMR: 22.13 and 22.18 ($\underline{C}H_3C{=}$), 161.3 and 161.6 ($O{-}\underline{C}{=}C$), 98.75 ($CO{-}\underline{C}{=}C$), 168.2 and 168.5 (C=O 3-carboethoxy), 58.61 and 58.67 (OCH_2 3-carboethoxy), 13.36 and 13.42 (CH_3 3-carboethoxy), 75.0 and 75.6 (4-C of ring), 18.82 and 18.86 (4-CH_3), 42.95 (4-CH_2), 171.2 (C =O in 4-CH_2COOEt), 59.24 and 59.36 ($CH_2CO{-}O\underline{C}H_2{-}CH_3$), 13.19 ($\underline{C}H_3CH_2OOCCH_2$), 23.75 (5-$CH_2$), 45.73 (6-CH), 166.1 (C =O 6-carbomethoxy), 50.7 and 50.9 ($\underline{C}H_3OOC$). The doubling of most of the signals indicates that the substance consists of a mixture of cis and trans isomers.

Addition Reaction of EAA with Acrylonitrile. This reaction was carried out in an analogous manner starting with 26.4 g (0.2 mole) of EAA, 10.7 g (0.2 mole) acrylonitrile, 1.96 g (10 mmole) $Fe(CO)_5$, and 1.6 g (10 mmole) Br_2 under a stream of N_2. Isolated products: 1) γ-carboethoxy-γ-acetylbutyronitrile (Ib), 9.9 g (27%), bp 108°C (1 mm), n_D^{20} 1.4475, d_4^{20} 1.0770. Found: C 58.60; H 7.12; N 8.48%. MR 45.49. $C_9H_{13}NO_3$. Calculated: C 59.00; H 7.15; N 7.70%. MR 45.25. PMR and ^{13}C-NMR spectra are given in Table 2. Mass spectrum, m/z: M^+ 183 (2.1), M + H − $COCH_3$ 141 (41.7), 138 (19.2), M − $COOC_2H_5$ 110 (2.1), 101 (66.9), 97 (13.7), $COOC_2H_5$ 73 (35.1), 55 (45.5), CO_2 44 (11.3), CH_3CO 43 (100), CH_2CH_2CH 41 (12.3), C_2H_5 29 (24.1).

2) 3-carboethoxy-6-cyano-4-(carboethoxymethyl)-2,4-dimethyl-5,6-dihydropyran (IV), 4.65 g (16%), bp 165-167°C (1 mm). Found: C 60.80; H 7.05; N 4.60%. $C_{15}H_{21}NO_5$. Calculated: C 61.02; H 7.06; N 4.75%. PMR spectrum: 1.11 and 1.51 t (CH_3 of the two ethoxy groups), 4.17 q (OCH_2), 2.10 s ($\underline{C}H_3C{=}$), 2.29 t (CH), 1.58 s ($CH_3{-}C_{quat}$). ^{13}C-NMR spectrum: 21.6 and 21.9 ($CH_3C{=}$), 161.7 and 161.9 ($O{-}C{=}$), 97.9 ($={\underline{C}}{-}CO$), 167.8 and 168.2 (3-COOEt), 60.2 (OCH_2 3-carboethoxy group), 13.4 (CH_3 in C_2H_5O), 74.4 (4-C_{ring}), 19.4 (4-CH_3), 41.4 (4-$\underline{C}H_2COO$), 166.6 (4-$CH_2{-}CO$), 59.4 (4-$CH_2COO\underline{C}H_2$), 22.7 (CH_2, ring), 41.0 (CH_{ring}), 118.4 (CN). According to the characteristics of the ^{13}C signals, the substance consists of a mixture of cis and trans isomers. For the IR spectrum see Table 3.

Addition Reaction of EAA with Methyl Methacrylate. A mixture of 100 g (1 mole) methyl methacrylate, 130 g (1 mole) EAA, 9.8 g (50 mmole) $Fe(CO)_5$, and 8 g (50 mmole) Br_2 was heated at 130°C for 4 h in a 0.5-liter rocking steel autoclave. After dilution with $CHCl_3$, washing with 10% HCl, drying over $CaCl_2$, and evaporation of unreacted starting materials the mixture afforded 28.2 g of a fraction boiling in the range 95-125°C (1 mm) which, according to GLC, contained 17 g of one diastereomer of the adduct, 10 g of the other diastereomer, and 1 g of (V). The reaction products were separated by preparative GLC. Methyl α-methyl-γ-carboethoxy-γ-acetylbutyrate was isolated from a fraction with bp 100-105°C (1 mm) as a mixture of two forms with combined yield 12%. Form A (predominant isomer), n_D^{20} 1.4435, d_4^{20} 1.0799. Found: C 57.22; H 7.77%. MR 56.69. $C_{11}H_{18}O_5$. Calculated: C 57.38; H 7.88%. MR 56.32. PMR and ^{13}C-NMR spectra, see Table 2. Form B (minor constituent of the mixture), n_D^{20} 1.4485, d_4^{20} 1.0947. Found: O 57.53; H 7.70%. MR 56.36, $C_{11}H_{18}O_5$. Calculated: C 57.38; H. 7.88%. MR 56.32. Mass spectrum of a 1:1 mixture of A and B: M^+ 230 (1.1), M + H − CH_3CO 188 (50.5), 152 (38.4), 114 (38.2), 101 (48.3), 88 (66.7), COOEt 73 (26.2), COOMe 59 (10.6), 56 (25.9), 55 (35.6), CH_3CO 43 (100), C_2H_5 29 (20.6). A higher boiling fraction afforded ethyl 2,6-dihydroxy-4-methylbenzoate (V), mp 59.5-60°C (from alcohol); this compound has been described previously [18] under the name ethyl orsellinate, mp 61°C (from petroleum ether). Found: C 61.20; H 6.22%. $C_{10}H_{12}O_4$. Calculated: C 61.22; H 6.16%. PMR spectrum: 2.20 s (4-CH_3), 1.42 t (3H, CH_3CH_2), 4.46 q (2H, CH_2O), 9.41 s (2H, OH), 6.13 s (CH =). ^{13}C-NMR spectrum: 13.9 (CH_3 carboethoxy group), 61.8 (OCH_2), 169.2 (COO), 97.4 (1-C), 160.6 (2,6-C), 108.6 (3,5-C), 147.2 (4-C).

Addition Reaction of Acetylacetone with Methyl Acrylate. The experiment was carried out in four 35-ml glass ampoules, each filled one-third full under an Ar atmosphere; each ampoule was charged with 5 g (50 mmole) acetylacetone, 4.3 g (50 mmole) methyl acrylate, 0.049 g (0.25 mmole) $Fe(CO)_5$, and 0.04 g (0.25 mmole) Br_2. The mixtures were heated at 120°C for 2 h; workup of the combined reaction mixtures afforded 13.9 g of recovered acetylacetone (31% conversion). Distillation at 85°C (1 mm) gave 10.2 g (27%) of methyl γ, γ-diacetylbutyrate (IIa), n_D^{20} 1.4613, d_4^{20} 1.1149. Found: C 58.42; H 7.46%. MR 45.86. $C_9H_{14}O_4$. Calculated: C 58.05; H 7.58%. MR 45.44. For the PMR and ^{13}C-NMR spectra, see Table 2.

CONCLUSIONS

The iron pentacarbonyl – bromine system initiates the addition reactions of ethyl acetoacetate and acetylacetone with the double bonds of acrylic monomers.

LITERATURE CITED

1. F. K. Velichko and L. V. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., 1107 (1982).
2. G. R. Zellars and R. J. Levine, J. Org. Chem., 13, 911 (1948).

3. I. Smrt and F. Shorm, Collect. Czech. Chem. Commun., 18, 131 (1953).
4. H. Timmler and R. Wegler, Angew. Chem., 72, 1001 (1960).
5. A. P. Terent'ev and A. N. Kost, Reactions and Methods of Investigating Organic Compounds [in Russian], Vol. 2, Goskhimizdat, Moscow–Leningrad (1952), p. 63.
6. H. H. Henecka, Chem. Ber., 81, 197 (1948).
7. S. S. Berestova, N. N. Shanet'ko, D. N. Shigorin, V. G. Medvedeva, A. P. Skoldinov, B. D. Plikhina, and Yu. S. Andreichikov, Teor. Éksp. Khim., 15, 575 (1979).
8. N. N. Shanet'ko, Yu. S. Bogachev, S. S. Berestova, V. G. Medvedeva, A. P. Skoldinov, and D. N. Shigorin, Teor. Éksp. Khim., 17, 186 (1981).
9. A. B. Ternt'ev, V. I. Dostovalova, and R. Kh. Freidlina, Org. Magn. Reson., 9, 301 (1977).
10. E. P. Prokof'ev and Zh. A. Krasnaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1011 (1980).
11. N. K. Freeman, J. Am. Chem. Soc., 75, 1859 (1953).
12. N. B. Colthup, J. Opt. Soc. Am., 40, 397 (1950).
13. S. A. Francis, J. Chem. Phys., 19, 942 (1951).
14. L. Bellamy, Infrared Spectra of Complex Molecules, Wiley (1954).
15. J. P. Maher and K. P. Samers, J. Chem. Soc., Dalton Trans., 579 (1980).
16. S. F. A. Kettle and L. E. Orgel, Chem. Ind., 49 (1960).
17. E. Weiss, K. Stark, L. F. Lankaster, and H. D. Murdoch, Helv. Chim. Acta, 46, 288 (1963).
18. A. Lipp and E. Scheller, Chem. Ber., 42, 1967 (1909).

1,3-DISUBSTITUTED 1,1,5,5-TETRANITROPENTANE-3-NITRONIC ACIDS

L. T. Eremenko, G. V. Oreshko,
M. A. Fadeev, G. V. Lagodzinskaya,
and V. I. Shestov

UDC 542.91:547.414

Usually nitroalkanenitronic acids of the aliphatic series cannot be isolated because of their extremely strong tendency to isomerize to true polynitro compounds. But by the addition of trinitromethane to 2-nitroalkenes the respective nitroalkanenitronic acids could be isolated individually [1]. Yet similar reactions of trinitromethane [2], fluorodinitromethane [3], and other nitroalkanes [4] with derivatives of 2-nitroallyl alcohol yield not the nitronic acids, but the symmetrical polynitroalkanes:

$$\mathrm{MeCOOCH_2C(NO_2){=}CH_2 + RH \rightarrow (RCH_2)_2CHNO_2}$$
$$\mathrm{R = C(NO_2)_3,\ \ FC(NO_2)_2\ \ MeC(NO_2)_2.}$$

We have found that salts of symmetrical polynitropentanes – 1,1,1,3,5,5,5-hepta- and 1,5-difluoro-1,1,3,5,5-pentanitropentane – under the influence of CF_3COOH in CCl_4 with cooling form 1,1,1,5,5,5-hexa- (I) and 1,5-difluoro-1,1,5,5-tetranitropentane-3-nitronic acids (II):

$$\mathrm{(RCH_2)_2C{=}NO_2^{-}AH^{+} \xrightarrow{CF_3COOH} \underset{(I),\ (II)}{(RCH_2)_2C{=}NOOH}}$$
$$\mathrm{A = NH_3,\ C_5H_5N;\ R = C(NO_2)_3\ (I);\ CF(NO_2)_2\ (II).}$$

In contrast to those described in [1, 5], these crystalline nitronic acids go over to the nitro form, the true nitro compounds, at ~20°. In air the (II) crystals isomerize in 10-15 min without decomposing, while (I) does so in 3-4 h with a small release of nitrogen oxides. When cooled to ~ −50°, (I) and (II) do not change for several days. The isomerization is quite fast in solution (ether, unsubstituted organic acids, and other solvents); this makes recrystallization of these compounds impossible. In trinitromethane solution the isomerization is substantially retarded, but it is accelerated by the addition of water. Therefore the PMR spectra

---

Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka Branch. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2555-2557, November, 1984. Original article submitted August 22, 1983.