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Abstract

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REDUCTIVE DIMERIZATION OF DERIVATIVES OF α, β-UNSATURATED ACIDS

It was established earlier by us (^{1}) that, under certain conditions, the principal product of the indirect electrochemical reduction of acrylonitrile is adipic acid dinitrile. Since the method found for reductive dimerization is distinguished by good reproducibility of the results and makes it possible to carry out the reduction under comparable conditions on various amalgams, it appeared possible to study the dependence of the hydrodimerization phenomenon on the structure of the compounds being reduced and on the nature of the amalgams.

With this aim, reductive dimerization was carried out for a series of different derivatives of α, β-unsaturated acids.

Reductive dimerization was performed in an apparatus consisting of a combination of an electrolyzer for obtaining amalgams with a reaction vessel, in which the amalgams obtained interacted with the reaction mixture (Fig. 1). The surface of the mercury cathode was 1.80 dm^2, and the surface of the amalgam in the reaction vessel was 2.35 dm^2. The amalgams were obtained by electrolysis of 40% solutions of sodium or potassium hydroxides and of a saturated LiCl solution at a current of 8-9 A and a temperature of 14-16°. The reaction mixtures consisted of the substances being reduced and 20% HCl (1 : 2.5 mol.). The reactions were interrupted after the appearance of an alkaline reaction to phenolphthalein.

Fig. 1. *A* –reaction vessel, *B* –electrolyzer

The investigation showed that one of the factors influencing the formation of hydrodimers is the character of the conjugated system of the substances being reduced. This observation cannot be considered unexpected if one assumes that formation of the hydrodimer is preceded by reduction of the molecules to intermediate radicals with their subsequent dimerization according to the scheme:

$$e + \mathrm{CH_2{=}CH{-}C}\left(\frac{\mathrm{O}}{\mathrm{OR}}\right) + \mathrm{H^+} \longrightarrow \cdot\mathrm{CH_2CH_2COOR}$$

$$2 \cdot \mathrm{CH_2CH_2COOR} \longrightarrow (\mathrm{CH_2CH_2COOR})_2$$

It is known that unconjugated ethylenic bonds are not reduced by amalgams. Using styrene and vinyl acetate as examples, we established that

conjugation of the ethylenic bond with the benzene nucleus or with the unshared pair of electrons of the oxygen atom is also insufficient for reduction of the double bond on potassium or lithium amalgams. In the case of amides and diethylamides of α, β-unsaturated acids, the conjugation of the C–C and C–O groups is apparently considerably weakened by the competing conjugation of the unshared pair of electrons of the nitrogen atom with the π-electrons of the C–O bond:

$$\mathrm{CH_2{=}CH{-}C({=}\,O)NR_2} \tag{2}$$

This may explain the fact that the amides and diethylamides of acrylic and crotonic acids are reduced only with great difficulty and do not give hydrodimers, while the amide and diethylamide of methacrylic acid are not reduced.

In the diethylamide and diphenylamide of cinnamic acid there is conjugation of the π-electrons of the carbonyl group, the ethylenic bond, and the benzene nucleus:

$$\mathrm{C_6H_5{-}CH{=}CH{-}C({=}\,O)NR_2} \tag{3}$$

as a result of which the competing conjugation is apparently less pronounced. From Table 1 it is seen that these compounds, along with the products of normal reduction, give hydrodimers.

The foregoing is in agreement with the literature data (2) on the hydrodimerization of α, β-unsaturated acids, in which competing conjugation is also present:

$$\mathrm{CH_2{=}CH{-}C({=}\,O)OH} \tag{4}$$

In this case also the phenomenon of reductive dimerization is characteristic only of acids in which, in the β-position, there are $\mathrm{C_6H_5{-}CH_2{=}CH{-}}$ and similar groupings. The connection between the phenomenon of conjugation and the ability to form hydrodimers is also observed in the series of esters and nitriles of α, β-unsaturated acids (see Table 1). Thus, for example, diethyl maleate, in which the conjugated system is somewhat disturbed (3), gives a hydrodimer in lower yield than diethyl fumarate. The decrease in the yield of hydrodimer in the case of methyl methacrylate and the absence of reduction upon hydrogenation of methacrylonitrile with potassium and lithium amalgams can be explained by a decrease in the conjugation of the multiple bond with the carbonyl group owing to the hyperconjugation effect of the methyl group. At the same time, from the data obtained it is evident that other factors may also have a decisive influence on the phenomenon of reductive dimerization. Thus, the absence of reduction upon treatment of the ethyl ester of β, β-dimethylacrylic acid with sodium and potassium amalgams is apparently explained by the shielding of the β-position by two methyl groups. With increasing molecular weight of the alcoholic residue in the series of acrylic esters, the yield of hydrodimer decreases; finally, the fact of the increased stability of nitriles of α,β-unsaturated acids, as compared with the corresponding esters, toward the action of amalgams of alkali metals is difficult to explain.

From the results obtained by us it follows that amalgams differ sharply in their ability to reduce derivatives of α,β-unsaturated acids.

Table 1

Starting compound	Reducing agent	Structure of hydrodimer	Yield, %
$CH_2{=}CHCOOCH_3$	K(Hg)	$(CH_2CH_2COOCH_3)_2$	26,7
$CH_2{=}CHCOOC_2H_5$	K(Hg)	$(CH_2CH_2COOC_2H_5)_2$	52,0
$CH_2{=}CHCOOC_3H_7$-n	K(Hg)	$(CH_2CH_2COOC_3H_7$-n$)_2$	34,9
$CH_2{=}CHCOOC_4H_9$-n	K(Hg)	$(CH_2CH_2COOC_4H_9$-n$)_2$	27,8
$CH_2{=}C(CH_3)COOCH_3$	K(Hg)	$(CH_2CH(CH_3)COOCH_3)_2$	23,1
$CH_2{=}C(CH_3)COOCH_3$	Na(Hg)	$(CH_2CH(CH_3)COOCH_3)_2$	16,1
$CH_3CH{=}CHCOOC_2H_5$	K(Hg)	$(CH_3CHCH_2COOC_2H_5)_2$	71,0
$(CH_3)_2C{=}CHCOOC_2H_5$	Li(Hg)	$[(CH_3)_2CCH_2COOC_2H_5]_2$ *	31,4
$(CH_3)_2C{=}CHCOOC_2H_5$	Na(Hg); K(Hg)	$(C_2H_5OOCCHCH_2COOC_2H_5)_2$	**
$C_2H_5OOCCH{=}CHCOOC_2H_5$, cis	K(Hg)	$(C_2H_5OOCCHCH_2COOC_2H_5)_2$	7,3
$C_2H_5OOCCH{=}CHCOOC_2H_5$, cis	Al(Hg)	–	0,0
$C_2H_5OOCCH{=}CHCOOC_2H_5$, trans	K(Hg)	$(C_2H_5OOCCHCH_2COOC_2H_5)_2$	28,6
$C_2H_5OOCCH{=}CHCOOC_2H_5$, trans	Al(Hg)	$(C_2H_5OOCCHCH_2COOC_2H_5)_2$	12,7
$C_6H_5CH{=}CHCOOC_2H_5$	K(Hg)	$(C_6H_5CHCH_2COOC_2H_5)_2$	51,3
$CH_2{=}C(C_6H_5)COOC_2H_5$	K(Hg)	$(CH_2CH(C_6H_5)COOC_2H_5)_2$ *	27,8
$CH_2{=}CClCN$	K(Hg)	$(CH_2CH_2CN)_2$	68,1
$CH_3CH{=}CHCN$	Li(Hg)	$(CH_3CHCH_2CN)_2$ *	37,0
$CH_3CH{=}CHCN$	Na(Hg); K(Hg)	–	**
$(CH_3)_2C{=}CHCN$	K(Hg); Li(Hg)	–	**
$CH_2{=}C(CH_3)CN$	K(Hg); Li(Hg)	–	**
$C_6H_5CH{=}CHCN$	K(Hg)	$(C_6H_5CHCH_2CN)_2$ *	60,0
$C_6H_5CH{=}CHCN$	Al(Hg)	$(C_6H_5CHCH_2CN)_2$	22,2
$C_6H_5CH{=}CHCON(C_2H_5)_2$ ***	K(Hg)	$[C_6H_5CHCH_2CON(C_2H_5)_2]_2$ *	22,7

Starting compound	Reducing agent	Structure of hydrodimer	Yield, %
$C_6H_5CH=CHCON(C_6H_5)_2$ ***	K(Hg)	$[C_6H_5CHCH_2CON(C_6H_5)_2]_2$ *	5,2

* Compounds obtained for the first time.
** The starting compounds are not reduced.
*** The reduction was carried out in a 30% solution of CH_3COOH in alcohol.

acids with formation of hydrodimers. Of the compounds investigated (see Table 1), on aluminum amalgam in moist ether by the method of Wilds and Shunk$^{(4)}$, only the esters of maleic and fumaric acids and derivatives of cinnamic acid undergo hydrodimerization. In the case of alkali-metal amalgams, the reactivity increases from sodium amalgam to lithium amalgam, i.e., parallel to the increase in the normal potential of these amalgams.

Table 2

Formula	b.p., °C	Pressure, mm Hg	n_D^{20}	d_4^{20}	C, % found	C, % calcd.	H, % found	H, % calcd.	N, % found	N, % calcd.
$(CH_2CH_2COOCH_3)_2$	110–113	10	1,4288	1,0642	55,38	55,16	8,00	8,10	–	–
$(CH_2CH_2COOC_2H_5)_2$	113–116	8	1,4283	1,0085	59,18	59,38	9,04	8,97	–	–
$(CH_2CH_2COOC_3H_7\text{-n})_2$	152–154	13	1,4301	0,9804	62,75	62,58	9,44	9,63	–	–
$(CH_2CH_2COOC_4H_9\text{-n})_2$	140–143	4	1,4375	0,9631	65,32	65,08	10,21	10,14	–	–
$(CH_2CH(CH_3)COOCH_3)_2$	108–112	12	1,4334	1,0188	59,23	59,38	8,93	8,97	–	–
$(CH_3CHCH_2COOC_2H_5)_2$	109–115	4	1,4350	0,9886	62,40	62,58	9,58	9,63	–	–
$[(CH_3)_2CCH_2COOC_2H_5]_2$	117–118	2	1,4521	0,9950	64,81	65,08	10,12	10,14	–	–
$(C_2H_5OOCCHCH_2COOC_2H_5)_2$ *	179–182	4	1,0468	1,4475	55,34	55,46	7,45	7,50	–	–

Formula	b.p., °C	Pressure, mm Hg	n_D^{20}	d_4^{20}	C, % found	C, % calcd.	H, % found	H, % calcd.	N, % found	N, % calcd.
$(C_2H_5OOCCHCH_2COOC_2H_5)_2$ **	178–179	3	1,0467	1,4464	55,17	55,46	7,59	7,50	–	–
$(CH_2CH_2CN)_2$	140–142	41	1,4418	0,9528	66,87	66,65	7,61	7,45	25,73	25,89
$(CH_3CHCH_2CN)_2$	121	3	1,4524	0,9524	70,76	70,56	8,71	8,88	20,39	20,56

* Obtained by reductive dimerization of diethyl maleate.
** Product of hydrodimerization of diethyl fumarate.

On lithium amalgam, in particular, it proved possible to carry out the reductive dimerization of ethyl β,β-dimethylacrylate and crotonic acid nitrile, which are not reduced on other amalgams. Under comparable conditions on sodium amalgam the yield of hydrodimer is 10–20% lower than on potassium amalgam. The structure of the hydrodimers obtained was confirmed by identification of the acids and by formation from the acids of the corresponding cyclopentanones. The investigation showed that reductive dimerization, where possible, leads to formation of a mixture of stereoisomers. Hydrodimerization of α-chloroacrylonitrile (see Table 1) is accompanied by replacement of the halide by hydrogen. The products

Table 3

Formula	M.p., °C	Solvent for crystallization	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
$(C_6H_5CHCH_2COOC_2H_5)_2$	116–117	Alcohol	74.21	74.54	7.41	7.40	–	–
$(CH_2CH(C_6H_5)COOC_2H_5)_2$*	111–113	Alcohol	74.2	74.54	7.51	7.40	–	–
$(CH_2CH(C_6H_5)COOC_2H_5)_2$**	36–38	Alcohol	74.40	74.54	7.48	7.40	–	–
$(C_6H_5CHCH_2CN)_2$*	213–215	Acetone	83.31	83.05	6.26	6.20	11.08	10.75
$(C_6H_5CHCH_2CN)_2$*	153–155	Alcohol	82.91	83.05	6.32	6.20	11.01	10.75
$[C_6H_5CHCH_2CON(C_2H_5)_2]_2$	175–177	Ethyl acetate	70.11	76.43	8.74	8.88	6.62	6.85

Formula	M.p., °C	Solvent for crystallization	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
$[C_6H_5CHCH_2{-}CON(C_6H_5)_2]_2$	288-289	Dimethylformamide	83.68	83.97	6.09	6.04	4.60	4.66

* Fractional crystallization yielded meso- and d, l-forms. In the remaining cases, the melting points are given for the forms less soluble in the indicated solvents.

The products of the reaction are adipodinitrile and propionitrile. In parallel with the reductive dimerization of methyl acrylate, a process of its saponification takes place, which greatly lowers the yield of the hydrodimer. The properties of the hydrodimers obtained are presented in Tables 2 and 3.

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1. I. L. Knunyants, N. S. Vyazankin, *Izv. AN SSSR, OKhN*, 1957, No. 2.
2. I. L. Knunyants, N. P. Gambaryan, *Usp. khim.*, **23**, 781 (1954).
3. D. G. J. Felton, S. F. D. Orr, *J. Chem. Soc.*, 1955, 2170.
4. A. L. Wilds, R. E. Sutton, *J. Org. Chem.*, **16**, 1371 (1951).

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