# CONCLUSIONS

1. The reaction of a dialkyl(chloromethyl)amine with lithium o-carboranes gave the N,N-dialkylaminomethyl-o-carboranes (or the N,N,N-dialkyl-o-carboranylmethylamines).

2. In contrast to  $\text{LiAlH}_4$ ,  $\text{AlClH}_2$  reduces the N,N-dialkylamides of o-carboranecarboxylic acid to the corresponding amines without cleaving the C-C bond between the carborane nucleus and the amide group.

### LITERATURE CITED

1. L. I. Zakharkin and V. S. Kozlova, Izv. Akad. Nauk SSSR, Ser. Khim., 1973, 1185.

2. L. I. Zakharkin, V. S. Kozlova, and S. A. Babich, Zh. Obshch. Khim., 44, 1891 (1974).

3. L. I. Żakharkin and Yu. A. Chapovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1964, 772.

4. L. I. Zakharkin, V. A. Brattsev, and Yu. A. Chapovskii, Zh. Obshch. Khim., 35, 2160 (1965).

# ADDITION OF 2-CARBOXYETHYL RADICALS

### TO 1-ALKENES AND 1-ALKYNES

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The electrophilic 1-carboxyalkyl radicals RCHCOOH have been studied extensively in the addition reactions to 1-alkenes [1]. They also add to 1-alkynes [2]. The nucleophilic radicals  $RCH(CH_2)_nCOOH$  ( $n \ge 1$ ) easily add to acrylic monomers due to manifestation of the polar effect [3]. Their reactions with alkenes and alkynes are unknown.

The addition of 2-carboxyethyl radicals, generated from peroxydisuccinic acid (PDSA) using  $FeSO_4$  [4], to 1-alkenes and 1-alkynes is discussed in the present paper. In the absence of an acceptor the  $CH_2CH_2COOH$  radicals obtained in this manner recombine predominantly to adipic acid [4]. Recombination also occurs in the presence of unsaturated hydrocarbons (Table 1). However, at a high concentration of the unsaturated hydrocarbon (6 moles per mole of peroxide), only 20-30% of the generated 2-carboxethyl radicals are converted to adipic acid, while 35-50% of the radicals add to the alkene or alkyne.

 $\begin{array}{l} (\mathrm{HOOCCH}_{2}\mathrm{CH}_{2}\mathrm{COO})_{2} + \mathrm{Fe}(\mathrm{II}) \rightarrow \mathrm{HOOCCH}_{2}\mathrm{CH}_{2}\mathrm{COO}^{-} + \mathrm{Fe}(\mathrm{III}) + \\ & + \mathrm{CO}_{2} + \mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{COOH} \\ \mathrm{RCH}_{2}\mathrm{CH} = \mathrm{CH}_{2} + \mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{COOH} \rightarrow \mathrm{RCH}_{2}\mathrm{CHCH}_{2}\mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{COOH} \\ & (\mathrm{I}) \\ (\mathrm{I}) + \mathrm{Fe}(\mathrm{III}) - \\ & - \\ & - \\ \mathrm{RCH}_{2}\mathrm{CH} = \mathrm{CHCH}_{2}\mathrm{CH}_{2}\mathrm{COOH} \\ & (\mathrm{II}) \\ & + \\ \mathrm{Fe}(\mathrm{III}) + \mathrm{H}^{+} \\ & - \\ \mathrm{RCH} = \mathrm{CHCH}_{2}\mathrm{CH}_{2}\mathrm{COOH} + \mathrm{Fe}(\mathrm{II}) + \mathrm{H}^{+} \\ & (\mathrm{III}) \\ & (\mathrm{I}) + \mathrm{SH} \rightarrow \mathrm{R} (\mathrm{CH}_{2})_{5}\mathrm{COOH} + \mathrm{S}^{*} \\ & (\mathrm{IV}) \\ \mathrm{R} = \mathrm{C}_{2}\mathrm{H}_{7} (\mathrm{a}), \ \mathrm{C}_{5}\mathrm{H}_{11} (\mathrm{b}) \end{array}$ 

The formed secondary adduct-radicals(I) are oxidized predominantly by Fe(III) ions and, in addition, cleave a hydrogen atom from the H donor (SH-succinic acid, hydrocarbon, methanol-solvent). As a result, unsaturated (II), (III) and saturated (IV) acids are obtained, (II) +(III):(IV) ~ 5:3. Acids (II) and (III) are formed in a 1:3 ratio. This ratio was established by the NMR method for the methyl esters of acids (II) and (III) on the basis of the integral intensity of the signals at 3.55 and 3.50 ppm (CH<sub>3</sub>O). On the example of the methyl ester of cis-, trans-(II) (R = C<sub>3</sub>H<sub>7</sub>), which was synthesized as described in [5], it was shown that the steric isomers have the same chemical shift for the protons of the CH<sub>3</sub>O group. The predominant formation of the isomer with the multiple bond furthest away from the functional group when carboxyalkyl radicals are oxidized by Cu(II) ions was mentioned in [6]; it is assumed, due to the steric shielding of the radical center.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2625-2628, November, 1977. Original article submitted May 17, 1977.

	Decomposition products, mole/mole of peroxide					
Hydrocarbon	HO <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H	HO <sub>2</sub> C (CH <sub>2</sub> ) <sub>4</sub> CO <sub>2</sub> H	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> H 0,10 Not determined Ditro 0,09 0,10			
1-Hexene 1-Hexene* 1-Octene 1-Hexyne 1-Octyne	0,97 1,35 0,98 0,96 0,94	0,14 0,09 0,16 0,10 0,11				
	$RCH_2CH = CH(CH_2)_2CO_2H$	RCH=CH(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H	R (CH <sub>2</sub> ) 5CO <sub>2</sub> H			
1-Hexene 1-Hexene <sup>*</sup> 1-Octene 1-Hexyne 1-Octyne	0,06 0,03 0,05 0,53 0,46	0,18 0,08 0,15 	0,15 0,11 0,13 - -			

TABLE 1. Main Decomposition Products of PDSA under Influence of FeSO<sub>4</sub> in Presence of 1-Alkenes and 1-Alkynes  $[R = C_3H_7$  (hexene, hexyne),  $C_5H_1$  (octene, octyne)]

\*In presence of NaF.

TABLE 2. Decomposition Products of Peroxydiglutaric Acid under Influence of  $FeSO_4$  in Aqueous Solutions [peroxide : salt = 1:1 (molar)]

Solvent	Decomposition products, mole/mole of peroxide									
	CO2	glutaric acid		suberic acid		human	y-butyro-	vinyl-		
		total	labeled	total	labeled	acid	lactone	acetic acid		
H <sub>2</sub> O * D <sub>2</sub> O	0,98 0,99	0,98 0,97	0,02	0,17 0,18	0,015	0,33 0,32	0,18 0,17	0,01		

\*Hexane-1,3,6-tricarboxylic acid was isolated in an amount of 0.06 mole/mole of peroxide.

The oxidative mechanism for the formation of unsaturated acids is confirmed by the fact that their yield decreases when NaF is added to the reaction system:  $PDSA - FeSO_4 - 1$ -hexene (see Table 1). The fluorine ions partially bind the Fe(III) ions into an insoluble complex [7], thus lowering their oxidative capacity and increasing the contribution made to the overall process of converting the radicals by the competing reaction of hydrogen transfer.

1-Hexyne and 1-octyne capture the 2-carboxyethyl radicals more efficiently than do the corresponding alkenes:

$$\begin{aligned} \text{RCH}_2\text{C} \equiv \text{CH} + \text{CH}_2\text{CH}_2\text{COOH} \rightarrow & \text{RCH}_2\text{C} = \text{CHCH}_2\text{CH}_2\text{COOH} \\ & (\text{V}) \\ & (\text{V}) + \text{SH} \rightarrow (\text{II}) \end{aligned}$$

The intermediate vinyl adduct-radicals (V) are not oxidized by Fe(III) ions. They predominantly cleave hydrogen from the H donor and are converted to  $\Delta^{4,5}$ -alkenoic acids (II). The yield of these acids is ~50%.

According to [8], the succinic acid that is formed during the decomposition of PDSA can function as a hydrogen donor toward free radicals. We obtained additional data regarding reactions of this type on the example of peroxydiglutaric acid (PDGA), whose main decomposition products were studied in [8].  $\alpha$ -D-Glutaric and  $\alpha$ -D-suberic acids are obtained when PDGA is reacted with FeSO<sub>4</sub> in D<sub>2</sub>O (Table 2). From this it may be concluded that the 3-carboxypropyl radicals generated from PDGA react with the decomposition products of PDGA, namely the glutaric and suberic acids, while the newly formed (VI) radicals are partially reduced by Fe(II) ions:

$$\begin{array}{rcl} \text{HOOC}(\text{CH}_2)_n \text{COOH} \ + \ \text{CH}_2(\text{CH}_2)_2 \text{COOH} \ \rightarrow \ \text{HOOCCH}(\text{CH}_2)_{n-1} \text{COOH} \ + \\ & & (\text{VI}) \\ & + \ \text{CH}_3(\text{CH}_2)_2 \text{COOH} \\ & & (\text{VI}) \ + \ \text{Fe}(\text{II}) \xrightarrow{D_2\text{O}} \text{HOOCCHD}(\text{CH}_2)_{n-1} \text{COOH} \ + \ \text{Fe}(\text{III}) \\ & & n = 3 \text{ or } 6 \end{array}$$

The other transformation products of PDGA in D<sub>2</sub>O are given in Table 2.

## EXPERIMENTAL

The GLC analysis was run on an LKhM-8M chromatograph equipped with a flame-ionization detector and a 4 m  $\times$ 3 mm column packed with 15% PEGS deposited on Chromosorb W, 40-60 mesh. The NMR spectra were obtained on an XL-100 instrument (solvent = CCl<sub>4</sub>, internal standard = HMDS), while the mass spectra were taken on an MI-1305 instrument. The peroxy diacids were synthesized as described in [9]; CO<sub>2</sub> was determined gravimetrically.

Addition of 2-Carboxyethyl Radicals to 1-Alkenes and 1-Alkynes. To a mixture of 0.02 mole of PDSA and 0.10 mole of unsaturated compound in 15 ml of MeOH was added in 1 h a solution of 0.02 mole of  $FeSO_4$ . 7H<sub>2</sub>O in 60 ml of MeOH at 20°C. The solvent and unreacted unsaturated compound were distilled off and the residue was esterified with methanol in the presence of conc. H<sub>2</sub>SO<sub>4</sub>. The fraction of the mixed acid esters was isolated by distillation. The quantitative yield of the products was determined by GLC using internal standards (see Table 1).

A fraction with bp 90-100° (15 mm) was obtained in the reaction with 1-hexene, from which by preparative GLC we isolated a mixture of the methyl esters of nonen-4-oic (IIa) and nonen-5-oic (IIIa) acids in a 1:3 ratio (NMR data). NMR spectrum ( $\delta$ , ppm): 5.36-5.16 m (CH = CH); 3.55 s [OCH<sub>3</sub> in (IIa)]; 3.50 s [OCH<sub>3</sub> in (IIIa)]; 2.19 m (CH<sub>2</sub>C=O); 2.05-1.76 m (CH<sub>2</sub>CH = CHCH<sub>2</sub>); 1.34-1.10 m (CH<sub>2</sub>CH<sub>2</sub>CH); 0.8 t (CH<sub>3</sub>).

The structure of the methyl esters of undecenoic acids (IIb) and (IIIb) was confirmed by their conversion to methyl undecanoate by hydrogenation over Raney Ni.

Decomposition of Peroxydiglutaric Acid in  $D_2O$ . To exchange the crystallization water for  $D_2O$  the FeSO<sub>4</sub> heptahydrate was heated (110-120°, 5 h) in vacuo, after which it was treated with  $D_2O$  and dehydrated again. The operation was repeated four times. The reaction and isolation of the products were run the same as described in [8]. The amount of deuterium in the acid diesters was determined by mass spectrometry on the basis of the intensity of the peaks that are formed when the OCH<sub>3</sub> groups are cleaved. For the isolated dimethyl esters of glutaric and suberic acids the m/e (relative intensity, %) is, respectively: 129 (100), 130 (8.3), 131 (0.5) and 171 (100), 172 (13.4) 173 (0.93). To calculate the amount of the natural C<sup>13</sup> and D isotopes we took the spectra of control samples of the diesters of these acids, m/e (relative intensity, %): 129 (100), 130 (6.8), 131 (0.4) and 171 (100), 172 (9.4), 173 (0.85).

## CONCLUSIONS

1. 2-Carboxyethyl radicals, generated in the system peroxydisuccinic acid-Fe(III) sulfate, add to 1alkenes. The intermediately formed adduct-radicals are oxidized by Fe(III) ions to give  $\Delta^{4,5}$ - and  $\Delta^{5,6}$ -alkenoic acids.

2. The vinyl adduct-radicals, obtained by the addition of 2-carboxyethyl radicals to 1-alkynes, predominantly cleave hydrogen from the H donor in the presence of Fe(III) ions.

3.  $\alpha$ -Carboxyalkyl radicals are capable of being reduced by Fe(II) ions in water to the corresponding acids.

#### LITERATURE CITED

1. H. H. Vogel, Synthesis, <u>1970</u>, 99.

2. Yu. N. Ogibin and G. I. Nikishin, Zh. Organ. Khim., 2, 1565 (1966).

- 3. F. Minisci and U. Pallini, Gazz. Chim. Ital., 89, 1030 (1961).
- 4. G. I. Nikishin, S. I. Moryasheva, and E. K. Starostin, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1975</u>, 2501.
- 5. G. I. Nikishin, M. G. Vinogradov, and T. M. Fedorova, Chem. Commun., 1973, 693.
- 6. M. G. Vinogradov, T. M. Fedorova, and G. I. Nikishin, Zh. Organ. Khim., <u>11</u>, 1380 (1975).
- 7. I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, MacMillan (1952).
- 8. E.K. Starostin, S. I. Moryasheva, and G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Khim., 1974, 2048.

9. W. Karnozhitskii, Organic Peroxides [Russian translation], IL (1961), p. 66.