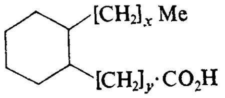
Diels–Alder Reactions of Long-chain Unsaturated Fatty Acids

By **G. F. Whitfield**,† Unilever Research Laboratory, The Frythe, Welwyn, Hertfordshire

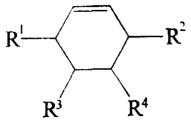
Methyl 9,12-dioxo-octadeca-*trans*-10-enoate undergoes Diels-Alder reaction with isoprene, with 2,3-dimethylbutadiene, and with methyl octadeca-*trans*-9,*trans*-11-dienoate to give substituted cyclohexenes. Clemmensen reduction of the cycloaddition product from the last-mentioned compound does not proceed normally, but yields a dihydroisobenzofuran compound by cyclodehydration. Diels–Alder reaction of 12-oxo-octadec-*trans*-10-enoic acid and octadeca-*trans*-9,*trans*-11-dienoic acid does not proceed to completion, but Clemmensen reduction of the cycloaddition product occurs normally to give the C_{36} cyclic di-acid.

THE importance of the Diels–Alder reaction as a preparative method in organic chemistry is widely recognised[1] and its ramifications in the lipid field have also been intensively investigated.[2,3] Heat treatment of linseed oil (which contains the triglyceride of octadeca-*cis*-9,*cis*-12,*cis*-15-trienoic acid) in the presence of alkali, followed by hydrogenation, gives rise to a series of C_{18} cyclic acids, of general structure (I). Their structure has been demonstrated by Friedrich,[4] who synthesised a number of the possible isomers ($x = 0$, 1, 2, or 3) and showed that 2-(8-carboxyoctyl)-1-propylcyclohexane was the major component. This substantiated the earlier work of Hutchison *et al.*,[5] who synthesised the aromatic analogue, ($x = 0$).



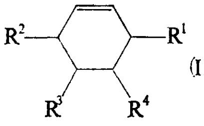
(I) $x + y = 10$

Intermolecular Diels–Alder reactions occur when methyl 10-*trans*,12-*trans*-octadecadienoate[6] or methyl 9-*cis*,12-*cis*-octadecadienoate[7] is heated, to give the diesters of C_{36} cyclic acids of general structures (II) and (III).



(II)

$R^1 = [CH_2]_a \cdot CO_2Me$
$R^2 = Me[CH_2]_b$
$a + b = 12$



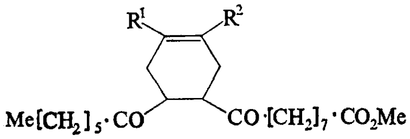
(III)

$R^3 = Me[CH_2]_c$
and $R^4 = CH{:}CH \cdot [CH_2]_d \cdot CO_2Me$
with $c + d = 12$
or $R^3 = Me[CH_2]_e \cdot CH{:}CH$
and $R^4 = [CH_2]_f \cdot CO_2Me$
with $e + f = 12$

The structures of these cyclic esters were deduced by degradation and spectral measurements. They have not yet been confirmed by synthesis. The work reported here is concerned with the synthesis, by intermolecular Diels–Alder reactions, of cyclohexenes structurally analogous to the compounds (I), (II), and (III).

Diels–Alder reaction of methyl 9,12-dioxo-octadeca-*trans*-10-enoate (IV)[8] with isoprene gave a mixture of products, methyl 5-heptanoyl-1-methylcyclohexene-4-(9-oxononanoate) (Va) and the 2-methyl analogue (Vb).

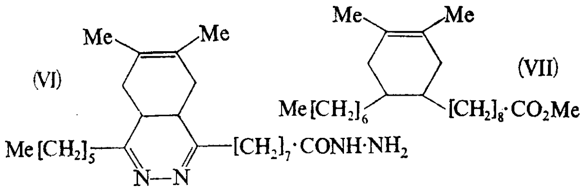
$Me[CH_2]_5 \cdot CO \cdot CH{:}CH \cdot CO \cdot [CH_2]_7 \cdot CO_2Me$ (IV)



(V)

a; $R^1 = Me$; $R^2 = H$
b; $R^1 = H$; $R^2 = Me$
c; $R^1 = R^2 = Me$

Reaction of compound (IV) with 2,3-dimethylbutadiene gave the 1,2-dimethylcyclohexene (Vc) (98%). Treatment of compound (Vc) with hydrazine hydrate yielded 4-hexyl-6,7-dimethyl-4a,5,8,8a-tetrahydrophthalazine-1-octanohydrazide (VI), whilst (Vc) was reduced to methyl 5-heptyl-1,2-dimethylcyclohexene-4-nonanoate (VII) (40%) by the Clemmensen reaction.



(VI)

(VII)

Attention was next directed to the diesters of C_{36} cyclic acids. Diels–Alder reaction of methyl octadeca-*trans*-9,*trans*-11-dienoate (IX)[9] with the dienophile (IV) gave methyl 5-heptanoyl-6-hexyl-3-(7-methoxycarbonylheptyl)cyclohexene-4-(9-oxononanoate) (Xa) and the isomer arising from 'antiparallel' addition (Xb), in 90% yield. T.l.c. of the mixture of (Xa) and (Xb) revealed two partially resolved spots, (R_F 0·55 and 0·59).

Clemmensen reduction of the mixture of (Xa) and (Xb) gave a mixture of products, which on t.l.c. was resolved into four components, evident as two pairs of spots (on silica–silver nitrate). The faster-running pair were dimethyl 3,4-dihexyl-4,5,6,7-tetrahydroisobenzofuran-1,7-dioctanoate (XIa) and its 'antiparallel'

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† *Present address:* Department of Chemistry, Queen Mary College (University of London), Mile End Road, London E.1.

[1] S. B. Needleman and M. C. Chang Kuo, *Chem. Rev.*, 1962, **62**, 405.

[2] H. P. Kaufmann, *Fette, Seifen, Anstrichm.*, 1962, **64**, 1115.

[3] L. F. Byrne, *Off. Dig. Fed. Soc. Paint Technol.*, 1962, **34**, 229.

[4] J. P. Friedrich, *J. Amer. Oil Chemists' Soc.*, 1967, **44**, 244.

[5] R. B. Hutchison and J. C. Alexander, *J. Org. Chem.*, 1963, **28**, 2522.

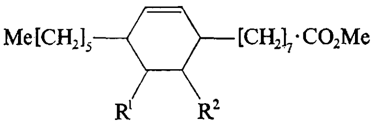
[6] R. F. Paschke, L. E. Peterson, and D. H. Wheeler, *J. Amer. Oil Chemists' Soc.*, 1964, **41**, 723.

[7] D. H. Wheeler and J. White, *J. Amer. Oil Chemists' Soc.*, 1967, **44**, 298.

[8] R. Kouhoupt, *J. Org. Chem.*, 1960, **25**, 1042.

[9] W. J. Schneider, L. E. Gast, and H. M. Teeter, *J. Amer. Oil Chemists' Soc.*, 1964, **41**, 605.

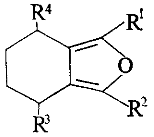
$\mathrm{Me[CH_2]_5{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}CO_2R}$ (VIII) R = H
(IX) R = Me



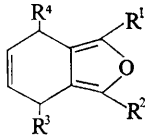
(X)

a; $\mathrm{R^1 = Me[CH_2]_5{\cdot}CO}$
$\mathrm{R^2 = CO{\cdot}[CH_2]_7{\cdot}CO_2Me}$
b: $\mathrm{R^1 = CO[CH_2]_7{\cdot}CO_2Me}$
$\mathrm{R^2 = Me[CH_2]_5{\cdot}CO}$

analogue (XIb). The slower-running pair were dimethyl 3,4-dihexyl-4,7-dihydroisobenzofuran-1,7-dioctanoate (XIIa) and its ' antiparallel ' analogue (XIIb).



(XI)



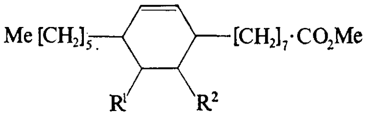
(XII)

a; $\mathrm{R^1 = R^4 = [CH_2]_7{\cdot}CO_2Me}$
$\mathrm{R^2 = R^3 = Me[CH_2]_5}$
b; $\mathrm{R^1 = R^3 = Me[CH_2]_5}$
$\mathrm{R^2 = R^4 = [CH_2]_7{\cdot}CO_2Me}$

The intramolecular cyclodehydration probably occurs by way of the dienolic forms of (Xa) and (Xb), with saturation of the cyclohexene double bond as a prominent side reaction. A shift of the exocylic double bonds then yields the isobenzofuran system.

Diels–Alder reaction of 12-oxo-octadeca-*trans*-10-enoic acid (XIII)[10] and octadeca-*trans*-9-*trans*-11-dienoic acid (VIII)[9] proceeded slowly and incompletely. The reaction mixture was esterified and the two cycloaddition products, methyl 5-heptanoyl-6-hexyl-3-(7-methoxycarbonylheptyl)cyclohexene-4-nonanoate (XIVa) and its ' antiparallel ' isomer (XIVb) were isolated by preparative t.l.c.

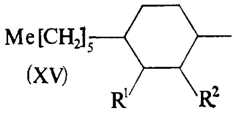
$\mathrm{Me[CH_3]_5{\cdot}CO{\cdot}CH{:}CH{\cdot}[CH_2]_8{\cdot}CO_2H}$
(XIII)



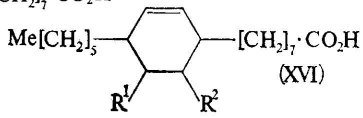
(XIV)

a; $\mathrm{R^1 = Me[CH_2]_5{\cdot}CO}$
$\mathrm{R^2 = [CH_2]_8{\cdot}CO_2Me}$
b; $\mathrm{R^1 = [CH_2]_8{\cdot}CO_2Me}$
$\mathrm{R^2 = Me[CH_2]_5{\cdot}CO}$

Clemmensen reduction of a mixture of compound (XIII) and the two cyclohexenes (XIVa) and (XIVb) gave four main products, evident as two pairs of spots on t.l.c. The slower-running pair were 3-(7-carboxyheptyl)-5-heptyl-6-hexylcyclohexene-4-nonanoic acid (XVIa) and its ' antiparallel ' analogue (XVIb), and the faster-running pair comprised 5-heptyl-6-hexyl-3-(7-carboxyheptyl)cyclohexane-4-nonanoic acid (XVa) and its anti-parallel analogue (XVb). Resolution of these four compounds on preparative t.l.c. permitted their separation into the two classes (XV) and (XVI), but was insufficient to allow further resolution of the (a) and (b) components of each.



(XV)

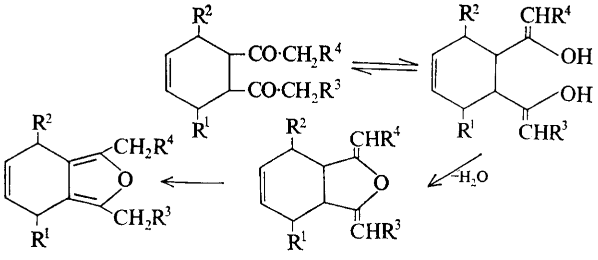


(XVI)

a; $\mathrm{R^1 = Me[CH_2]_6}$
$\mathrm{R^2 = [CH_2]_8{\cdot}CO_2H}$
b; $\mathrm{R^1 = [CH_2]_8{\cdot}CO_2H}$
$\mathrm{R^2 = Me[CH_2]_6}$

In agreement with Kloetzal's general rules[11] for Diels–Alder reactions, reaction of the unsaturated diketone (IV) with 2-methylbutadiene proceeded less readily than that with 2,3-dimethylbutadiene. By use of the 1,4-substituted butadiene (IX), the reaction could be forced to completion only by using a higher temperature and longer reaction time, whilst Diels–Alder reaction with the unsaturated monoketone (XIII) and the diene (VIII) gave a mixture containing *ca.* 26% of the cycloaddition product. With regard to the Clemmensen reduction of the Diels–Alder adducts, our results suggest that there is little significant steric hindrance to the approach of the metal in the 1,2,4,5-tetrasubstituted cyclohexene (Vc), and reduction is fairly smooth. With the 3,4,5,6-tetrasubstituted cyclohexene (XIV), which contains one keto-group, the bulky substituents at positions 3, 4, and 6 constitute a significant steric compression and reduction is slower. In the case of the tetrasubstituted cyclohexene (X), which contains two keto-groups, the steric compression provided by the 3- and 6-substituents and the proximity of the two hydroxy-groups [dienolic form of (X)] constitute especially favourable conditions for dehydration rather than reduction (see Scheme).

It has been noted[12] that compounds of type (X) (*e.g.* 1,2-dimethyl-4,5-diacetylcyclohexene) when subjected to dehydrating conditions (zinc chloride at 230°) yield dihydroisobenzofuran derivatives of type (XII).



SCHEME

EXPERIMENTAL

Methyl-5-Heptanoyl-1-methylcyclohexene-4-(9-oxononanoate) (Va) *and its 2-Methyl Analogue* (Vb).—A mixture of redistilled isoprene (0·55 g., 5 mol.), methyl 9,12-dioxo-

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[10] J. Nichols and E. Schipper, *J. Amer. Chem. Soc.*, 1958, **80**, 5708.

[11] M. C. Kloetzal, *Org. Reactions*, 1948, **4**, ch. 1.

[12] G. O. Schenck, *Chem. Ber.*, 1947, **80**, 226, 289.

octadeca-*trans*-10-enoate [8] (0·54 g., 1 mol.), and dry benzene (4 ml.) was left at 20° for 6 days. A mixture of (Va) and (Vb) was isolated by preparative t.l.c. on silicic acid as a clear oil, m.p. *ca.* −20° (Found: C, 73·4; H, 10·8. Calc. for $C_{24}H_{40}O_4$: C, 73·4; H, 10·7%), $\nu_{max.}$ (liquid) 1748 (CO_2Me), 1721 (C=O), and 783 (trisubstituted cyclohexene) $cm.^{-1}$, no u.v. absorption at $\lambda_{max.}$ 228 mμ (absence of ene-dione system).

Methyl 5-*Heptanoyl*-1,2-*dimethylcyclohexene*-4-(9-*oxononanoate*) (Vc).—A mixture of redistilled 2,3-dimethylbutadiene [13] (10·1 g., 4 mol.), methyl 9,12-dioxo-octadeca-*trans*-10-enoate (10·0 g., 1 mol.), and ethanol (150 ml.) was warmed to give a clear solution, and left at 20° for 48 hr. A small amount of solid appeared, which was filtered off. Ethanol was distilled off *in vacuo* to yield the *cyclohexene* (Vc) (12·3 g., 98%), n_D^{26} 1·4749, b.p. 196°/0·04 mm. (Found: C, 73·9; H, 10·6. $C_{25}H_{42}O_4$ requires C, 73·85; H, 10·4%). The product, a clear oil, gave a single spot on t.l.c. (silicic acid), $\nu_{max.}$ (liquid) 1748 (CO_2Me) and 1715 (C=O) $cm.^{-1}$, τ ($CDCl_3$) 6·36 (s, CO_2Me) 7·02 (t, ring CH), 7·60 (m, $CO{\cdot}CH_2$, $CH_2{\cdot}CO_2R$, ring CH_2) 8·38 (s, MeC:), 8·68 (s, long chain CH_2), and 9·03 (t, Me).

4-*Hexyl*-6,7-*dimethyl*-4a,5,8,8a-*tetrahydrophthalazine*-1-*octanohydrazide* (VI).—Hydrazine hydrate (100%; 0·25 g., 4 mol.), the 1,2,4,5-tetrasubstituted cyclohexene (Vc), (0·50 g., 1 mol.), and ethanol (5 ml.) were mixed at room temperature. A white precipitate appeared which redissolved within a few min. The mixture was heated under reflux under nitrogen for 2 hr. at 80°; when cooled to −20° it deposited a white *solid*, m.p. 122° [from benzene–light petroleum (1 : 1)] (Found: C, 71·65; H, 10·3; N, 13·65. $C_{24}H_{42}N_4O$ requires C, 71·6; H, 10·45; N, 13·9%), $\nu_{max.}$ ($CHCl_3$) 3390, 3247 (NH_2 stretch), 1664 (hydrazide C=O), and 1616 (C=N–N=C) $cm.^{-1}$, $\lambda_{max.}$ 260 mμ (ε 1338) (C=N–N=C).

Methyl 5-*heptyl*-1,2-*dimethylcyclohexene*-4-*nonanoate* (VII).—A mixture of zinc amalgam [14] (4·0 g., 12·4 mol.), the 1,2,4,5-tetrasubstituted cyclohexene (Vc), (2·0 g., 1 mol.), toluene (5 ml.), concentrated hydrochloric acid (5 ml.), water (4 ml.), and acetic acid (0·5 ml.) was heated under reflux for 64 hr. At intermediate stages of the reduction, small amounts of concentrated hydrochloric acid, toluene, water, and acetic acid were added. The organic and aqueous layers were separated, and the latter was extracted with ether. The organic solutions were combined, washed with water, and dried ($MgSO_4$), and the solvent was distilled off *in vacuo*. Ethereal diazomethane was added to the residue to convert any free acid present into the methyl ester. Ether was removed and the crude product was chromatographed on a silica gel column (Davidson 950) with benzene as eluent. The second peak eluted was the *cyclohexene* (VII) (0·72 g., 38·8%) (Found: C, 79·35; H, 11·8. $C_{25}H_{46}O_2$ requires C, 79·3; H, 12·25%), $\lambda_{max.}$ (liquid) 1745 (CO_2Me) and 880 (C–H deformation in a 1,2,4,5-tetrasubstituted cyclohexene) $cm.^{-1}$, $\lambda_{max.}$ 215 mμ (ε 8900) (cyclohexene C=C), *m*/*e* 378 (M^+), 374 ($M - 4H$), 279 ($M - CH_3{\cdot}[CH_2]_6$), and 207 ($M - [CH_2]_8{\cdot}CO_2Me$), no retro-Diels–Alder cleavage observed.

Methyl 5-*Heptanoyl*-6-*hexyl*-3-(7-*methoxycarbonylheptyl*)-*cyclohexene*-4-(9-*oxononanoate*) (Xa) *and its 'Antiparallel' Isomer* (Xb).—A mixture of methyl octadeca-*trans*-9,*trans*-11-dienoate (IX) (4·40 g., 1 mol.), methyl 9,12-dioxo-octadeca-*trans*-10-enoate (IV) (5·78 g., 1·21 mol.) and toluene (40 ml.) was heated under reflux for 191 hr. Toluene was distilled off under reduced pressure and the residue (10·0 g.) was chromatographed on a silica gel column with benzene containing increasing amounts of ether (2, 4, and 8%) as eluent. The product, a clear oil, was a mixture of (Xa) and (Xb) (9·20 g., 90%) (Found: C, 73·35; H, 10·6. Calc. for $C_{38}H_{66}O_6$: C, 73·6; H, 10·75%), $\nu_{max.}$ (liquid) 1748 (CO_2Me) and 1712 (C=O) $cm.^{-1}$, no absorption in the 990—970 $cm.^{-1}$ region [indicating the absence of (IX) and (IV); also confirmed by the u.v. spectrum], τ ($CDCl_3$) 4·40 (s, CH=CH), 6·40 (s, CO_2Me), 7·73 (m, $CO{\cdot}CH_2$, $CH_2{\cdot}CO_2R$, ring CH), 8·69 (s, long chain CH_2), and 9·10 (t, Me), *m*/*e* 618 (M^+), 600 [$M - H_2O$; (X) $\longrightarrow$ (XII)], 533 ($M - Me[CH_2]_5$), 505 ($M - Me[CH_2]_5{\cdot}CO$), 416 ($M - [CH_2]_7{\cdot}CO_2Me$), and 433 ($M - CO{\cdot}[CH_2]_7{\cdot}CO_2Me$), no retro-Diels–Alder cleavage observed. T.l.c. of the mixture of (Xa) and (Xb) on silica showed two partially resolved spots, R_F 0·55 and 0·59.

Dimethyl 3,4-*dihexyl*-4,5,6,7-*tetrahydroisobenzofuran*-1,7-*dioctanoate* (XIa) *and its 'Antiparallel' Isomer* (XIb) *and their Dihydroisobenzofuran Analogues* (XIIa) *and* (XIIb).—A mixture of (Xa) and (Xb) (9·0 g.,1 mol.), zinc amalgam (22·0 g., 23 mol.), toluene (21·5 ml.), concentrated hydrochloric acid (2·7 ml.), distilled water (16·5 ml.), and acetic acid (1 ml.) was heated under reflux for 65 hr. At intermediate stages of the reaction, small amounts of concentrated hydrochloric acid, toluene, water, and acetic acid were added. The reaction product was worked up as described for compound (VII). The crude product was esterified with ethereal diazomethane and then subjected to preparative t.l.c. on silica–silver nitrate (in 3% ether–benzene). A mixture of (XIa) and (XIb) (12·7 mg.) and a mixture of (XIIa) and (XIIb) (4·6 mg.) were obtained.

The dihydroisobenzofurans (XIIa) and (XIIb) had $\nu_{max.}$ (liquid) 1745 (CO_2Me) and 1582 (cyclic C=C–C=C; furan absorbs at 1590) $cm.^{-1}$, $\lambda_{max.}$ 233 mμ (1,3-diphenyldihydroisobenzofuran and 5,6-dimethyl-1,3-diphenyldihydroisobenzofuran [15] both have $\lambda_{max.}$ 230 mμ), τ (CCl_4) 4·40 (s, CH:CH), 6·40 (s, CO_2Me), 7·65 (m, CH_2CO_2R, ring CH and CH_2 α to furan ring), 8·66 (s, long chain CH_2), and 9·10 (t, Me), *m*/*e* 600 (M^+), 598 ($M - 2H$), 515 ($M - Me[CH_2]_5$), 443 ($M - [CH_2]_7{\cdot}CO_2Me$), and 359 ($M - \{CH_3[CH_2]_5 + [CH_2]_7{\cdot}CO_2Me\} + H$). The tetrahydroisobenzofurans (XIa) and (XIb) had i.r. and u.v. spectra similar to those of their dihydroisobenzofuran analogues. N.m.r. spectrum (CCl_4): τ 6·40 (s, CO_2Me), 7·71 (m, $CH_2{\cdot}CO_2R$, ring CH, CH_2 α to furan ring), 8·66 (s, long chain CH_2), and 9·08 (t, Me). Mass spectrum: *m*/*e* 602 (M^+), 598 ($M - 4H$), 517 ($M - Me[CH_2]_5$), 445 ($M - [CH_2]_7{\cdot}CO_2Me$), and 361 ($M - \{Me[CH_2]_5 + [CH_2]_7{\cdot}CO_2Me\} + H$).

Methyl 5-*Heptanoyl*-6-*hexyl*-3-(7-*methoxycarbonylheptyl*)-*cyclohexene*-4-*nonanoate* (XIVa) *and its 'Antiparallel' Isomer* (XIVb).—A mixture of 12-oxo-octadec-*trans*-10-enoic acid (XIII) [10] (0·65 g., 2 mol.), octadeca-*trans*-9,*trans*-11-dienoic acid (VIII) [9] (0·31 g., 1 mol.), and redistilled anisole (10 ml.) was heated under reflux under nitrogen for 113 hr. Anisole was distilled off *in vacuo* and a small sample of the residue was converted into the methyl ester with ethereal diazomethane. G.l.c. analysis of the methylated product gave the following result [retention time (min.) in parentheses]: (IX) 41·7% (12·2), (XIII) methyl ester 32·6%

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[13] C. F. H. Allen and A. Bell, *Org. Synth.*, Coll. Vol. III, 1955, p. 312.

[14] E. L. Martin, *Org. Reactions*, 1942, **1**, ch. 7.

[15] R. Adams and M. H. Gold, *J. Amer. Chem. Soc.*, 1940, **62**, 2038.

(24·0), (XIVa) + (XIVb) 25·7% (17·7). (A Wilkins 1522 instrument was used with a column of 5% Se 30 on Chrom-W 80/100, at 150° and nitrogen flow rate 33 ml./min.). A mixture of (XIVa) and (XIVb) (6·2 mg.) was isolated from the methylated reaction product by preparative t.l.c. on silica–silver nitrate (solvent 8% ether–benzene; detection with u.v. light); $\nu_{\text{max.}}$ (liquid) 1736 (CO_2Me), 1715 (acyclic C=O), and 1613 (C=C) cm.$^{-1}$, τ (CCl_4) 4·53 (s, CH:CH), 6·38 (s, CO_2Me), 7·66 (m, $CH_2CO_2R,CH_2\cdot CO$, ring CH), 8·71 (s, long chain CH_2), and 9·08 (t, Me), *m/e* 604 (M^+), 600 ($M - 4H$), 547 ($M - Me[CH_2]_3$) 533 ($M - Me[CH_2]_4$), 519 ($M - Me[CH_2]_5$), 491 ($M - Me[CH_2]_5\cdot CO$), 447 ($M - [CH_2]_7\cdot CO_2Me$), and 113 ($Me[CH_2]_5\cdot CO$).

3-(7-*Carboxyheptyl*)-5-*heptyl*-6-*hexylcyclohexene*-4-*nonanoic Acid* (XVIa), *its Antiparallel Isomer* (XVIb), *and their Cyclohexane Analogues* (XVa) *and* (XVb).—The Diels–Alder reaction was repeated with (VIII) 3·3 g., 1 mol.), (XIII) (7·0 g., 2 mol.), and re-distilled anisole (100 ml.), The mixture was heated under reflux for 113 hr. as before, and anisole was distilled off *in vacuo*. The residue was chromatographed on a column of silicic acid impregnated with oxalic acid [16] with 2% ether–benzene as eluent. In this way (VIII) was removed from the reaction product, and a mixture of (XIII), (XIVa), and (XIVb) was obtained (3·09 g., 51·5%). G.l.c. analysis showed the mixture to contain (XIII) (55·9%) and (XIVa) + (XIVb) (44·1%). The mixture of all three (302·9 mg.) in toluene (5 ml.) was added to zinc amalgam (5 g.), concentrated hydrochloric acid (5 ml.), distilled water (4 ml.), and acetic acid (0·5 ml.). The mixture was heated under reflux under nitrogen for 53 hr.; during the reaction, small amounts of hydrochloric acid, toluene, and acetic acid were added. The solution was decanted from the zinc amalgam and the aqueous layer was diluted with water and extracted with ether. The toluene layer and ether extracts were combined, washed with water, and dried ($MgSO_4$), and the solvent was distilled off *in vacuo* to give the crude product (53·7 mg.). This was chromatographed on a column of silicic acid impregnated with oxalic acid with benzene containing increasing amounts of ether as eluent. One of the peaks eluted was identified as a mixture of (XVIa), (XVIb), (XVa), and (XVb) (2·8 mg., 2·4%), τ ($CDCl_3$) 0·7 (s, CO_2H), 4·59 (s, CH=CH), 7·84 (m, $CH_2\cdot CO_2H$ and allylic ring protons), 8·74 (s, long chain CH_2), and 9·12 (t, Me). The mixture was converted into the methyl esters with ethereal diazomethane, and then subjected to preparative t.l.c. on silica–silver nitrate, (solvent 3% ether–benzene; detection by u.v. light). Thus the cyclohexenes (XVIa) and (XVIb) were separated from their cyclohexane analogues (XVa) and (XVb).

The mixture of (XVIa) and (XVIb) gave the following mass spectral peaks: *m/e* 590 (M^+), 505 ($M - Me[CH_2]_5$), 491 ($M - Me[CH_2]_6$), 433 ($M - [CH_2]_7\cdot CO_2Me$), and 419 ($M - [CH_2]_8\cdot CO_2Me$). A peak at 478 was attributed to allylic ring cleavage ($M - Me[CH_2]_6\cdot CH$) and the occurrence of retro-Diels–Alder cleavage was indicated by a peak at 294.

The mass spectrum of (XVa) and (XVb) showed *m/e* 592 (M^+), 507 ($M - Me[CH_2]_5$), 493 ($M - Me[CH_2]_6$), 435 ($M - [CH_2]_7\cdot CO_2Me$), and 421 ($M - [CH_2]_8\cdot CO_2Me$); no retro-Diels–Alder cleavage observed.

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