Reference Samples. 5,5-Diethyl-2,2-dimethyl-3-nonene (2). —In a flask fitted with a reflux condenser was placed a mixture of 5,5-diethyl-2,2-dimethyl-3-nonanol (1, R = H) (0.85 g, 0.0037 mol) and 3.0 g of potassium hydrogen sulfate. The mixture was then heated at 170–180° for 20 hr. After allowing the mixture to cool, it was distilled at reduced pressure to give 0.70 g (89% yield) of 5,5-diethyl-2,2-dimethyl-3-nonene (2), bp 63–65° (1.0 mm) [lit.[2] bp 120–121° (40 mm)]. The nmr showed signals at δ 5.2 (AB quartet, 2 H, J = 16 Hz), 1.0 (s, 9 H, tert-butyl group), and 0.5–1.8 (m, 19 H).

5,5-Diethyl-2,2-dimethyl-3-nonyl Acetate.—The acetate was prepared by refluxing 5,5-diethyl-2,2-dimethyl-3-nonanol (0.5 g, 0.0022 mol) with acetic anhydride (2.0 g, 0.019 mol) in 5.0 ml of dry pyridine for 2 hr. The mixture was cooled, poured onto ice water, and extracted with pentane. The pentane layer was washed with 10% hydrochloric acid, 5% sodium bicarbonate, and finally with water. The pentane solution was dried over magnesium sulfate and then distilled to give 0.3 g (50% yield)

of 5,5-diethyl-2,2-dimethyl-3-nonyl acetate, bp 80–82° (0.5 mm). The infrared spectrum showed evidence of slight alcohol impurity, but the characteristic strong acetate absorption was present at 1735 cm^{-1}. The nmr spectrum showed signals at δ 4.8 (q, 1 H, -CHOH), 1.95 (s, 3 H, CH$_3$C=O), 0.9 (s, 9 H, tert-butyl group), and 0.7–1.5 (m, 21 H).

The Decarboxylation and Rearrangement of 3,3-Dialkyl-2-oxocarboxylic Acids[1]

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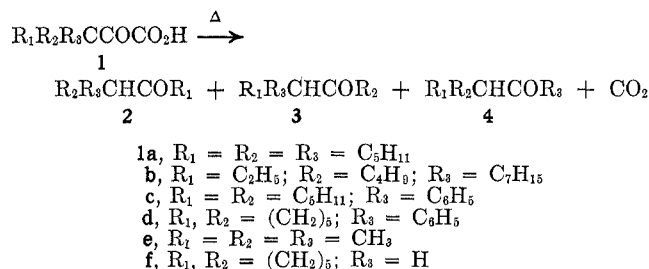
Received May 21, 1970

The thermal decomposition of 3,3-dialkyl-2-oxocarboxylic acids (1) has been shown to lead to decarboxylation and rearrangement. Although 3,3-dimethyl-2-oxobutyric acid (1e) undergoes decarbonylation, 2-oxo acids with larger groups in the 3 position, 1a–d, afforded mixtures of ketones by 1,2 shifts. Ethyl, butyl, and heptyl groups migrated with similar ease, 1b, while phenyl was found to have essentially the same migratory aptitude as pentyl in 2-oxo-3-pentyl-3-phenyloctanoic acid (1c). However, the phenyl group shifted almost exclusively, in preference to ring expansion, in 1-phenylcyclohexaneglyoxylic acid (1d). These results are ascribed to the bulk and conformational effects of the groups in the 3 position of 1. It is suggested that either a zwitterionic or a concerted process (Scheme 1) best explains the experimental observations.

In a related investigation,[3] it was observed that a small amount of a low-boiling material was obtained on distillation of the product from the base-catalyzed autoxidation of ethyl 2-cyano-3,3-dipentyloctanoate. Since vpc analysis of the crude mixture showed that the only volatile products were unchanged cyano ester and the corresponding 2-keto ester, and these are known to be stable at distillation temperatures, it appeared that the pyrolysis of some nonvolatile species in the reaction mixture was responsible for the low-boiling unknown. The latter was present when either DMF or DMSO–tert-BuOH was used as the reaction medium, which eliminated condensation products of dimethyl sulfoxide[4] as possible precursors.

The ir spectrum of the crude autoxidation mixture had broad absorptions at 3200–3600 and 2550–2700 cm^{-1} which suggested the presence of a carboxylic acid. This was confirmed by the preparation of 3,3-dipentyl-2-oxooctanoic acid (1a) which on attempted distillation gave a 77% yield of the unknown pyrolysate. It was identified as 7-pentyl-6-dodecanone (2a) by comparison of its spectral properties with those of an authentic sample of this ketone.

Although the decarbonylation of 2-oxo esters is well known,[5] the decarboxylation of the corresponding acids has received relatively little attention. In those cases

which have been studied,[6] aldehydes have been obtained as the common products. The present paper describes the investigation of the thermal decarboxylation and accompanying rearrangement of a number of 3,3-dialkyl-2-oxocarboxylic acids, 1, to ketones 2, 3, and 4. In

$$R_1R_2R_3CCOCO_2H \xrightarrow{\Delta}$$
$$1$$
$$R_2R_3CHCOR_1 + R_1R_3CHCOR_2 + R_1R_2CHCOR_3 + CO_2$$
$$2 \qquad\qquad 3 \qquad\qquad 4$$

1a, R$_1$ = R$_2$ = R$_3$ = C$_5$H$_{11}$
b, R$_1$ = C$_2$H$_5$; R$_2$ = C$_4$H$_9$; R$_3$ = C$_7$H$_{15}$
c, R$_1$ = R$_2$ = C$_5$H$_{11}$; R$_3$ = C$_6$H$_5$
d, R$_1$, R$_2$ = (CH$_2$)$_5$; R$_3$ = C$_6$H$_5$
e, R$_1$ = R$_2$ = R$_3$ = CH$_3$
f, R$_1$, R$_2$ = (CH$_2$)$_5$; R$_3$ = H

addition, exploratory experiments were carried out in an attempt to elucidate the mechanism of the reaction.

The pyrolysis of 1a–d on attempted distillation afforded the corresponding 2, 3, and 4, whereas 1e was decarbonylated to pivalic acid; the less highly substituted acid, 1f, produced a mixture of four components.

Attempts to analyze and separate the mixture of ketones from 1b by vpc on several different columns were not successful, but nmr analysis suggested that 2, 3, and 4 were present in the approximate ratio of 40:30:30, respectively. Compound 1c gave 7-phenyl-6-dodecanone (2c, pentyl migration) and 2-pentylheptanophenone (4c, phenyl migration) in the ratio of 66:34. The migratory abilities of the phenyl and pentyl groups then are approximately equal in this case since pentyl migration is favored statistically by a factor of 2:1.

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(1) Taken from the Ph.D. Thesis of C. A. Harbert, 1967, and presented in part at the 3rd Midwest Regional American Chemical Society Meeting, Columbia, Mo., Nov 2–3, 1967.

(2) NDEA Fellow, 1963–1966.

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(5) A. C. Cope, H. L. Holmes, and H. O. House, in R. Adams, "Organic Reactions," Vol. 9, Wiley, New York, N. Y., 1957, p 147.

(6) G. Darzens and A. Levy, *C. R. Acad. Sci., Ser. C*, **204**, 272 (1937); G. Barger and A. P. T. Easson, *J. Chem. Soc.*, 2100 (1938); J. Cymerman-Craig, J. W. Loder, and B. Moore, *Aust. J. Chem.*, **9**, 222 (1965).

Acid **1d**, which offers the possibility of ring expansion, required a temperature of 200–220° (5 mm) for decomposition, and the product consisted of cyclohexyl phenyl ketone, **4d** (phenyl migration), and trace amounts of 2-phenylcycloheptanone (alkyl migration) and 1-phenyl-cyclohexanecarboxaldehyde (decarboxylation), as indicated by nmr.

The above limited data are to be compared with the diversity of migratory aptitudes reported for other systems. Although aryl and other unsaturated groups generally migrate more readily than alkyl groups in 1,2-cationic rearrangements,[7] Parham and Czuba[8] have found the ratio of phenyl to cyclohexyl migration to be 0.2–0.9:1 in the ring expansion of a hexahydrofluorenone with diazomethane and the related Tiffeneau–Demjanov type of ring expansion of an ether of an aminomethylhexahydrofluorenone with nitrous acid. They ascribed these results to the geometric requirements of phenyl migration. Recent studies by Miller and coworkers[9] on the thermal sigmatropic rearrangement of substituted indenes indicate an order of H > C_6H_5 > CH_3 which contrasts with those of 1,2-cationic,[7] anionic,[10] and free-radical rearrangements.[11] Dubois and Bauer[12] have investigated bis-*tert*-alkyl ketone rearrangements in sulfuric acid and have shown that the migrating tendency of an ethyl group relative to methyl varies from 1.2 to 5.0 depending on the structure of the ketone. The widely varying data for different rearrangements suggest that the migratory aptitudes of groups are greatly dependent upon the system involved and the structural environment of the origin and terminus of the migration.

The steric bulk at the 3 position of **1** seems to be an important factor which influences the course of the thermal decomposition of these compounds. This is demonstrated by the failure of **1e** and **1f** to rearrange under conditions in which **1a–d** afforded ketones **2–4**. Also, the phenyl to pentyl migration ratio for **1c** is lower than normal for a carbonium ion process; however, as indicated previously other such examples are known[8] including the acid-catalyzed rearrangement of trisubstituted acetaldehydes to ketones.[13] The origin of this effect in the present case seems to be largely steric in nature. If it is assumed that a migrating phenyl group must be perpendicular to the plane described by the migrating carbon, the migration origin and the migration terminus,[14] then it follows that the preferred conformation for phenyl group migration in **1c** is that depicted by the Newman projection **5c** in which the phenyl group lies in the plane of the paper as viewed from atoms C_2–C_3. Since this conformation should be of higher energy than **6c**, in which the phenyl ring is twisted to avoid interaction with the pentyl groups, it follows that the activation energy for phenyl migration would be in-

creased by the difference in energy between conformations **5c** and **6c**. This could explain the nearly statistical phenyl to pentyl migration ratio observed on pyrolysis of **1c**.
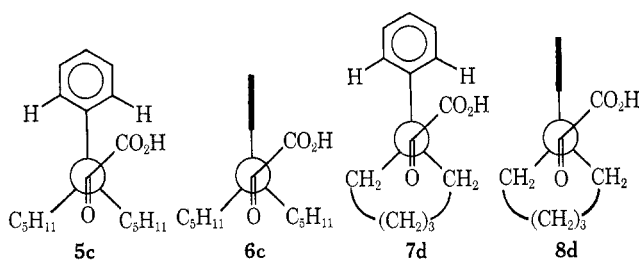
The pyrolysis of **1d** might be considered in a similar manner. The interacting methylene groups in **7d** are held rigid by the ring, thereby lowering the energy of this conformation relative to that of **8d**. However, additional driving force for phenyl migration in this case should arise from the loss of 1,3-diaxial interactions in **1d**. The fact that higher temperatures were required to rearrange **1d** than **1c** suggests that the former is a more strain-free system and the driving force of relief of strain is less in this compound.

The information available concerning relative migration tendencies of alkyl groups is quite limited.[15] Ethyl migrates better than methyl in the pinacol rearrangement and in the acetolysis of neopentyl-type brosylates; however, the opposite order has been reported for the solvolysis of 3,4-dimethyl-4-phenyl-3-hexyl *p*-bromobenzoate, and the acetolysis of some alkyl-substituted neopentyl brosylates.[16] In the latter study it was shown that lengthening an alkyl group without branching (C_2H_5, *n*-C_3H_7, and *n*-C_4H_9) has no effect on the relative rate of acetolysis of molecules of this type. A similar situation might be expected to obtain in **1b**, and this was borne out by the results obtained on thermolysis of **1b**, where essentially equal amounts of the expected rearranged ketones, **2–4**, were formed.

A detailed mechanistic study of the thermal decomposition of **1** was not carried out. Such an investigation would be complicated by the pyrolysis conditions which are not amenable to the trapping or identification of possible intermediates. At least four possible mechanisms can be considered for the pyrolysis and rearrangement of **1**: (1) a free-radical process, (2) an initial decarboxylation to aldehydes which subsequently rearrange to ketonic products, (3) a zwitterionic mechanism, and (4) a concerted decarboxylation rearrangement. Free-radical processes seem unlikely since homolytic decarboxylations usually require radical initiators and/or metal catalysts.[17] This is supported by the observation that no noticeable increase in ketone formation, as compared to an uncatalyzed reaction, was observed when the pyrolysis of **1a** was conducted in the presence of di-*tert*-butyl peroxide. Furthermore, it might be expected that an acyl free radical $R_1R_2R_3\overset{\cdot}{C}{=}O$, formed either by decarboxylation of a carboxylate radical, $R_1R_2R_3CO$-$CO_2\cdot$, or by direct homolysis, would decarbonylate rather than rearrange. This was confirmed by heating

(7) For leading references, see (a) G. W. Wheland, "Advanced Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1960, pp 573–597; (b) Y. Pocker, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 22–24; (c) C. F. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 724–744; (d) N. F. Phelan, H. H. Jaffé, and M. Orchin, *J. Chem. Educ.*, **44**, 626 (1967).

(8) W. E. Parham and L. J. Czuba, *J. Amer. Chem. Soc.*, **90**, 4030 (1968).

(9) L. L. Miller, R. Greisinger, and R. F. Boyer, *ibid.*, **91**, 1578 (1969).

(10) H. E. Zimmerman, in ref 7b, pp 391–399; ref 7c, pp 787–792.

(11) C. Walling, in ref 7b, pp 409–423.

(12) J. E. Dubois and P. Bauer, *J. Amer. Chem. Soc.*, **90**, 4511 (1968).

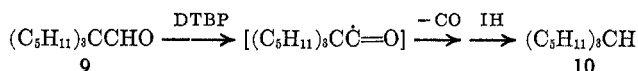(13) Reference 7a, pp 549, 580, 592; C. J. Collins, *Quart. Rev. (London)*, **14**, 357 (1960).

(14) For a discussion, see ref 7d and 8.

(15) For leading references, see R. L. Heidke and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **88**, 5816 (1966).

(16) E. N. McElrath, R. M. Fritz, C. Brown, C. Y. LeGall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1960).

(17) W. H. Starnes, Jr., *ibid.*, **31**, 1436 (1966).

2,2-dipentylheptanal (9) with di-*tert*-butyl peroxide. Only the expected 10 was obtained (75%), and carbonyl products could not be detected.

$$(C_5H_{11})_3CCHO \xrightarrow{\text{DTBP}} [(C_5H_{11})_3C\dot{C}{=}O] \xrightarrow{-CO} \xrightarrow{\text{IH}} (C_5H_{11})_3CH$$
$$9 \hspace{6cm} 10$$

The intermediacy of trisubstituted acetaldehydes was tested by pyrolyzing 1a in the presence of the corresponding aldehyde, 9. Approximately 80% of the latter was recovered which suggests that this species is not an intermediate in the pyrolysis of 1a. It should be noted, however, that this does not rule out the possibility of a vibrationally excited aldehyde intermediate.

The related zwitterionic and concerted pathways, Scheme I, appear to offer reasonable explanations for

SCHEME I

A

B
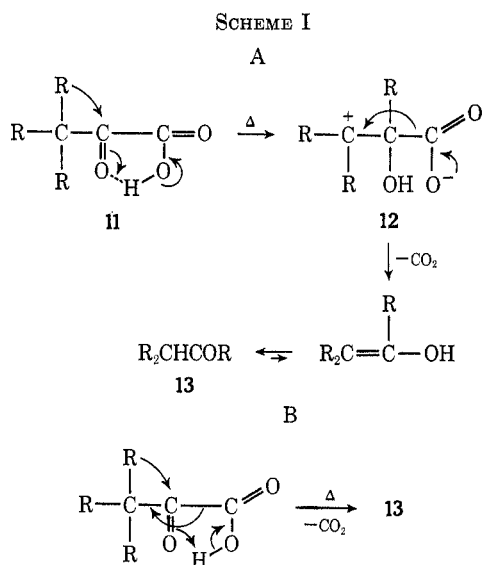
the decarboxylation of 1 and the accompanying rearrangement to ketones. The combination of hydrogen bonding[18] and steric compression in 11 should facilitate thermally induced rearrangement. The migration of R in a stepwise process (Scheme I, A) would be expected to produce zwitterion 12, which upon loss of carbon dioxide would lead to the enol form of ketone 13. If rearrangement and loss of carbon dioxide were to occur simultaneously, the mechanism can be depicted by the concerted process as shown in Scheme I, B. Similar mechanisms have been suggested for the decarboxylation of glycidic acids[19] and β-keto acids.[20] It is not possible to distinguish between mechanisms A and B on the basis of the present investigation; however, it seems that the true mechanism lies somewhere between these extremes, and probably closer to the concerted process.

Experimental Section[21]

Materials.—The 3,3-disubstituted 2-oxocarboxylates used in this study were prepared by the autoxidation of the corresponding

ethyl 2-cyano-3,3-disubstituted anions,[3] with the exception of ethyl 3,3-dimethyl-2-oxobutyrate which was obtained from the reaction of *tert*-butylmagnesium chloride with diethyl oxalate.

Saponification of Ethyl 3,3-Dipentyl-2-oxooctanoate and Pyrolysis of the Resulting Acid, 1a.—A solution of 16.3 g (0.05 mol) of ethyl 3,3-dipentyl-2-oxooctanoate, 14 g (0.21 mol) of 85% KOH pellets, 15 ml of H_2O, and 90 ml of C_2H_5OH was heated at reflux for 4 hr. The C_2H_5OH was removed by distillation, the residue was treated with 100 ml of 10% HCl, and the mixture was extracted with three 30-ml portions of ether. The combined extracts were worked up to give a pale yellow oil: $n^{25}D$ 1.4528; nmr (CCl$_4$) δ 10.82 (s, 1, CO_2H), 1.6 (m, 6, CH_2), and 0.6–1.5 (m, 27, CH_2, CH_3); ir (neat) 3100–3450 (m, CO_2H), 2500–2700 (m, bonded OH), and 1710–1750 cm^{-1} (s, C=O).

Anal. Calcd for $C_{18}H_{34}O_3$: C, 72.43; H, 11.48. Found: C, 72.53; H, 11.68.

The attempted distillation of 7.5 g of crude 1a through a spinning-band column resulted in considerable foaming and gave 4.9 g (77%) of a product: bp 70–75° (0.05 mm); $n^{25}D$ 1.4389; nmr (neat) δ 2.38 (t, 3, CHCOCH$_2$) and 0.6–1.8 (m, 31, CH_2, CH_3); ir (neat) 1715 cm^{-1} (s, C=O). These spectra are identical with those of an authentic sample of 7-pentyl-6-dodecanone (2a), which was synthesized by the condensation of pentylmagnesium bromide with 2-pentylheptanenitrile: bp 135–138° (3 mm); $n^{25}D$ 1.4388.

Anal. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47. Found: C, 80.40; H, 13.20.

The 2-pentylheptanenitrile was prepared by the dialkylation of acetonitrile with pentyl bromide and sodium amide according to the method of Newberry and Webster:[22] bp 83–84° (1.5 mm); $n^{25}D$ 1.4308.

Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79. Found: C, 79.66; H, 12.58.

Pyrolysis of 3-Butyl-3-ethyl-2-oxodecanoic Acid (1b).—The saponification of 11.9 g of ethyl 3-butyl-3-ethyl-2-oxodecanoate according to the method in the preceding experiment afforded 11 g of crude 1b. Attempted distillation of this material caused pronounced foaming and gave 6.4 g (72%) of product: bp 83–85° (0.1 mm); $n^{25}D$ 1.4359.

Anal. Calcd for $C_{15}H_{30}O$: C, 79.57; H, 13.36. Found: C, 79.55; H, 13.16.

The ir of the pyrolysate had an absorption at 1715 cm^{-1} (C=O) and nmr (neat) δ 2.38 (m, 3, CHCOCH$_2$) and 0.6–1.8 (m, 27, CH_2, CH_3). The assignment for the downfield multiplet was based on the ability of these protons to exchange with D_2O under basic conditions. The nmr (CCl$_4$) of a synthetic mixture of 2b, 3b, and 4b in the ratio of 40:30:30, respectively, was identical with the spectrum (CCl$_4$) of the pyrolysate.

The reaction of a benzene solution of heptyl bromide with hexanenitrile in the presence of sodium amide[22] afforded 2-butylnonanenitrile (72%): bp 115–117° (2.5 mm); $n^{25}D$ 1.4337.

Anal. Calcd for $C_{13}H_{25}N$: C, 79.93; H, 12.90. Found: C, 80.21; H, 12.65.

This nitrile was caused to react with ethylmagnesium bromide to give 2b (44%): bp 146–147° (40 mm); $n^{25}D$ 1.4360.

Anal. Calcd for $C_{15}H_{30}O$: C, 79.57; H, 13.36. Found: C, 79.74; H, 13.18.

The ketone, 3b, bp 148–150° (20 mm), $n^{25}D$ 1.4360 (*Anal.* Calcd for $C_{15}H_{30}O$: C, 79.57; H, 13.36. Found: C, 79.36; H, 13.12), was obtained (48%) in a similar fashion from *n*-butylmagnesium bromide and 2-ethylnonanenitrile. The latter, bp 113–114° (10 mm), $n^{25}D$ 1.4279, was prepared (59%) from butyronitrile, heptyl bromide, and sodium amide by the previously described procedure.[22]

Anal. Calcd for $C_{11}H_{21}N$: C, 78.97; H, 12.65. Found: C, 79.06; H, 12.91.

Ketone 4b, bp 111–112° (4 mm), $n^{25}D$ 1.4358, was prepared (35%) by the reaction of heptylmagnesium bromide with 2-ethylhexanenitrile: bp 115–117° (135 mm), $n^{25}D$ 1.4142 [lit.[23] bp 98–100° (50 mm), $n^{25}D$ 1.4148].

(18) Intramolecular hydrogen bonding has been well demonstrated for 2-oxo acids, although the bonding decreases as the steric bulk increases at the 3 position: *cf.* M. Hirota and F. Shinozaki, *Bull. Chem. Soc. Jap.*, **42**, 2614 (1969); G. Oehme, G. Fischer, and A. Schellenberger, *Chem. Ber.*, **100**, 425 (1967); A. Schellenberger and G. Oehme, *Z. Phys. Chem. (Leipzig)*, **227**, 112 (1964).

(19) V. J. Shiner, Jr., and B. Martin, *J. Amer. Chem. Soc.*, **84**, 4824 (1962).

(20) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, pp 303–309.

(21) The infrared spectra were recorded on a Perkin-Elmer Model 237-B spectrophotometer and the nmr spectra were run on a Varian A-60 spectrometer employing tetramethylsilane as an internal standard. Elemental microanalyses were performed by Drs. Weiler and Strauss, Oxford, England, and Galbraith Laboratories, Inc., Knoxville, Tenn. Analytical vpc was done on a Wilkens Aerograph A90-P3 and a Microtek 2000-R gas chromatograph. All boiling points are uncorrected.

(22) G. Newberry and W. Webster, *J. Chem. Soc.*, 738 (1937).

(23) P. A. Levene and M. Kuna, *J. Biol. Chem.*, **140**, 263 (1941).

Anal. Calcd for $C_{15}H_{30}O$: C, 79.57; H, 13.36. Found: C, 79.38; H, 13.24.

Decarboxylation and Rearrangement of Other 3,3-Disubstituted 2-Oxocarboxylic Acids, 1.—The acids were prepared by the saponification of the corresponding ethyl esters in the manner described for **1a** and heated under a spinning-band column until distillation occurred.

A. 2-Oxo-3-pentyl-3-phenyloctanoic Acid (1c).—Distillation of the crude acid (from 15.5 g of the ester) gave 81% of a product, bp 110–115° (0.5 mm), which consisted of two components. The spectra of the low-boiling fraction [n^{25}D 1.4869; nmr (CCl₄) δ 7.18 (s, 5, aromatic), 3.56 (t, 1, CH), 2.28 (t, 2, CH₂CO), and 0.6–1.5 (m, 20, CH₂, CH₃); ir (neat) 1715 cm⁻¹ (C=O)] are identical with those of authentic 7-phenyl-6-dodecanone. The latter was synthesized by the reaction of 2-phenylheptanenitrile, bp 141–143° (4 mm), n^{25}D 1.4970 [lit.[24] bp 165–168° (22.5 mm), n^{25}D 1.4996], with pentylmagnesium bromide, bp 119–120° (0.5 mm), n^{25}D 1.4877.

Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 83.15; H, 10.60.

The higher boiling fraction, n^{25}D 1.4928, was approximately 85% pure: nmr (CCl₄) δ 7.3–7.5 and 7.8–8.1 (m, 5, aromatic), 3.1–3.6 (s, 1, CH), and 0.6–1.9 (m, 22, CH₂, CH₃). Small signals at δ 7.18 and 2.28 were attributed to the presence of the lower boiling compound. The nmr and ir (neat), 1685 (s) and 1715 (m) cm⁻¹ carbonyl absorptions, spectra were essentially identical with those of authentic 2-pentylheptanophenone, when allowance was made for the absorptions arising from the 7-phenyl-6-dodecanone.

The 2-pentylheptanophenone was prepared (88%) by condensing 2-pentylheptanenitrile with phenylmagnesium bromide, bp 116–119° (0.4 mm), n^{25}D 1.4940.

Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 83.29; H, 10.86.

B. 1-Phenylcyclohexaneglyoxylic Acid (1d).—An 8-g portion of the crude acid was distilled through a spinning-band column to give 3.7 g of product [bp 97–99° (0.2 mm); n^{25}D 1.5435; nmr (CCl₄) δ 10.60 (s, 1, CO₂H), 7.17 (m, 5, aromatic), and 1.0–2.7 (m, 10, CH₂), ir (neat) 3000–3400 (s), 2500–2700 (m), and 1700–1750 cm⁻¹ (s)] and a tarry residue.

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.49; H, 7.17.

Distillation of 7 g of the crude acid at a pot temperature of 200–220° produced 2.7 g (48%) of material: bp 135–139° (5 mm); n^{25}D 1.5490; nmr (CCl₄) δ 7.0–8.0 (m, 5, aromatic), 3.0–3.5 (m, 1, CHCO), and 1.0–2.0 (m, 10, CH₂). The absorptions are consistent with those of cyclohexyl phenyl ketone.

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.79; H, 8.56.

Weak signals in the nmr at δ 9.25 and 5.5–6.5 were attributed to impurities which presumably included 1-phenylcyclohexanecarboxaldehyde and 2-phenylcycloheptanone, respectively.

C. 3,3-Dimethyl-2-oxobutyric Acid (1e).—A 6-g sample of freshly distilled **1e**, bp 74–76° (15 mm), n^{25}D 1.4222 [lit.[25] bp 80° (15 mm)], was distilled through a spinning-band column with a pot temperature of 220–240°. Considerable foaming occurred and there was obtained 1.9 g of a liquid, bp 120–130°, n^{25}D 1.3982 (lit.[26] $n^{36.5}$D 1.3931), for pivalic acid. This material also had the same retention time as does pivalic acid on a silicone rubber vpc column. Approximately 3 g of a brown oil remained in the distillation flask, and vpc analysis indicated that the volatile material was mainly pivalic acid. No ketonic products were detected.

D. Cyclohexaneglyoxylic Acid (1f).—The attempted distillation of the crude acid from 5.2 g of ethyl cyclohexylglyoxylate produced a mixture of at least four products and a considerable

amount of a tarry residue. No cycloheptanone could be detected by vpc comparison with an authentic sample, and no effort was made to identify the components of the mixture.

Ethyl 3,3-Dimethyl-2-oxobutyrate.—A Grignard reagent, prepared from 49.5 g (0.54 mol) of *tert*-butyl chloride, 13.2 g (0.54 g-atom) of Mg, and 300 ml of dry ether was added to a solution of 197 g (1.35 mol) of diethyl oxalate in 200 ml of dry ether while the temperature was maintained at −50 to −60°. The mixture was allowed to warm to 0° and was decomposed by pouring it onto iced, dilute HCl. It was worked up in the usual manner and distilled through a Podbielniak column to give 48 g (56%) of product, bp 156–158°, n^{25}D 1.4070 [lit.[27] bp 65–66° (15 mm), n^{25}D 1.4096].

Pyrolysis of 3,3-Dipentyl-2-oxooctanoic Acid (1a) in the Presence of Di-*tert*-butyl Peroxide.—A mixture of 3 g (0.01 mol) of crude **1a** and 0.22 g (0.0015 mol) of di-*tert*-butyl peroxide was heated at 140° for 3.5 hr and an aliquot was analyzed by vpc using a 25% silicone rubber SE-30 on Chromosorb W column. The chromatogram was identical with that of a control sample of **1a** which had been heated under the same conditions without catalyst. An additional 0.8 g (0.008 mol) of peroxide was added to the reaction mixture and heating was continued for 5.5 hr at 160°. Only a slight change in the relative peak areas of 7-pentyl-6-dodecanone (**2a**) was observed for the heated samples, with and without peroxide, as compared to a chromatogram of crude **1a** which had not been heated.

2,2-Dipentylheptanal (9).—A mixture of 75 g (0.28 mol) of 2,2-dipentylheptanoic acid, bp 149–152° (0.75 mm), n^{25}D 1.4485 [lit.[28] bp 167–168° (2 mm)], and 119 g (1 mol) of thionyl chloride afforded 65 g (82%) of the acid chloride, bp 137–139° (0.5 mm), n^{25}D 1.4530.

Anal. Calcd for $C_{17}H_{33}ClO$: C, 70.66; H, 11.43. Found: C, 70.56; H, 11.26.

A mixture of 60 g (0.21 mol) of 2,2-dipentylheptanoyl chloride, 150 ml of dry xylene, 8.4 g of Pd–BaSO₄ catalyst, and 0.9 g of quinoline–sulfur poison was heated at 150° while H₂ was passed through it for 60 hr according to the procedure of Hershberg and Cason.[29] It was worked up in the usual way to give 39 g (75%) of aldehyde, bp 105–108° (1 mm), n^{25}D 1.4435.

Anal. Calcd for $C_{17}H_{34}O$: C, 80.24; H, 13.47. Found: C, 80.40; H, 13.36.

Reaction of 2,2-Dipentylheptanal (9) with Di-*tert*-butyl Peroxide.—A modification of the method of Wilt and Philip[30] was adopted. A mixture of 10.2 g (0.04 mol) of **9** and 0.58 g (0.004 mol) of di-*tert*-butyl peroxide was heated at 140° for 9 hr, allowed to cool, and distilled. There was obtained 7.1 g (78%) of 6-pentylundecane (**10**), bp 136–138° (15 mm), n^{25}D 1.4332.

Anal. Calcd for $C_{16}H_{34}$: C, 84.86; H, 15.14. Found: C, 85.06; H, 14.98.

Pyrolysis of 3,3-Dipentyl-2-oxooctanoic Acid (1a) in the Presence of 3,3-Dipentylheptanal (9).—A mixture of 7 g of crude **1a** and 1.25 g of **9** was distilled through a spinning-band column to give a mixture of unchanged **9** and 7-pentyl-6-dodecanone (**2a**). The relative amounts of aldehyde and ketone were determined by the nmr integration ratios of the aldehyde absorption at δ 9.33 and the ketone absorption at δ 2.38. It was determined that 0.95 g (76%) of the aldehyde, 9, had been recovered.

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