drying was recrystallized from ethyl ether, dried, and the crystals (m.p. 77.0°)[12] mounted directly on a sample pan and counted for C^{14} in a windowless, Q-gas flow counting tube operated in the Geiger–Müller region. No radioactivity could be detected within the limits of the precision of the measurements. A second determination yielded the same result.

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Synthesis of Odd-numbered Keto Dibasic Acids and Corresponding Saturated Acids

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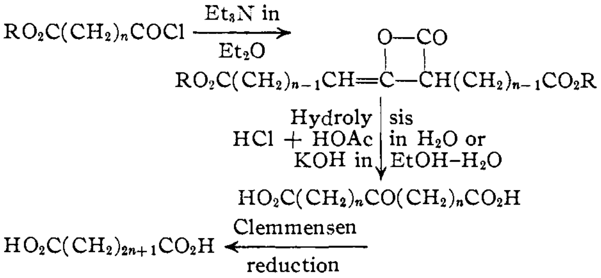
Odd-numbered keto dibasic acids of the type $HO_2C(CH_2)_nCO(CH_2)_nCO_2H$ and related saturated acids, $HO_2C(CH_2)_{2n+1}CO_2H$, were desired as intermediates for syntheses of many-membered carbon rings. Recently Leonard and Goode[1] described the preparation of several acids of this kind *via* the dialkylation of acetonedicarboxylic ester with ω-halogen esters, a procedure first reported by von Pechmann and Sidgwick.[2] However, it seemed that the desired acids might be obtained in quantity more conveniently through application of the method used by Sauer in his preparation of 6-oxo-1,11-hendecanedioic acid from δ-carbethoxyvaleryl chloride through γ-carbethoxypropylketene dimer.[3] The method in general terms is indicated in the following diagram.



By this method δ-ketoazelaic acid (I) was obtained as its diethyl ester in 42–52% yield from γ-carbomethoxybutyryl chloride. In this synthesis the best results were obtained by hydrolyzing the intermediate ketene dimer with hydrochloric acid in acetic acid–water, thus avoiding intramolecular condensation of the keto acid. The higher keto dibasic acids, 9-oxo-1,17-heptadecanedioic acid (II) and 10-oxo-1,19-nonadecanedioic acid (III), were obtained in excellent yield (85–95%) from the appropriate acid chlorides. The intermediate ketene dimers were best hydrolyzed by an ethanol–water solution of potassium hydroxide.[3]

Clemmensen reduction of II and III gave 1,17-heptadecanedioic acid and 1,19-nonadecanedioic acid in yields of 80 and 63%, respectively.

The availability of ω-carbalkoxy acid chlorides and the ease with which they may be transformed *via* the ketene dimers to the corresponding keto dibasic acids, recommends Sauer's method as a useful one for preparing the odd-numbered symmetrical keto dibasic acids. The Clemmensen reduction of these keto acids to saturated odd-numbered dibasic acids is also a satisfactory process.

Experimental[4]

Materials.—Thionyl chloride, anhydrous ether and triethylamine were purified as previously described.[5] Acid chlorides of mono esters of dibasic acids were prepared by treating the carbalkoxy acids with thionyl chloride. Those used showed the following properties: γ-carbomethoxybutyryl chloride, b.p. 105–110° (20 mm.), $n^{20}{}_D$ 1.444–1.446; ω-carbomethoxycaprylyl chloride, b.p. 127.5–130° (3.3 mm.); ω-carbethoxypelargonyl chloride, b.p. 174–176° (15 mm.).

δ-Ketoazelaic Acid (I).—The procedure used was similar to that described by Sauer for the preparation of 6-oxo-1,11-hendecanedioic acid[3] but some important modifications were made. γ-Carbomethoxybutyryl chloride (330 g., 2 moles) was added rapidly to a cooled, well stirred solution of 242 g. (2.4 moles) of triethylamine in 2 l. of anhydrous ether, all under an atmosphere of purified nitrogen. After completion of the addition, stirring of the mixture under nitrogen was continued for 24 hr. at room temperature. Then 40–50 ml. of a solution of 350 ml. of concentrated hydrochloric acid in 490 ml. of glacial acetic was added with stirring, followed by the addition of 300 ml. of water. The ether layer was separated and the aqueous layer extracted with four 300-ml. portions of ether. Tarry material, which separated during the acidification and which was insoluble both in ether and in water, was dissolved in acetone and combined with 100 ml. each of concentrated hydrochloric acid and acetic acid. This mixture was evaporated on the steam-bath and the resulting residue combined later with the main hydrolysate. The combined ether solutions were added to *ca.* 800 ml. of the hydrochloric acid–acetic acid solution described above and, after distillation of the ether, the residue was refluxed 6 hr. This residue, combined with the hydrolyzed tars mentioned previously, was evaporated on the steam-bath. A mixture of 200 ml. each of concentrated hydrochloric acid and acetic acid was added to the non-volatile residue and the whole evaporated again on the steam-bath. Subsequently 200 ml. of water was added to the residue and the mixture again evaporated on the steam-bath. After repeating this last treatment and finally heating the residue on the steam-bath for 12 hr. there was obtained 225–235 g. of crude I suitable for esterification.

Pure I was obtained by extracting the crude acid with chloroform, adding petroleum ether to the extract, and recrystallizing the precipitated acid from water: m.p. 109–109.6°; neut. equiv., 100.5; phenylhydrazone deriv., m.p. 149–151.1°.[1,2,6]

Diethyl δ-ketoazelate was prepared following the procedure of Leonard and Goode[1] using the crude I described above. The crude I obtained from 330 g. (2 moles) of γ-carbomethoxybutyryl chloride gave 110–135 g. of the ester: b.p. 137–155° (0.5 mm.). This 42–52% yield for the two steps from the acid chloride is based on twenty preparations. A sample of this diester redistilled showed the following properties: b.p. 142° (0.3 mm.); $n^{20}{}_D$ 1.4459; $d^{20}{}_4$ 1.0545; sapn. no. 126.8, 125.4; semicarbazone deriv., m.p. 78.5–79° from chloroform–ligroin.[1]

9-Oxo-1,17-heptadecanedioic Acid (II) **and 10-Oxo-1,19-nonadecanedioic Acid** (III).—Following essentially the procedure of Sauer,[3] ω-carbomethoxycaprylyl chloride and ω-carbethoxypelargonyl chloride were dehydrochlorinated to give the corresponding crude ketene dimers. These dimers were then hydrolyzed using a solution of potassium hydroxide in ethanol–water, also as described by Sauer.[3]

The unrecrystallized III obtained (98.5% yield) showed m.p. 117–119.5°.[7] II after one recrystallization from ethanol showed m.p. 113–115°.[8]

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1,17-Heptadecanedioic Acid and 1,19-Nonadecanedioic Acid.—Reduction of the crude keto dibasic acids II and III by the Clemmensen method[9] gave 1,17-heptadecanedioic acid showing m.p. 118–118.5° with sintering at 117.5°[10] in 80.5% yield after two recrystallizations and 1,19-nonadecanedioic acid showing m.p. 118–119°[10] in 63% yield after two recrystallizations. The m.ps. of these acids when mixed with their related keto dibasic acids were lowered markedly; depressions of 6–10° were observed.

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Zero-point Vibrational Contributions to the Optical Rotatory Power of Isotopically Dissymmetric Molcules

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Recently, several optically active compounds of the type R_1R_2CHD have been prepared.[1,2] The optical rotations, while small, are apparently well established experimentally and are of the order of magnitude to be expected from the isotopic mass dissymmetry. The rotations of such compounds are amenable to theoretical calculation within the framework of Kirkwood's theory of optical rotatory power[3] if the vibrational contributions are explicitly taken into account.

The Born–Oppenheimer approximation[4] may be used to express the molecular wave functions as products of wave functions for the electronic and nuclear motions. For the equilibrium configuration of the nuclei the potential function for the electronic motion possesses a plane of symmetry. The vibrational wave functions, on the other hand, will be sensibly dissymmetric because of the isotopic mass difference.

Kirkwood's theory[3] can be applied to the case of isotopic dissymmetry through explicit representation of the quantities of interest as expectation values over the molecular ground state wave function. We start with Kirkwood's Eq. (32) for $g^{(0)}$

$$g^{(0)} = -\sum_{i \neq h = 1}^{N} ([\overrightarrow{a_3}\alpha^{(i)}\mathrm{T}_{ik}\alpha^{(k)}\overrightarrow{a_2}][\overrightarrow{R_k}\overrightarrow{a_1}])_{\mathrm{Av.}} \quad (1)$$

in which the sum extends over the N intrinsically inactive groups into which the molecule is divided for the purpose of calculation; α is the group polarizability tensor; and $\overrightarrow{R}$ denotes the position of the group center of mass referred to the molecular center of mass. The unit vectors $\overrightarrow{a}$ define a rectangular coördinate system fixed in space, and the subscript Av. indicates an averaging over all molecular orientations. Expanding $g^{(0)}$ in the normal coördinates of vibration about the equilibrium positions, we obtain

$$g^{(0)} = \sum_{i \neq h = 1} [(\overrightarrow{a_3}\alpha^{(i)}\mathrm{T}_{ik}\alpha^{(k)}\overrightarrow{a_2})(\{\sum_l\left(\frac{\partial \overrightarrow{R_k}}{\partial q_l}\right)_0 q_l\}\overrightarrow{a_1})$$

$$+ (\overrightarrow{R_k}\overrightarrow{a_1})_0(\overrightarrow{a_3}\alpha^{(i)}\{(\sum_l\left(\frac{\partial \mathrm{T}_{ik}}{\partial q_l}\right)_0 q_l)\alpha^{(k)} + \mathrm{T}_{ik}(\sum_l\left(\frac{\partial \alpha^{(k)}}{\partial q_l}\right) q_l)\}a_2)$$

$$+ (\overrightarrow{R_k}a_1)_0(a_3\alpha^{(i)}\{\sum_l\left(\frac{\partial \mathrm{T}_{ik}}{\partial q_l}\right)_0 q_l\}\{\sum_n\left(\frac{\partial \alpha^{(k)}}{\partial q_n}\right)_0 q_n\}\overrightarrow{a_2}) + \ldots]_{\mathrm{Av.}}$$

where the q's represent the normal coördinates. We have supposed here that in any one mode of vibration the polarizability of only one group of each pair is appreciably affected by the vibration. The remaining second order terms are neglected for various reasons. The averaging process is carried out as before[3] and for groups with optical symmetry, the result for $\langle g^{(0)} \rangle$, the expectation value of $g^{(0)}$, is analogous to Kirkwood's corrected[5] Eq. (35)

$$\langle g^{(0)} \rangle = \frac{1}{6}\sum_{i \neq k = 1}^{N} \alpha_i\beta_i\Bigl[\Bigl(\sum_l \alpha_l^{(k)\prime}\beta_l^{(k)\prime}\langle q_l\rangle\Bigr)$$

$$(G_{ik} + G'_{ik})(\overrightarrow{R_{ik}}\cdot(\overrightarrow{b_i}\times\overrightarrow{b_k}))$$

$$+ \alpha_i\beta_i(G'_{ik}\overrightarrow{R_{ik}} + G_{ik}\Bigl(\sum_l\left(\frac{\partial \overrightarrow{R_{ik}}}{\partial q_l}\right)\langle q_l\rangle\Bigr)))\cdot(\overrightarrow{b_i}\times\overrightarrow{b_k})\Bigr] \quad (3)$$

$$\alpha_l^{(k)\prime} = \frac{1}{3}\left\{\left(\frac{\partial \alpha_{11}^{(k)}}{\partial q_l}\right)_0 + 2\left(\frac{\partial \alpha_{22}^{(k)}}{\partial q_l}\right)_0\right\};\ \alpha_l^{(k)\prime}\beta_l^{(k)\prime} = \left(\frac{\partial \alpha_{11}^{(k)}}{\partial q_l}\right)_0 - \left(\frac{\partial \alpha_{22}^{(k)}}{\partial q_l}\right)_0$$

$$G'_{ik} = \overrightarrow{b_i'}\left\{\sum_l\left(\frac{\partial \mathrm{T}_{ik}}{\partial q_l}\right)_0\langle q_l\rangle\right\}\overrightarrow{b_k}$$

where α_{11} and α_{22} are the components of the group polarizability tensor parallel and perpendicular to the optical axis of the group, $\overrightarrow{b}$ is the unit vector along the optical axis, and $\overrightarrow{b'}$ is the corresponding quantity for the derived tensor.

For R_1R_2CHD the principal contributions probably come from C–H and C–D stretching; for this motion the triple vector product in the fourth term of Eq. (3) vanishes, and the third term is found to be small, so that, to a first approximation

$$\langle q^{(0)}\rangle = \frac{1}{6}\sum_i \alpha_i\beta_i[\alpha^{(H)\prime}\beta^{(H)\prime}(G_{i\mathrm{H}} + G'_{i\mathrm{H}})(R_{i\mathrm{H}}\cdot(\overrightarrow{b_i}\times\overrightarrow{b_{\mathrm{H}}})\langle X_{\mathrm{H}}\rangle + \alpha^{(\mathrm{D})\prime}\beta^{(\mathrm{D})\prime}(G_{i\mathrm{D}} + G'_{i\mathrm{D}})(\overrightarrow{R_{i\mathrm{D}}}\cdot(b_i\times\overrightarrow{b_{\mathrm{D}}})\langle x_{\mathrm{D}}\rangle] \quad (4)$$

where x represents the elongation of the bond from its equilibrium distance and the sum extends over all groups other than H and D.

The value of $(\alpha^{(\mathrm{H})\prime}\langle x_{\mathrm{H}}\rangle)$, 0.028 Å.[3] for one C–H bond, has been obtained from the polarizabilities of CH_4 and CD_4.[6] The quantity β' is related to the degree of depolarization of a Raman line in the same way that the quantity β is related to the degree of depolarization of ordinary (Rayleigh) scattered light.[7] It was obtained from the depolarization factor for the ν_1, A_1 line of chloroform.[8] The value $\rho = 0.3$, taken as representative, gives $\beta' = 1.9$. By way of comparison, the value for hydrogen,[6,9] $\rho = 0.14$, gives $\beta' = 1.2$ for the H–H

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