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DEGRADATION OF CARBOXYLIC ACIDS BY ONE CARBON ATOM

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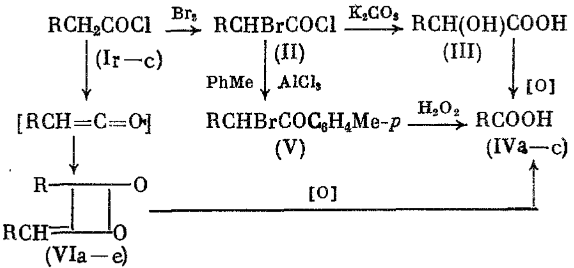
To degrade carboxylic acids by one C atom, the Barbier–Wieland method is mainly used. This is based on the Grignard reaction of phenylmagnesium bromide with esters, followed by oxidation of the intermediate 1-alkyl-2,2-diphenylethylenes [1-3].

To search for other paths for degrading the carboxylic acids by one C atom, in the present work we studied the transformation of n-decanoyl chloride (Ia) into the lower homolog, pelargonic acid (IVa)



R = C_8H_{17} (Ia), (II), (III), (IVa), (V), (VIa); C_7H_{15} (Ib), (IVb), (VIb); C_4H_9 (Ic), (IVc), (VIc).

α-Bromodecanoyl chloride (II) was obtained by brominating acid chloride (Ia) according to [4]. Compound (II) was then hydrolyzed in aqueous DMFA to α-hydroxy acid (III). The oxidative splitting of (III) by the action of $KMnO_4$ or a chromic mixture in AcOH leads to the formation of acid (IVa) with an admixture of lower carboxylic acids (Table 1, expts. 2 and 3). The (III) → (IV) transformation by the action of $KMnO_4$ in acetone, i.e., under the conditions of oxidative splitting of α-hydroxycarboxylic acids according to [5], proceeds much less selectively.

Bromo-ketone (V) was obtained by the Friedel–Crafts reaction of acid chloride (II) with toluene in the presence of $AlCl_3$, and was subjected to alkaline splitting by alkaline H_2O_2 in an aqueous–alcoholic solution. Under these conditions, besides p-toluic acid, acid (IVa) was isolated with a similar admixture of lower carboxylic acids than in the preceding experiments (see Table 1, expt. 4). Transformation (V) → (IVa) probably proceeds via successive stages of nucleophilic substitution of the Br atom by a hydroperoxide residue, decomposition of hydroperoxide (VII), and further oxidation of the intermediate α-diketone (VIII) according to the scheme

TABLE 1. Oxidative Splitting of Functional Derivatives (III), (V), (VIa-c), and (XI)

No. of expt.	Substrate	Oxidizing agent	Main oxidation product	Ratio of (IVa-c) and admixtures of lower carboxylic acids	Yield of oxidation products, %
1	(III)	$KMnO_4$ in acetone	(IVa)	44 : 56	32
2	(III)	$KMnO_4$ in AcOH	(IVa)	78 : 22	42
3	(III)	Chromic mixture in AcOH	(IVa)	80 : 20	30
4	(V)	H_2O_2/KOH in aqueous alcohol	(IVa)	93 : 7	38
5	(VIa)	$KMnO_4$ in AcOH	(IVa)	95 : 5	30
6	(VIb)	$KMnO_4$ in AcOH	(IVb)	95 : 5	25
7	(VIc)	$KMnO_4/Na_2CO_3$ in H_2O	(IVc)	95 : 5	28
8	(XI)	CrO_3 in aqueous AcOH	(IVa)	96 : 4	44

*According to data of GLC analysis of methyl esters.

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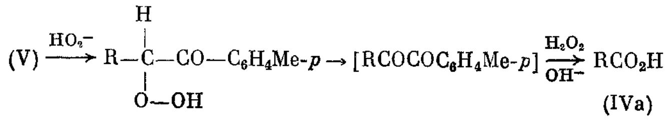

$$(V) \xrightarrow{HO_2^-} R-\overset{H}{\underset{O-OH}{C}}-CO-C_6H_4Me\text{-}p \rightarrow [RCOCOC_6H_4Me\text{-}p] \xrightarrow[OH^-]{H_2O_2} \underset{(IVa)}{RCO_2H}$$

The oxidative splitting of diketone (VIa), synthesized by dehydrochlorination of (Ia) by the action of Et_3N [6], proceeds more selectively. By treating diketene (VIa) with $KMnO_4$ in AcOH, acid (IVa) was isolated, which contains a small amount of lower carboxylic acids as an admixture (expt. 5). The selective oxidation of diketene (VIa) is favored by the presence of an ethylene bridge and an acidic CH group in (VIa), which are sensitive to the action of oxidizing agents.

Similarly, the corresponding caprylic and valeric acids are formed in the oxidation of diketene, obtained from pelargonic acid (VIb) by the action of $KMnO_4$ in AcOH, and a diketene obtained from caproic acid (VIc) by treatment with $KMnO_4$ in an aqueous solution of Na_2CO_3, respectively (expts. 6 and 7). Attempts to split diketenes (VIa-c) by other oxidizing agents (CrO_3, chromic mixture, H_2O_2) did not give satisfactory results.

To compare the diketene method of degradation of carboxylic acids by one C atom with the Barbier–Wieland method [3], we used the latter method in the synthesis of acid (IVa) from methyl caprate (IX). The reaction of ester (IX) with phenylmagnesium bromide, followed by splitting the carbinol (X) gives ethylene (XI), which on oxidation by CrO_3 in aqueous AcOH gave acid (IVa).

$$\underset{(IX)}{RCH_2COOMe} \xrightarrow{PhMgBr} \underset{(X)}{RCH_2C(OH)Ph_2} \xrightarrow{-H_2O} RCH{=}CPh_2 \xrightarrow{CrO_3} (IVa)$$

Acid (IVa) was obtained by this three-stage scheme in an overall yield of 23%, based on ester (IX) (expt. 8). In its yield and purity of the end product, the diketene method is comparable with the classical Barbier–Wieland method.

The carboxylic acids which were synthesized were identified in the form of methyl esters by mass spectroscopy [7] and GLC methods.

EXPERIMENTAL

The GLC analysis of the methyl esters of the carboxylic acids was carried out on an LKhM-8 MD chromatograph with a flame-ionization detector, using a 1 m × 3 mm stainless steel column with 5% silicone SE-30 on Chromaton N-AW, 0.160-0.200 mm (120°C); carrier gas N_2.

The PMR spectra were run on a Tesla BS-497 spectrometer (in CCl_4 with reference to TMS as internal standard); the mass spectra were run on a Varian MATCH-6 apparatus.

α-Hydroxydecanoic Acid (III). A 14-g portion of capric acid and 6 ml of Br_2 were successively added to 10 ml of $SOCl_2$, and the mixture was held for 4 h at 20°C. It was then heated for 10 h at 70-75°C (here and below the bath temperature), and evaporated, and the residue was distilled in vacuo. Yield, 17 g (76%) of α-bromodecanoyl chloride (II), bp 100-101°C (4 mm), n_D^{20} 1.4720. PMR spectrum (δ, ppm): 0.83 m (Me), 1.23 br. s ($(CH_2)_6$), 1.96 m (CH_2), 4.34 t (CHBr, J = 7 Hz).

A mixture of 2.4 g of (II), 2 ml of H_2O, 3 g of K_2CO_3, and 10 ml of DMFA was heated for 5 h at 140-145°C, then cooled to 20°C, diluted by 80 ml of H_2O, acidified by dilute (1:1) HCl, and extracted by ether. The extract was dried over $MgSO_4$ and evaporated. Yield, 1.3 g (80%) of (III), mp 70-72°C (from ether at −70°C).

PMR spectrum (δ, ppm): 0.87 t (Me, J = 5 Hz), 1.28 br. s [$(CH_2)_7$], 4.20 t (CH, J = 4 Hz). The compound (III) synthesized does not give a depression of the melting point of a mixed probe with a known sample, obtained by hydrolysis of α-bromodecanoic acid by aqueous KOH [8].

Oxidative Splitting of α-Hydroxydecanoic Acid (III). A 20-g portion of finely ground $KMnO_4$ was added gradually, with stirring, to a solution of 6 g of (III) in 140 ml of AcOH. The mixture was held, with periodic stirring, for 48 h at 20°C, and then was diluted by 1 liter of water. A 50-ml portion of conc. HCl was added and the mixture was left to stand for 24 h at 20°C, and then was extracted by ether. The extract was dried over $MgSO_4$ and evaporated, and the residue was fractionally distilled at atmospheric pressure. Yield, 2.1 g (42%) of pelargonic acid (IVa) (bp 248-252°C (750 mm), n_D^{20} 1.4302) with an admixture of lower carboxylic acids (see Table 1, expt. 2).

A 30-ml portion of concentrated H_2SO_4 was added gradually, with stirring, to a solution of 5 g of (III) in 200 ml of AcOH, and then 30 ml of an aqueous solution containing 14 g of $Na_2Cr_2O_7$ were added. The mixture was stirred for 4 h at 20°C, poured into water, and extracted by ethyl acetate. The extract was dried over $MgSO_4$ and evaporated, and the residue was fractionally distilled at atmospheric pressure. Yield, 1.2 g (30%) of (IVa) (bp 245-249°C (745 mm), n_D^{20} 1.4303) with an admixture of lower carboxylic acids (expt. 3).

Preparation of p-(α-Bromodecanoyl)toluene (V). A 5-g portion of anhydrous $AlCl_3$ was gradually added, with stirring, to a solution of 6 g of acid chloride (II) in 15 ml of toluene. The mixture was stirred for another 20 min at 20°C, then poured into water and extracted by ether. The extract was dried over $MgSO_4$ and evaporated. Yield, 7 g (89%) of (V), mp 33-35°C (from ether, at −70°C). PMR spectrum (δ, ppm): 0.92 m (Me), 1.28 br. s ($-(CH_2)_6-$), 2.00 m (CH_2CHBr), 2.38 s (Me), 4.97 t (CHBr, J = 7 Hz), 6.06 d and 7.10 d (arom. ring, J = 10 Hz). Found: C 62.79; H 8.03; Br 24.64%. $C_{17}H_{25}BrO$. Calculated: C 62.77; H 7.69; Br 24.62%.

Oxidative Splitting of p-(α-Bromodecanoyl)toluene (V). A 4.6-g portion of bromoketone (V) was added, with stirring, to a solution of 8 g of KOH in 40 ml of alcohol, and then 15 ml of perhydrol were added in the course of 30 min. The reaction mixture was held, with periodic stirring, for 24 h, then diluted by water, acidified by concentrated HCl, and extracted by benzene. The extract was dried over $MgSO_4$ and evaporated, and the residue was treated with hexane at 0°C. The precipitate of p-toluic acid (mp 178-179°C) was separated, the mother liquor was evaporated, and the residue was fractionally distilled at atmospheric pressure. Yield, 1 g (38%) of (IVa) (bp 249-252°C (750 mm), n_D^{20} 1.4308) with an admixture of products of more extensive decomposition (expt. 4). When bromo-ketone (V) was oxidized by other oxidizing agents ($KMnO_4$, CrO_3, $Na_2Cr_2O_7$ + H_2SO_4), mixtures of carboxylic acids were isolated with a low content of (IVa).

Oxidative Splitting of Diketene Obtained from Capric Acid (VIa). Diketene (VIa) was obtained according to [6] with certain changes. A 15-g portion of capric acid was added to 10 ml of $SOCl_2$, and the mixture was held for 24 h at 20°C, and then was heated for 2 h at 60-70°C. Excess $SOCl_2$ was evaporated *in vacuo* and the residue was dissolved in 100 ml of benzene, and 17 ml of dry Et_3N were added gradually and with ice-cooling. The reaction mixture was held for 24 h at 0°C and treated with ice water. The benzene layer was separated, and the aqueous solution was extracted by benzene. The combined benzene solutions were dried over $MgSO_4$ and evaporated. After distillation of the residue *in vacuo*, 9.3 g (70%) of diketene (VIa) were obtained (bp 180-184°C (4 mm)), which was used at the following stage without additional purification.

Finely ground $KMnO_4$ was added gradually, with stirring and cooling with water, to a solution of 8 g of diketene (VIa) in 160 ml of AcOH. At the end of the exothermal reaction, the mixture was held for 24 h, with periodic stirring, at 20°C. The mixture was then diluted by water, excess $KMnO_4$ was decomposed by Na_2SO_3, and 80 ml of concentrated HCl were added. The reaction mixture was left to stand for 24 h at 20°C, and then was extracted by benzene. The benzene extract was dried over $MgSO_4$ and evaporated. The residue was fractionally distilled *in vacuo* to yield 2.5 g (30%) of (IVa), bp 145-148°C (20 mm), n_D^{20} 1.4306 (expt. 5).

Oxidative Splitting of Diketene Obtained from Pelargonic Acid (VIb). The synthesis of diketene (VIb) and its oxidation by $KMnO_4$ in AcOH were carried out as described in the preceding experiment. From 8 g of pelargonic acid, diketene (VIb) was obtained, which was used, without distillation, at the following stage. Oxidation of (VIb) gave 1.8 g (25%) of caprylic acid (IVb), bp 233-235°C (750 mm), n_D^{20} 1.4276 (expt. 6).

Oxidative Splitting of Diketene Obtained from Caproic Acid (VIc). A 9.8-g portion of diketene (VIc) [6] was added to a solution of 30 g of Na_2CO_3 in 350 ml of water, and then, with stirring and cooling by water, 40 g of finely ground $KMnO_4$ were gradually added. The mixture was held for 96 h, with periodic stirring, at 20°C. Excess $KMnO_4$ was decomposed by Na_2SO_3, and the MnO_2 precipitate was filtered and washed with an aqueous solution of KOH. The mother liquor was acidified with concentrated HCl and extracted by ether. The extract was dried over $MgSO_4$ and evaporated. The residue was fractionally distilled at atmospheric pressure. Yield, 2.8 g (28%) of (IVc), bp 181-183°C (750 mm), n_D^{20} 1.4075 (expt. 7).

Oxidation of diketene (VIc) in $KMnO_4$ in AcOH gave a mixture of carboxylic acids with a lower content of the desired (IVc).

Oxidative Splitting of 1,1-Diphenyl-1-decene (XI). By carrying out the reaction as described in [3], 5 g of methyl caprate (IX) gave 3.78 g (52%) of (XI), bp 160-164°C (3 mm), n_D^{20} 1.5492. Found: C 90.08; H 9.61%. $C_{22}H_{28}$. Calculated: C 90.35; H 9.65%.

Oxidation of 3.5 g of (XI) according to [3] gave 1.39 g (44%) of (IVa), bp 162-167°C (30 mm) (expt. 8). The overall yield of (IVa), calculated for (IVa) is 23% (based on (XI)).

CONCLUSIONS

1. Methods of degradation of carboxylic acids by one carbon atom by oxidizing the corresponding diketenes by potassium permanganate have been developed.

2. The transformation of decanoyl chloride into pelargonic acid via intermediate stages of oxidative splitting of α-hydroxydecanoic acid by $KMnO_4$ and chromic mixture, or oxidation by alkaline H_2O_2 of a product of a Friedel—Crafts reaction of α-bromodecanoyl chloride with toluene, were studied.

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SYNTHESIS AND VALENCE ISOMERIZATION OF δ-DIMETHYLAMINO-γ-CHLORODIENONES TO 2-DIMETHYLAMINO-3-CHLORO-2H-PYRANS. ^{1}H AND ^{13}C NMR AND UV SPECTROSCOPIC STUDY

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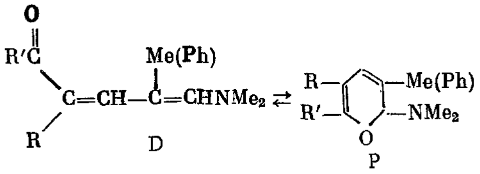
952.1:547.81

We have previously reported the synthesis of dienylic δ-dimethylamino carbonyl compounds containing Me or Ph substituents in the γ position, and have observed the valence isomerization of the δ-aminodienone moiety to a 2-amino-2H-pyran derivative [1-4].



Because the reversible cleavage of the C—O bond is the underlying principle behind the photochromism of spiropyrans, one of the most important classes of photochromic materials, with broad practical applications, we have continued our research in the development of synthetic methods for various types of δ-aminodienones, and have subjected these compounds to a systematic study of their solvation, thermal, and photochromic properties.

Our goal in the present paper was to synthesize δ-dimethylamino-γ-chlorodienones and investigate their valence isomerization.

The starting materials used in this study were the previously unknown aminal (Ia) and aminoacetal (Ib) of α-chloro-β-dimethylaminoacrolein; these compounds were obtained

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