842. *The Elimination of Carbon Monoxide from Acid Derivatives. Part II.* Friedel–Crafts Reactions (i) with αα-Dialkylglutaric Anhydrides, (ii) involving Cyclisation with Elimination*

By Eugene Rothstein and William G. Schofield

(i) In benzene solution, αα-dimethylglutaric anhydride reacts with aluminium chloride to give a mixture of γ-benzoyl-αα-dimethylbutyric and γ-methyl-γ-phenylvaleric acids, the corresponding amount of carbon monoxide being eliminated. On the other hand, the αα-diethyl homologue yields carbon monoxide quantitatively, the chief products being 4-ethyl-4-phenylhexanoic acid, and a rearranged aliphatic acid, identified as iso-octanoic acid.

(ii) δ-Phenyl-αα-dimethylvaleryl chloride eliminates carbon monoxide when cyclised by aluminium chloride and yields 1,1-dimethyltetralin, which is also obtained by a similar cyclisation followed by reduction of γ-methyl-γ-phenylvaleryl chloride. αα-Diethyl-δ-*p*-methoxy-phenylvaleryl chloride behaves in the same way as the αα-dimethyl compound and affords 1,1-diethyl-7-methoxytetralin with evolution of carbon monoxide. Two separate aspects of the Friedel–Crafts reaction are included in this Paper and are discussed in different sections, but the associated experimental work cannot be conveniently divided in this way.

REACTIONS OF α,α-DIALKYLGLUTARIC ANHYDRIDE

FRIEDEL–CRAFTS reactions with α,α-dialkyl dibasic-acid anhydrides usually afford a ketonic acid (I), reaction taking place at the least alkylated carbonyl group. In certain cases carbon monoxide is eliminated forming a carbonium ion (II) which can yield an arylated acid (III) which is sometimes the product of a preliminary rearrangement.

$$Ar \cdot CO \cdot CHR' \cdot [CH_2]_n \cdot CR_2 \cdot CO_2H \quad (I) \qquad \overset{+}{C}R_2 \cdot [CH_2]_n \cdot CHR' \cdot CO_2H \quad (II)$$

$$CR_2Ar \cdot [CH_2]_n \cdot CHR' \cdot CO_2H \quad (III)$$

In anisole the ketone (I) is nearly always obtained, indicating that if rearrangement does occur it is dependent on the production of the carbonium-ion intermediate (II). The reaction in inert solvents yields unsaturated derivatives with loss of carbon monoxide, this being the case with camphoric anhydride,[1] *as*-dimethylsuccinic anhydride, and αα-dimethylglutaric anhydride.[2] Evolution of carbon monoxide can be quite slow and at any time during the reaction it is possible to decompose the anhydride–catalyst complex with mineral acid with recovery of unchanged material. As a consequence, *as*-dimethyl-, *as*-diethyl-, and trimethyl-succinic anhydrides afford ketones only, even when the somewhat inert benzene is the aromatic component of the reaction.[3] Even for the diethyl compound the yield of carbon monoxide is not greater than 4% in contrast to triethylacetyl chloride which is decarbonylated seventy times faster than pivaloyl chloride though the two parent acids could be regarded as monodecarboxylated succinic acids.[4] It seems that the slow decomposition of the succinic anhydrides must be attributed to the close proximity of the second carbonyl group; nevertheless, tetramethylsuccinic anhydride rapidly decomposes both in benzene and in toluene, giving quantitative yields of the α-aryl-ααβ-trimethyl-butyric acid.[5] The reactions of camphoric anhydride are intermediate in character between those of *as*-dimethyl- and tetramethyl-succinic anhydrides since in benzene solution there

* Part I, M. E. Grundy, Wei-Hwa Hsü, and E. Rothstein, *J.*, 1960, 372.
[1] F. H. Lees and W. H. Perkin, *J.*, 1901, **79**, 341.
[2] M. Desfontaines, *Compt. rend.*, 1902, **134**, 295.
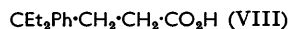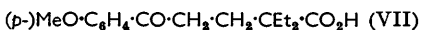[3] S. C. Sengupta, *J. prakt. Chem.*, 1938, [2], **151**, 581.
[4] M. E. Grundy, Wei-Hwa Hsü, and E. Rothstein, *J.*, 1958, 581.
[5] E. Rothstein and M. A. Saboor, *J.*, 1943, 425.

is a quantitative elimination of carbon monoxide, but in toluene the ketone is the only product.   In this respect it resembles the glutaric acid derivatives described below, and it does not appear that its cyclic structure is of great importance.   A mixture of αα-dimethyl-glutaric anhydride, benzene, and aluminium chloride rapidly evolved carbon monoxide at room temperature, in variable yield.   The extent of decarbonylation was to some extent dependent on conditions, and in general approximately equal quantities of γ-benzoyl-αα-dimethylbutyric acid, (IV), and of γ-methyl-γ-phenylvaleric acid, (V), were isolated. There were also small amounts of 4,4-dimethyltetralone, derived by cyclisation of the acid (V), as well as of an acid isomeric with the ketonic acid (IV) which may have become parti-ally rearranged.   Reduction of the acid (IV) yielded αα-dimethyl-σ-phenylvaleric acid, identical with the acid synthesised by alkylating isobutyrophenone with 3-phenylpropyl bromide followed by fission of the resultant ketone with sodamide.[6]

$$Ph·CO·CH_2·CH_2·CMe_2·CO_2H \text{ (IV)} \qquad\qquad CMe_2Ph·CH_2·CH_2·CO_2H \text{ (V)}$$
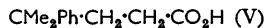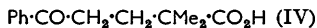
The reactions of αα-diethylglutaric anhydride were of greater interest.   Not only was the substitution of *gem*-diethyl for *gem*-dimethyl likely to accelerate the decarbonylation reaction, but extensive rearrangements dependent on the intermediate diethylalkyl carb-onium ion could be anticipated.   In the past such rearrangements have been encountered in connection with analogous carbonium ions derived from the tertiary alkyl halides.   Thus, Rylander and Meyerson [7] found that the ferric-chloride-catalysed reaction of 3-chloro-3-ethylpentane with benzene furnished principally 3-methyl-3-phenylhexane, but in addition there was present in 10% yield an isomeric hydrocarbon which the authors thought might be 2,3-dimethyl-2-phenylpentane, but which in the light of the present experiments could have been 2-methyl-2-phenylhexane.   Furthermore, Schuerch and Huntress [8] examined the reaction of triethylacetic acid with sodium azide and sulphuric acid.   Complete fission occurred, but most of the fragments were identified, and from them it was deduced that the initially formed triethylcarbonium ion was first rearranged, and then the resulting n-butyldimethylcarbonium ion $Bu^n·\overset{+}{C}Me_2$, (VI), disrupted.   In the present work, the loss of carbon monoxide from diethylglutaric anhydride has led to the isolation of a derivative of the carbonium ion (VI), but it may be noticed that the reaction of the anhydride with anisole yielded γ-*p*-anisoyl-αα-diethylbutyric acid (VII) in high yield and without re-arrangement.

$$(p-)MeO·C_6H_4·CO·CH_2·CH_2·CEt_2·CO_2H \text{ (VII)} \qquad\qquad CEt_2Ph·CH_2·CH_2·CO_2H \text{ (VIII)}$$

Thus the loss of carbon monoxide is an essential preliminary for this to occur.

The addition of aluminium chloride to a cold benzene solution of diethylglutaric anhydride caused immediate liberation of carbon monoxide in 94% yield.   A ketonic acid corresponding to the dimethyl derivative (IV) was not obtained.   Instead, a mixture of two principal constituents was isolated, the ratio of their amounts depending on the pro-portion of catalyst used.   The first was 4-ethyl-4-phenylhexanoic acid, (VIII), containing traces of isomeric and unsaturated acids which proton magnetic resonance (p.m.r.) spectra indicated to be the result of some rearrangement.   The second constituent was an aliphatic acid, together with a small proportion of phenyl ketone derived from it.   P.m.r. spectra showed that the terminal *gem*-diethyl group had been converted into isopentyl, the com-pound having undergone rearrangement in manner similar to that inferred by Schuerch and Huntress.   Thus, in this instance, iso-octanoic acid, $CHMe_2·[CH_2]_4·CO_2H$ (IX), together with some 1-benzoyl-5-methylhexane, $CHMe_2[·CH_2]_4·COPh$ (X), were produced, the second compound being obtained also by a Friedel–Crafts reaction on the acid chloride of (IX)   The structures of the rearranged substances were established by comparison of

[6] P. Ramart-Lucas and J. Hoch, *Bull. Soc. chim. France*, 1938, (v), **5**, 848.
[7] D. N. Rylander and S. Meyerson, *J. Amer. Chem. Soc.*, 1955, **77**, 6683.
[8] C. Schuerch and E. H. Huntress, *J. Amer. Chem. Soc.*, 1949, **71**, 2238.

the melting points, infrared, and proton magnetic spectra of the acid, the methyl ester, the amide, the ketone (X), and its semicarbazone, with those of independently synthesised specimens. On the other hand, there was no resemblance to the corresponding derivatives of 4-ethylhexanoic acid, $CHEt_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, (XI), or of 4,4-dimethylhexanoic acid, $CEtMe_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, (XII), which were also prepared by standard routes. Nevertheless, a small side-band on the gas chromatogram of the methyl ester of the acid (IX), using polyethylene glycol adipate as the stationary phase, was also detected for the ketone, and persisted even when the recrystallised amide was reconverted into the ester. It was presumably due to an isomer which was derived from neither of the acids (XI) or (XII) and had little noticeable effect on any of the physical properties referred to above. Except for this, there was no other evidence that an intermediate was formed, and indeed Schuerch and Huntress [8] have advanced a possible mechanism which does not require one. Protonation by benzene of a carbonium ion is not uncommon,[9] but biphenyl, which is often formed, was not detected in the higher-boiling fractions of the reaction product.

CYCLISATION REACTIONS INVOLVING ELIMINATION OF CARBON MONOXIDE

Tertiary aromatic side-chain acid chlorides, $Ar(CH_2)_n \cdot CR_2 \cdot COCl$ (XIII) can undergo four types of Friedel–Crafts reactions.[10] The formation of a cyclic ketone is the more usual one, but in the presence of a strongly nucleophilic reagent (*e.g.*, anisole), an open-chain derivative, $Ar(CH_2)_n \cdot CR_2 \cdot COAr'$, is usually but not invariably formed. If $n = 0$, or if the aromatic nucleus is deactivated (*e.g.*, by a nitro-group), a cyclic ketone is not obtained and carbon monoxide is eliminated.[11] Rothstein and Saville noticed that the acid chloride (XIII; R = Et or Me) always yielded the cyclic ketone when n was 1 or 2 and considered this to be a consequence of the proximity of the carbonyl group to the *ortho*-position of the nucleus and to the general stability of five- and six-membered rings. Hence it appeared that extension of the side-chain to four carbon atoms, *i.e.*, (XIII; $n = 3$), might lead to a fourth type of reaction, namely simultaneous elimination of carbon monoxide and cyclisation to a tetralin derivative. This reaction, which was the subject of a brief Communication some years ago,[12] has a formal analogy in the cyclisations of the *N*-benzenesulphonyl- and *N*-methyl derivatives of phenylalkylglycines, $Ph \cdot [CH_2]_n \cdot NR \cdot CH_2 \cdot CO_2H$ ($n = 2$ or 3), when successively reacted with phosphorus pentachloride and aluminium chloride. Elimination of carbon monoxide with formation of the corresponding derivatives of tetrahydroisoquinoline and tetrahydro-2-benzazepine occurs,[13] but unlike 4-phenylbutyryl chloride which affords tetralone, the *N*-substituted benzylglycine ($n = 1$) is not converted into isoquinolone, but instead eliminates carbon monoxide and formaldehyde, yielding secondary amine derivatives.[14] The reaction with $\alpha\alpha$-dimethyl-δ-phenylvaleryl chloride (XIII; $n = 3$) envisaged above was first carried out by Ramart-Lucas and Hoch [6] in the expectation of isolating 2,2-dimethylbenzocycloheptenone, (XV). They obtained, however, not the cycloheptenone but a compound which they considered might be the phenylcyclopentanone (XVI) in analogy with phenylcyclopentane (XVII) prepared by von Braun and Deutsch when cyclising 5-phenylpentyl chloride.[15]

The reaction with dimethyl-phenylvaleryl chloride appeared to require re-examination because Ramart-Lucas and Hoch did not publish an analysis of their compound (XVI) and they appear not to have noticed that carbon monoxide had been released. Repetition

[9] E. Rothstein and E. Vallely, unpublished work.
[10] E. Rothstein, *J.*, 1951, 1459.
[11] E. Rothstein and R. W. Saville, *J.*, 1949, 1946, 1950.
[12] E. Rothstein, *Chem. and Ind.*, 1954, 403.
[13] J. von Braun, G. Blessing, and R. S. Cahn, *Ber.*, 1924, **57**, 908; J. von Braun and W. Wirz, *Ber.*, 1927, **60**, 102.
[14] C. Mannich and R. Kuphal, *Ber.*, 1912, **45**, 1268.
[15] J. von Braun and H. Deutsch, *Ber.*, 1912, **45**, 1268; cf. also J. von Braun and M. Kuhn, *Ber.*, 1927, **60**, 2561.

of their experiment showed that this did in fact occur with resultant production of dimethyl-tetralin, (XVIII). Its structure was established by direct comparison of the dinitro-derivative with that of (*a*) the specimen obtained by reduction and nitration of 4,4-dimethyltetralone, mentioned above, and (*b*) the dinitro-derivative of dimethyltetralin prepared by cyclisation of 1,1-dimethyl-4-phenylbutanol. P.m.r. spectra agreed with the

(XV)   (XVI)   (XVII)   (XVIII)
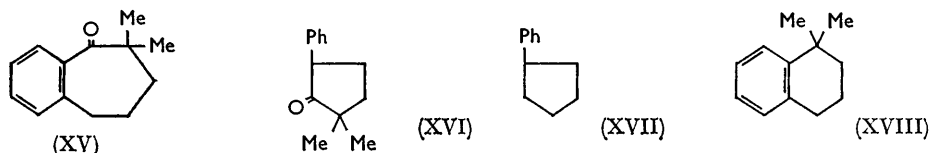
suggested structure and also showed that prolonged reaction with aluminium chloride led to rearrangement. Internal Friedel–Crafts acylations seem less prone to side-reactions than alkylations and, unlike the abnormal reaction observed by von Braun and Deutsch, δ-phenylvaleryl chloride afforded benzocycloheptenone.[6] Similarly, it is now found that γγ-dimethyl-δ-phenylvaleryl chloride, (XIX), cyclises normally to give 4,4-dimethyl-benzocycloheptenone, (XX), the structure being confirmed by p.m.r. (see Experimental section).

$$PhCH_2 \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot COCl \longrightarrow$$

(XIX)   (XX)
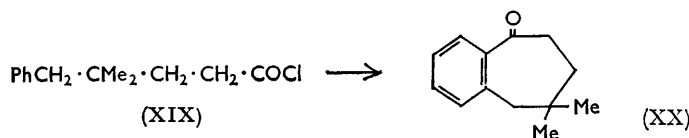
Similar cyclisations were observed in the diethyl series. Since the 4-ethyl-4-phenyl-hexanoyl chloride prepared from diethylglutaric anhydride contained isomers, it was synthesised by an independent route. The addition of ethyl 2-cyano-3,3-diethylacrylate to phenylmagnesium bromide gave ethyl 2-cyano-3-ethyl-3-phenylvalerate, $CEt_2Ph\cdot CHCN\cdot CO_2Et$ which on hydrolysis yielded β-ethyl-β-phenylvaleric acid. The acid chloride of this was reduced by aluminium lithium hydride and the 3-ethyl-3-phenyl-pentanol so obtained was converted first into the bromide and then into the Grignard derivative, which furnished the required acid when saturated with carbon dioxide. Cyclisation of the acid chloride yielded 4,4-diethyltetralone which was reduced to the tetralin, the latter being identical with the specimen obtained by cyclising 1,1-diethyl-4-phenyl-butanol. The reactions of αα-diethyl-γ-*p*-amisoyl-butyryl chloride (XXI) and of its

(XXI)   (XXII)   (XXIII)
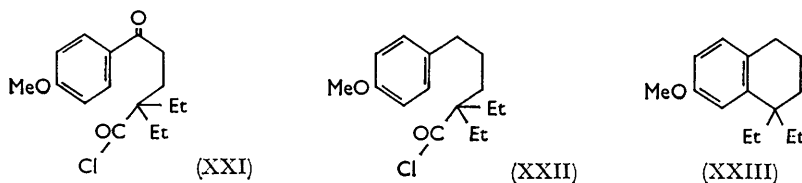
reduction product, αα-diethyl-δ-*p*-methoxyphenylvaleryl chloride, (XXII), were also examined. In both cases carbon monoxide was evolved but only the product of the second reaction was identified. This was 1,1-diethyl-7-methoxytetralin, (XXIII), the position of the methoxy-group being determined by the structures of the parent acids.

EXPERIMENTAL

Preparation and Friedel–Crafts Reaction of as-*Diethylsuccinic Anhydride.*—Ethyl 2-cyano-3,3-diethylacrylate[16] (18·1 g.) was dissolved in 50% ethanol (40 c.c.) and sodium cyanide (9·8 g.) added.[17] The liquid was heated (100°) for a few minutes, mixed with water and dilute

[16] A. C. Cope, C. M. Hofmann, C. Wyckoff, and E. Hardenbergh, *J. Amer. Chem. Soc.*, 1941, **63**, 3452.
[17] A. Lapworth and Wilson Baker, *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 451.

acid (HCl), and extracted with ether. The extract yielded ethyl α,β-dicyano-β,β-diethyl-propionate, b. p. 156—162°/11 mm. (63·5%), which was hydrolysed and decarboxylated in the conventional manner. The resulting recrystallised acid, m. p. 106° (63%), was converted into the anhydride, b. p. 116—120°/11 mm. (77%), by boiling it with acetyl chloride (Found: C, 61·6; H, 7·7. Calc. for $C_8H_{12}O_3$: C, 61·5; H, 7·7%). A solution of the anhydride (10 g., 0·064 mol.) in benzene (10 c.c.) was added to a stirred suspension of aluminium chloride (18 g., 0·14 mol.) in benzene (60 c.c.) under nitrogen, and the reaction completed by boiling the liquid under reflux for 30 min. The yield of carbon monoxide was 3·2% and that of β-benzoyl-αα-diethylpropionic acid which separated from light petroleum (b. p. 60—80°) as needles, m. p. 92—93°, 84%. In this as in subsequent Friedel-Crafts reactions, the catalyst was a free-flowing powder specially prepared by Messrs. British Drug Houses Limited.

Experiments with Derivatives of 2,2-Dimethylglutaric Acid.—*Preparation of 2,2-dimethylglutaric anhydride.* (i) Isolauronolic acid [18] (63 g.) was oxidised by warming it with a mixture of nitric acid (d 1·2; 470 c.c.) and water (470 c.c.).[19] The crude acid was repeatedly distilled with water to free it from the greater part of the unchanged nitric acid, dissolved in methanol, and saturated with dry hydrogen chloride. Fractionation of the product afforded methyl αα-dimethylglutarate, b. p. 90—98°/12 mm. together with a fraction, b. p. 110—150°/12 mm. which contained nitrogen and separated from light petroleum (b. p. 60—80°) in clusters of prisms, m. p. 84—85° (Found: C, 51·9; H, 7·2; N, 6·1. $C_{10}H_{17}NO_5$ requires C, 51·9; H, 7·4; N, 6·0%). Infrared absorptions indicated hydroxyl (3509 cm.$^{-1}$ in CCl_4) which was probably tertiary (1110 cm.$^{-1}$ in KCl), and also the presence of a nitro-group (absorptions at 1540, 1379, 1346, and 870 cm.$^{-1}$, in KCl). P.m.r. indicated that the substance was *methyl 1-hydroxy-2,3,3-trimethyl-2-nitrocyclopentanecarboxylate.* The four methyl-group signals were at (τ values) 9·12, 8·83, 8·35, and 6·29 p.p.m. The latter was clearly due to the methoxy-group and as regards the first three, the Varian spectrum for 2-methyl-2-nitropropanol [20] indicates that the absorption associated with methyl protons β to the nitro-group is at 8·41 p.p.m.; the observed difference from 8·35 could be attributed to the shielding effect of the cyclopentane ring. Also, in a rigid molecule, as in the present case, the 3,3-methyl groups are differently oriented with reference to the nitro-group, which accounts for the two signals observed. Finally, the hydroxyl proton had a frequency of 6·70 p.p.m. and the two methylenes were indicated by a symmetrical (A_2B_2) group of signals centred at 7·5 p.p.m.

Hydrolysis of the above methyl ester yielded αα-dimethylglutaric acid (22·6 g., 35%), treatment of which with acetyl chloride furnished the anhydride, b. p. 126°/10 mm., m. p. 37—38° (90%) (Found: C, 58·9; H, 6·8. Calc. for $C_7H_{10}O_3$: C, 59·2; H, 7·0%).

(ii) Cyanoethylation of isobutyraldehyde afforded γ-cyano-αα-dimethylbutyraldehyde,[21] and the latter (114 g.) was hydrolysed by boiling it under reflux, with stirring, with 10% sodium hydroxide (500 c.c.) until no more ammonia was evolved (6 hr.). Neutral products were removed from the diluted solution with ether and the alkaline aqueous layer acidified (HCl), extracted with ether, and the extract dried (Na_2SO_4). Distillation afforded γγ-dimethyl-δ-oxovaleric acid, b. p. 52°/0·05 mm. (26·5 g.), leaving a residue of αα-dimethylglutaric acid (14 g.). The dimethyl-oxovaleric acid (26·5 g.) was oxidised by warming its solution in 20% potassium hydroxide (200 g.) at 40° with a stirred suspension of potassium permanganate (48 g.) in water (400 g.) yielding αα-dimethylglutaric acid (28·6 g., 96%).

Reaction of αα-dimethylglutaric anhydride with benzene. A typical example was the addition of a solution of the anhydride (18 g.) in benzene (20 c.c.) to a stirred suspension of aluminium chloride (41 g.) in benzene (100 c.c.). The reaction was carried out under nitrogen, and arrangements were made to collect all the evolved gases over water. The yield of carbon monoxide was in some experiments as high as 77·1%. The product was decomposed by ice–water and acid (HCl) and the separated benzene layer extracted with aqueous sodium hydroxide. The following were obtained:

(i) The dried benzene layer afforded 4,4-dimethyltetralone (1·3 g.) to which reference is made below. The corresponding *semicarbazone* separated from dilute ethanol as needles, m. p. 197·5° (Found: C, 67·9; H, 7·7; N, 18·7. $C_{13}H_{17}N_3O$ requires C, 67·5; H, 7·4; N, 18·2%).

(ii) A solid product obtained by acidification of the aqueous alkaline layer was extracted

[18] B. Shive, J. T. Horeczy, and H. L. Lochte, *J. Amer. Chem. Soc.,* 1940, **62**, 2744.
[19] G. Blanc, *Bull. Soc. chim. France,* 1898, (3), **19**, 284.
[20] " N.M.R. Spectra Catalog," vol. 2, No. 422, Varian Associates, Palo Alto, California, 1963.
[21] D. Hoch and P. Karrer, *Helv. Chim. Acta,* 1954, **37**, 397.

with light petroleum (b. p. 40—60°); the residue was *γ-benzoyl-αα-dimethylbutyric acid* which separated from dilute ethanol or from benzene–light petroleum (b. p. 80—100°) as needles, m. p. 122—123° (7 g.) (Found: C, 71·4; H, 7·2. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). The *semicarbazone*, after repeated recrystallisations from ethanol, had m. p. 208° decomp. (Found: C, 60·8; H, 6·9; N, 15·2. $C_{14}H_{19}N_3O_3$ requires C, 60·7; H, 6·9; N, 15·2%). Clemmensen reduction yielded αα-dimethyl-δ-phenylvaleric acid, b. p. 132°/0·1 mm., m. p. 30° (Found: C, 75·4; H, 8·7. Calc. for $C_{13}H_{18}O_2$: C, 75·6; H, 8·7%). The identity of the acid was confirmed by comparison with the independently synthesised specimen. Condensation of isobutyrophenone with 3-phenylpropyl bromide using sodamide, followed by fission by the same reagent [6] gave αα-dimethyl-δ-phenylvaleramide m. p. 95° (Found: C, 76·1; H, 9·5; N, 6·7. Calc. for $C_{13}H_{19}NO$: C, 76·1; H, 9·3; N, 6·8%), which was hydrolysed by 48% hydrobromic acid. A mixture of the acid and thionyl chloride at room temperature yielded the acid chloride, b. p. 94°/0·1 mm., 80—82°/0·02 mm. (Found: C, 70·2; H, 8·0; Cl, 16·0. Calc. for $C_{13}H_{17}ClO$: C, 69·5; H, 7·6; Cl, 15·8%).

(iii) The petroleum extract yielded γ-methyl-γ-phenylvaleric acid, b. p. 134°/0·1 mm. (8·4 g.) (Found: C, 74·9; H, 8·4. Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·4%). It was identified by the anilide, m. p. 115—116°,[22] which was recrystallised from ethanol (Found: C, 80·5; H, 7·7; N, 5·3. Calc. for $C_{18}H_{21}NO$: C, 81·0; H, 7·9; N, 5·3%).

(iv) A high-boiling residue (1·7 g.) from (iii) was an acid, b. p. 165—170°/0·1 mm., m. p. 125—126° (from ethyl acetate). It appeared to be isomeric (Found: C, 70·5; H, 7·5%) with γ-benzoyl-αα-dimethylvaleric acid but depressed the m. p. of the latter.

Cyclisation of 4-methyl-4-phenylvaleric Acid and Reduction of the Tetralone.[23]—A mixture of the acid (10·1 g.) and purified thionyl chloride (7·5 g.) was set aside for 18 hr. yielding the acid chloride, b. p. 91—94°/0·1 mm. (95%). The latter (9·9 g.) dissolved in benzene (25 c.c.) was added to a stirred suspension of aluminium chloride (9·5 g.) in benzene (50 c.c.) under nitrogen. When addition was complete (75 min.) the mixture was stirred (1 hr.) and then stood overnight. Decomposition of the mixture with ice and dilute acid afforded the 4,4-dimethyltetralone, b. p. 129—131°/9 mm., 97—99°/0·3 mm. (92%) (Found: C, 82·6; H, 7·9. Calc. for $C_{12}H_{14}O$: C, 82·8; H, 8·1%), which gave the semicarbazone, m. p. 197—199° after two recrystallisations from ethanol and one from ethyl acetate. It was identical (mixed m. p.) with that described above (Found: C, 67·4; H, 7·3; N, 18·3%). The 2,4-dinitrophenylhydrazone had m. p. 220° somewhat above that (m. p. 217—218°) found by Arnold, Buckley, and Richter [24] who prepared the ketone by a Friedel–Crafts reaction with γγ-dimethylbutyrolactone. Clemmensen reduction of the dimethyltetralone afforded 1,1-dimethyltetralin, b. p. 91—92°/7 mm. (55%) (Found: C, 90·2; H, 10·0. Calc. for $C_{12}H_{16}$: C, 90·0; H, 10·0%). Nitration using a mixture of nitric acid (*d* 1·52) and phosphorus pentoxide,[25] yielded a dinitro-derivative when rubbed with light petroleum (b. p. 20—40°). It separated from dilute ethanol in micro-crystals, m. p. 66·5—67·0° (lit.,[25] 64·5°).

Cyclisation of 2,2-Dimethyl-5-phenylvaleryl Chloride.—A characteristic of the reaction was that prolonged action by the catalyst afforded a mixture of isomeric products. This was shown independently by heating the catalyst with solutions of 1,1-dimethyltetralin. The first cyclisation reaction carried out on a larger scale thus yielded two main isomeric fractions together with small quantities of other materials. The two reactions described below were carried out under more controlled conditions.

(*a*) The acid chloride (31·6 g.) was slowly added with cooling to a suspension of aluminium chloride (40 g.) in benzene (300 c.c.), carbon monoxide being rapidly evolved. The product, b. p. 85—110°/9 mm. (18·5 g., 82·5%), was fractionated through a column packed with glass helices and yielded the following substances: (i) b. p. 90°/0 mm. (Found: C, 89·1; H, 10·9%; *M*, 150. Calc. for $C_{12}H_{16}$: C, 90·0; H, 10·0%; *M*, 160). (ii) b. p. 110—111°/9 mm. (Found: C, 90·0; H, 9·5%). (iii) b. p. 140°/0.2 mm. (Found: C, 86·6; H, 9·0%).

(*b*) The acid chloride (2·3 g.) was added under nitrogen to a mixture of the catalyst (1·4 g.) and benzene (20 c.c.) at room temperature. The yield of carbon monoxide was 66%. After 1 hr. the mixture was decomposed in the usual way and the neutral product, b. p. 94—96°/

[22] E. Späth and P. Kainrath, *Ber.*, 1938, **71**B, 1662.
[23] Cf. R. D. Campbell and N. H. Cromwell, *J. Amer. Chem. Soc.*, 1955, **77**, 5169.
[24] R. T. Arnold, J. S. Buckley, and J. Richter, *J. Amer. Chem. Soc.*, 1947, **69**, 2323.
[25] M. T. Bogert, D. Davidson, and P. M. Apfelbaum, *J. Amer. Chem. Soc.*, 1934, **56**, 961; of. also M. T. Bogert and V. G. Fourmain, *ibid.*, 1933, **55**, 4670.

8 mm., was fractionated from metallic sodium. It appeared to be a mixture and did not afford a crystalline dinitro-derivative.

(c) Aluminium chloride (0·3 g.) was added from a container attached to the reaction flask by a small length of rubber tubing, to a stirred solution of the acid chloride (4·7 g.) in benzene (50 c.c.) under nitrogen. The mixture was stirred for 15 min. after carbon monoxide evolution had ceased, and was then decomposed with ice and acid. Distillation of the product from metallic sodium yielded pure 1,1-dimethyltetralin, b. p. 91—92°/7 mm. (57%). The dinitro-derivative, m. p. 66·5—67°, was identical (mixed m. p.) with that described below (Found: C, 58·0; H, 5·6; N, 11·4. Calc. for $C_{12}H_{14}N_2O_4$: C, 57·7; H, 5·6; N, 11·2%).

Independent Synthesis of 1,1-Dimethyltetralin.[25]—Ethereal 3-phenylpropylmagnesium bromide reacted with acetone to give 1,1-dimethyl-4-phenylbutanol, b. p. 126—130°/11 mm. (51%) (Found: C, 81·0; H, 9·8. Calc. for $C_{12}H_{18}O$: C, 81·0; H, 10·1%). Cyclisation of the alcohol with concentrated sulphuric acid afforded the dimethyltetralin, b. p. 96—98°/11 mm. (74·5%) (Found: C, 90·4; H, 10·1%), which gave the above dinitro-derivative, m. p. 66·5° (Found: C, 57·9; H, 5·7; N, 11·3%).

Cyclisation of γγ-Dimethyl-δ-phenylvaleryl Chloride.—4-Benzoyl-4-methylvaleric acid was prepared in improved yield by the cyanoethylation of isobutyrophenone followed by the hydrolysis of the resulting cyanide.[26] Acrylonitrile (17·2 g.) was added over 20 min. to a mixture of isobutyrophenone (48 g.), dioxan (50 g.), and benzyltrimethylammonium hydroxide (5 g.) kept at 25—35° by water-cooling. The mixture was stirred for a further 6 hr., acidified (HCl), diluted with water, and extracted with chloroform. The extract was freed from dioxan by washing it with water, and then dried ($CaCl_2$). Fractionation afforded the benzoylmethylvaleronitrile, b. p. 137°/0·1 mm. (37·5 g., 57%) (Found: C, 77·2; H, 7·1; N, 7·1. Calc. for $C_{13}H_{15}NO$: C, 77·6; H, 7·5; N, 7·0%). The *oxime* crystallised from dilute ethanol as needles, m. p. 127—129° (Found: C, 72·0; H, 7·4; N, 13·0. $C_{13}H_{16}N_2O$ requires C, 72·2; H, 7·4; N, 13·0%). The semicarbazone, which separated as needles, m. p. 203—204° (decomp.) (lit.,[26] 202—203°) (Found: C, 60·6; H, 6·8; N, 15·2. Calc. for $C_{14}H_{19}N_3O_3$: C, 60·7; H, 6·9; N, 15·2%) depressed the m. p. of the isomeric semicarbazone of γ-benzoyl-αα-dimethylbutyric acid. Neither the nitrile nor the acid was affected by sodamide in boiling benzene suspension, and hence they could not be used as sources of the corresponding dimethylglutaric acid derivatives. The *acid chloride*, b. p. 132°/0·4 mm., separated from light petroleum (b. p. 80—100°) in plates, m. p. 83—84° (Found: C, 66·0; H, 6·2; Cl, 14·3. $C_{13}H_{15}ClO_2$ requires C, 65·4; H, 6·3; Cl, 14·9%). The *amide*, m. p. 174—175°, was recrystallised from dilute ethanol (Found: C, 71·7; H, 7·5; N, 6·5. $C_{13}H_{17}NO_2$ requires C, 71·2; H, 7·7; N, 6·4%). Cyclisation of the acid chloride yielded unidentified products.

Clemmensen reduction of the acid afforded the corresponding γγ-dimethyl-δ-phenylvaleric acid, b. p. 129°/0·1 mm. (73%) which gave the acid chloride, b. p. 110—112°/0·05 mm. A solution of the latter (3·4 g.) in benzene (6 c.c.) was added at room temperature to aluminium chloride (3·6 g.) suspended in benzene (25 c.c.). The mixture was stirred for 2 hr. and then for a further 0·5 hr. at the boil. Carbon monoxide was not liberated and the principal product was 4,4-*dimethylbenzocycloheptenone* (2 g.), b. p. 90—94°/0·1 mm. (Found: C, 83·2; H, 8·5. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%); *semicarbazone* (from ethanol), m. p. 226° (Found: C, 68·5; H, 7·8; N, 17·0. $C_{13}H_{19}N_3O$ requires C, 68·5; H, 7·8; N, 17·1%); *oxime* (from dilute ethanol), m. p. 153—154° (Found: C, 76·5; H, 8·0; N, 7·3. $C_{13}H_{16}NO$ requires C, 76·8; H, 8·4; N, 6·9%). P.m.r. of the oxime and the ketone indicated that there were four aromatic protons and two isolated protons, giving single signals at 7·54 and 7·43 p.p.m., respectively, corresponding to the methylene groups in the 5-position, thus establishing the cycloheptenone structure.

Reaction of αα-Dimethyl-δ-phenylvaleryl Chloride with Anisole.—The only product isolated by the reaction of the acid chloride (9·2 g.), aluminium chloride (10 g.), and anisole (65 c.c.) was 2-p-*methoxybenzoyl-2-methyl-5-phenylpentane*, b. p. 183°/0·3 mm. (90%) (Found: C, 81·2; H, 8·3. $C_{20}H_{24}O_2$ requires C, 81·1; H, 8·1%). The *oxime* separated from ethanol as needles, m. p. 149—150° (Found: C, 76·8; H, 8·4; N, 4·6. $C_{20}H_{25}NO_2$ requires C, 77·2; H, 8·7; N, 4·5%). Carbon monoxide was not eliminated in this reaction.

Experiments with αα-Diethylglutaric Acid Derivatives.—αα-Diethylglutaric acid was prepared by the cyanoethylation of diethylacetaldehyde followed by hydrolysis and oxidation of the resulting 4-cyano-2,2-diethylbutyraldehyde.[27] The anhydride, b. p. 113—114°/0·08 mm.

[26] A. D. Campbell, C. Z. Carter, and S. N. Slator, *J.*, 1948, 1741.
[27] H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, 1944, **66**, 56.

(85%) (Found: C, 63·7; H, 8·3. Calc. for $C_9H_{14}O_3$: C, 63·5; H, 8·2%) was obtained by boiling the acid (78·5 g.) with acetyl chloride (62 g.).[28]

Reaction of αα-*diethylglutaric anhydride with anisole.* A solution of the anhydride (5 g.) in anisole (39 g.) was added at 0° to a mixture of anisole (24 g.) and aluminium chloride (10 g.) under nitrogen, and the reaction completed by heating the liquid at 100° for 1·5 hr. A trace of carbon monoxide (2·6%) was obtained. Recrystallisation of the product from benzene–light petroleum (b. p. 80—100°) gave αα-*diethyl-α-p-methoxy-benzoylbutyric acid,* m. p. 118° (62%). (Found: C, 68·9; H, 7·8. $C_{16}H_{22}O_4$ requires C, 69·1; H, 7·9%). The *methyl ester,* b. p. 140°/0·08 mm., separated from light petroleum (b. p. 60—80°) as prisms, m. p. 52·5° (Found: C, 70·2; H, 8·3. $C_{17}H_{24}O_4$ requires C, 69·9; H, 8·2%). The acid chloride, b. p. 180°/0·08 mm. (decomp.), eliminated carbon monoxide (24%) when it was added to a suspension of aluminium chloride in benzene, but the product was not identified.

Clemmensen reduction of the ketonic acid yielded the corresponding αα-diethyl-δ-*p*-methoxy-phenylvaleric acid (62%), which decomposed when distilled. In benzene solution, the acid chloride, b. p. 160°/0·025 mm. (1·06 g.), reacted with aluminium chloride (0·24 g.) to give carbon monoxide (53·5%), 1,1-*diethyl-7-methoxytetralin,* b. p. 100°/0·015 mm. (47%) (Found: C, 82·6; H, 10·0. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%), and some unreacted acid. The infrared absorption spectrum of the tetralin showed a complete absence of carbonyl bands.

Reaction of αα-*diethylglutaric anhydride with benzene.* This reaction, using a mixture of the anhydride (25 g., 0·15 mol.) aluminium chloride (50 g., 0·37 mol.), and benzene (250 c.c.) kept at the boil for 1·5 hr., yielded (i) carbon monoxide (94%); (ii) 6-methylheptanoic acid, b. p. 118—120°/7 mm. (34%) (Found: C, 66·8; H, 11·3. Calc. for $C_8H_{16}O_2$: C, 66·6; H, 11·2%), traces of isomeric acid were also present (see below); (iii) 4-ethyl-4-phenylhexanoic acid, b. p. 135—140°/0·02 mm. (9%), containing traces of isomeric acids (Found: C, 76·2; H, 8·8. Calc. for $C_{14}H_{20}O_2$: C, 76·3; H, 9·1%); (iv) 1-*benzoyl-5-methylhexane,* b. p. 110—115°/0·1 mm. (7·7%) (Found: C, 82·7; H, 10·0. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%). The *semicarbazone* separated from dilute ethanol as thin prisms, m. p. 142—143° (Found: C, 68·8; H, 8·6; N, 15·9. $C_{15}H_{23}N_3O$ requires C, 69·0; H, 8·8; N, 16·1%). A similar experiment employing a smaller molecular excess (1·5 : 1) of catalyst afforded yields of 13 and 68% of the aliphatic and aromatic acids, respectively.

Identification of the aliphatic acid (ii). The acid chloride, b. p. 73°/9 mm., was converted by gaseous ammonia into 6-methylheptanamide, m. p. 113—114°, after several recrystallisations from benzene (Found: C, 66·9; H, 11·8; N, 9·9. Calc. for $C_8H_{17}NO$: C, 67·1; H, 11·9; N, 9·8%). Its identity was established by comparing it (mixed m. p.) with the amide, m. p. 114—115° (Found: C, 67·2; H, 11·8; N, 9·8%) prepared from the authentic acid by condensing diethyl malonate with isohexyl iodide, followed by hydrolysis and decarboxylation of the resulting malonic ester derivative.[29] Their infrared absorption spectra were also identical, and there were only minor differences in the p.m.r. spectra. There was also a more soluble amide which separated from benzene–light petroleum (b. p. 60—80°) in flakes, m. p. 80—83° (Found: C, 66·9; H, 12·0; N, 10·0%). A mixture with the higher-melting compound had an intermediate m. p., but further recrystallisations left the substance unaltered. The infrared spectrum was somewhat less complex in the 1430-cm.[-1] region, but there were very slight differences only in the p.m.r. spectra. Similar comparisons with 4-ethyl- and 4,4-dimethyl-hexanamides (described below) exhibited no points of resemblance.

Methyl esters. Authentic *methyl 6-methylheptanoate,* b. p. 73°/10 mm. (Found: C, 68·2; H, 11·5. $C_9H_{18}O_2$ requires C, 68·4; H, 11·4%) was compared, using infrared absorption and gas chromatography, with the methyl ester, b. p. 75—78°/17 mm. (Found: C, 68·2; H, 11·3%) prepared from the Friedel–Crafts acid. The two were identical except that there was a fairly prominent side-band on the gas chromatogram (stationary phase, polyethylene glycol) in the latter case. A partial separation resulted when the amide, m. p. 113—114°, was converted back into the acid, re-esterified, and the methyl ester put through a preparative Carbowax 1500 column. A small side-band still persisted, though its presence was undetectable on either the infrared or p.m.r. spectra. The gas chromatograms, on the other hand, as well as the spectra of the methyl esters of 4-ethyl- and 4,4-dimethyl-hexanoic acids, were significantly different.

1-*Benzoyl-5-methylhexane.* This was prepared from the " synthetic " acid chloride (2 g.)

[28] N. M. Kishner, *J. Russ. Phys. Chem. Soc.,* 1911, **43**, 1154.
[29] P. A. Levene and C. H. Allen, *J. Biol. Chem.,* 1916, **27**, 433.

by adding its benzene solution to aluminium chloride (2·5 g.) in benzene (200 c.c.) and heating the mixture at the boil for 10 min. The resulting ketone, b. p. 103°/0·09 mm. (88%) (Found: C, 82·4; H, 9·9%) yielded the semicarbazone, m. p. 143—144° (Found: C, 68·9; H, 8·8; N, 16·1%) which was identical (mixed m. p.) with the specimen originally isolated, and also with one obtained by the Friedel–Crafts reaction on the acid chloride from diethylglutaric anhydride. The identity of all three compounds was also confirmed by comparison of their infrared and p.m.r. spectra, but here again the specimens which were derived from the anhydride gave gas-chromatographic traces with small side-bands indicating the presence of some isomeric material.

Derivatives of 4-ethylhexanoic acid. The acid was prepared by the catalytic hydrogenation of 4-ethylhex-2-enoic acid.[30] The *acid chloride*, b. p. 74—75°/13 mm. (Found: C, 59·1; H, 9·2. $C_8H_{15}ClO$ requires C, 59·0; H, 9·2%) afforded the *amide*, separating from water as wax-like plates, m. p. 82—83° (Found: C, 67·1; H, 11·8; N, 9·5. $C_8H_{17}NO$ requires C, 67·0; H, 11·9; N, 9·8%). The *methyl ester*, b. p. 74—77°/13 mm. (89%), was prepared by saturating a methanolic solution of the acid with hydrogen chloride (Found: C, 68·6; H, 11·5. $C_9H_{18}O_2$ requires C, 68·3; H, 11·5%). The corresponding p.m.r. spectrum was rather complex but the triplet and quartet of signals attributed to the ethyl groups could be clearly distinguished. A Friedel–Crafts reaction of 4-ethylhexanoyl chloride with benzene furnished the corresponding 1-*benzoyl*-3-*ethylpentane*, b. p. 108—109°/0·025 mm. (91%) (Found: C, 82·3; H, 10·1. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%), the evolved carbon monoxide being <3%. The *semicarbazone* separated from dilute ethanol as prisms, m. p. 135° (Found: C, 69·6; H, 9·0; N, 15·9. $C_{15}H_{23}N_3O$ requires C, 69·0; H, 8·8; N, 16·1%). A mixture of it with 1-benzoyl-5-methylhexane semicarbazone had m. p. 121—130°.

Derivatives of 4,4-dimethylhexanoic acid. The initial preparation of this acid by cyanoethylating methyl isopropyl ketone followed by Clemmensen reduction and hydrolysis[26] gave a product, b. p. 130—150°/16 mm., and was unsatisfactory. Therefore, 3,3-dimethylpentyl bromide[31] was converted into the Grignard derivative and an ethereal solution of the latter saturated with carbon dioxide. The acid was obtained as a colourless oil, b. p. 120—124°/14 mm. (57%) (Found: C, 66·6; H, 11·0. Calc. for $C_8H_{16}O_2$: C, 66·6; H, 11·2%); *acid chloride*, b. p. 71—73°/13 mm. (Found: C, 59·0; H, 9·5. $C_8H_{15}ClO$ requires C, 59·0; H, 9·2%); methyl ester, b. p. 74—76°/15 mm.; *amide*, waxy plates from dilute ethanol, m. p. 104° (Found: C, 66·9; H, 11·9; N, 10·1. $C_8H_{17}NO$ requires C, 67·1; H, 11·9; N, 9·8%). Aluminium chloride added to the benzene solution of the acid chloride afforded 1-*benzoyl*-3,3-*dimethylpentane*, b. p. 110—111°/0·04 mm. (Found: C, 82·1; H, 9·8. $C_{14}H_{20}O$ requires 82·4; H, 9·8%); the *semicarbazone* separated from dilute ethanol as needles, m. p. 130—131° (Found: C, 68·7; H, 8·7; N, 16·0. $C_{15}H_{23}N_3O$ requires C, 69·0; H, 8·8; N, 16·1%). The m. p. of a mixture with 1-benzoyl-5-methylhexane semicarbazone was 115—120°.

Preparation of 4-ethyl-4-phenylhexanoic acid. The addition of ethereal ethyl 2-cyano-3,3-diethylacrylate (63 g.) to ethereal phenylmagnesium bromide, prepared from magnesium (10 g.) and bromobenzene (75·5 g.), yielded ethyl α-cyano-β-ethyl-β-phenylvalerate as a heavy oil, b. p. 145—152°/0·1 mm. (57%). The ester (60·5 g.) was heated for 15—20 hr. under reflux with a solution of potassium hydroxide (52·5 g.) in ethylene glycol (320 g.) until the solution was homogeneous and no more ammonia was detected. 3-*Ethyl*-3-*phenylvaleric acid*, b. p. 120—130°/0·3 mm., crystallised on cooling, and after recrystallisation from dilute ethanol had m. p. 74—75° (Found: C, 75·5; H, 8·6. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7). Reaction with cold thionyl chloride gave the corresponding acid chloride, b. p. 96—98°/0·03 mm. (93%). Though there was little reaction with ethereal diazomethane, the acid chloride (71 g.) dissolved in ether (50 c.c.) was readily reduced by a solution of aluminium lithium hydride (9·0 g.) in the same solvent (50 c.c.). After the initial vigorous reaction had subsided, the mixture was warmed for 20 min., cooled to 0°, and decomposed by moist ether followed by ice and acid (10% H_2SO_4). Isolation of the product yielded 3-*ethyl*-3-*phenylpentanol*, b. p. 110—112°/0·06 mm. (52·2 g., 87%) (Found: C, 81·5; H, 10·4. $C_{13}H_{20}O$ requires C, 81·3; H, 10·4%). The alcohol was best converted into the bromide by adding it (18·1 g.) to a mixture of hydrobromic acid (48%; 30 g.) and concentrated sulphuric acid (5·6 g.). A further 0·94 g. of the latter was then added and the mixture boiled under reflux for 5·5 hr. The organic layer was washed with concentrated sulphuric acid,

[30] L. F. Fieser, M. T. Leffler, and their co-workers, *J. Amer. Chem. Soc.*, 1948, **70**, 3174.
[31] L. Schmerling, *J. Amer. Chem. Soc.*, 1945, **67**, 1152.

dilute alkali (Na_2CO_3), and water, and dried ($CaCl_2$). Distillation afforded the crude 3-*ethyl-3-phenylpentyl bromide*, b. p. 85—86°/0·015 mm. (64%) (Found: C, 62·4; H, 7·7. $C_{13}H_{19}Br$ requires C, 61·2; H, 7·5%). It was converted into the corresponding 3-ethyl-3-phenylpentyl-magnesium bromide which in turn yielded 4-*ethyl-4-phenyl-hexanoic acid*, b. p. 135—140°/0·04 mm. (60%), described above (Found: C, 76·1; 8·8. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·1%).

Cyclisation of 4-ethyl-4-phenylhexanoyl chloride (iii) *prepared from diethylglutaric anhydride.* A benzene (40 c.c.) solution of the acid chloride, b. p. 104—108°/0·03 mm. (11·2 g.), was gradually added to a benzene (100 c.c.) suspension of aluminium chloride (9·5 g.). A small amount of carbon monoxide (13%) was liberated, but the main product consisted largely of 4,4-*diethyl-tetralone*, b. p. 96—100°/0·04 mm. (56%) (Found: C, 83·4; H, 9·1. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%). The 2,4-*dinitrophenylhydrazone* separated from glacial acetic acid as deep orange plates, m. p. 188° (Found: 62·9; H, 5·8; N, 14·9. $C_{20}H_{22}N_4O_4$ requires C, 62·8; H, 5·8; N, 14·7%). Neither the oxime nor the semicarbazone could be obtained crystalline. Clemmensen reduction of the ketone yielded the corresponding 1,1-*diethyltetralin*, b. p. 70—71°/0·05 mm. (68%).

The above tetralone was also obtained from the sample of 4-ethyl-4-phenylhexanoyl chloride (b. p. 98—100°/0·02 mm.) prepared *via* 3-ethyl-3-phenylpentyl bromide, and had b. p. 94—96°/0·01 mm. (85%). The 2,4-dinitrophenylhydrazone, m. p. 189° (Found: C, 63·1; H, 6·1; N, 15·0%) was identical (mixed m. p.) with that described above.

Preparation of 1,1-*diethyltetralin.* The method used was similar to that employed for the dimethyl derivative, and started from diethyl ketone. 1,1-*Diethyl-4-phenylbutanol* having b. p. 130—138°/0·15 mm. (54%) (Found: C, 81·6; H, 10·1. $C_{14}H_{22}O$ requires C, 81·5; H, 10·1%), was cyclised by concentrated sulphuric acid and the product distilled from metallic sodium. 1,1-*Diethyltetralin* was obtained as an odourless oil, b. p. 69—71°/0·04 mm. (63·3%) (Found: C, 89·4; H, 10·4. $C_{14}H_{20}$ requires C, 89·4; H, 10·6%). Unlike the specimen obtained by the Friedel–Crafts reaction, it furnished 1,1-diethyl-5,6-dinitrotetralin, crystallising from dilute ethanol as needles, m. p. 117—118° (24%) (Found: C, 59·7; H, 6·7; N, 10·4. $C_{14}H_{18}N_2O_4$ requires C, 60·4; H, 6·5; N, 10·1%). The 5,6-dinitro-substitution is suggested because the remaining two aromatic protons give signals conforming to an AB system, the τ values being 2·50 and 2·03 ($J_{7,8} = 9·0$ c./sec.), and therefore they are adjacent. A 5,8-dinitro-structure would leave the protons adjacent but symmetrically placed, and therefore giving a single absorption. A similar AB structure is found for the adjacent protons of 2,5-dichloronitrobenzene. In this case the doublet is centred at 2·45 p.p.m. (corresponding to the 3- and 4-protons), but there is a triplet derived from the proton in the 6 position ($J = 1·5$ c./sec.) which interacts with the first two protons (giving an AX_2 system). No such splitting occurs in the dinitro-tetralin because the third isolated proton is not present. Tetralin itself is nitrated partly in the 5,6- and partly in the 5,7-positions but in the latter case, the greater solubility of the resulting dinitro-derivative makes it less easy to isolate.[32] Furthermore, since *p*-t-butyl-toluene is preferentially nitrated in the position *ortho* to methyl,[33] analogy suggests that the nitro-groups should be oriented away from the *gem*-diethyl groups of the other ring.

Proton Magnetic Resonance Spectra.—Some of the features of p.m.r. spectra used for various identification purposes are given in the Table, the figures being τ values (p.p.m.) They were measured on Varian A-60 spectrometer. The first six compounds were derived from dimethyl-glutaric anhydride and were characterised by the single unsplit signals given by the protons of the tertiary *gem*-dimethyl groups. In many cases the adjacent chain-methylene protons also gave single absorptions. The next five substances were connected with the rearrangement products of αα-diethylglutaric anhydride. With the exception of No. 7 where they were tertiary, the *gem*-dimethyl groups were of the *iso*-type at the end of chains and gave rise to doublets. The remaining six were *gem*-diethyl derivatives which all showed the typical triplet (with intensities in the ratio 1 : 3 : 2) and quartet of signals of methyl and methylene, respectively. The latter usually overlapped those of the chain methylenes but could nevertheless be distinguished. This was true also of No. 15, γ-*p*-anisoyl-αα-diethylbutyric acid, but the spectrum of the methyl ester (No. 16) showed a clear separation of the triplet, quartet, and the *single* signal corresponding to the two adjacent methylene groups, which in this respect resembled the *gem*-dimethyl derivatives. Assignments were largely based on analogy, and in particular, by

[32] G. Schroeter, *Annalen*, 1922, **426**, 44.
[33] M. Battegay and P. Haeffely, *Bull. Soc. chim. France*, 1924, (4), **35**, 985.

comparison with the spectrum of 4-methylpentanamide,[36] where the *gem*-dimethyl, the methylene adjacent to amido-, and the amido-group itself show absorptions at 9·1 (doublet), 7·80 (multiplet), and 3·81 (doublet), respectively. In general, only the centres of the A_2B_2 bands were measured. In the case of the benzoyl derivative (No. 4), tentative assignments based the

Proton magnetic resonance spectra (τ values)

No.	Compound	$-CH_2 \cdot CH_3$	$-CH_2-$	Chain $-CH_2-$	Other absorptions
1	γ-Methyl-γ-phenylvaleric acid	8·71s	—	7·97s (A_4)	2·71s (Ph), −1·71 (CO_2H)
2	anilide	8·74s	—	0·99s (A_4)	
3	$\alpha\alpha$-Dimethyl-δ-phenyl-valeric acid	8·75s	—	8·37s (A_4)	2·83s (Ph), −2·01 (CO_2H)
4	γ-Benzoyl-γ-methylvaleric acid	8·69s	—	762, 7·96 (A_2B_2) *	
5	1,1-Dimethyltetralin	8·75s	—	†	$\sim$2·9 m (Ph)
6	after treatment with $AlCl_3$	8·75s	—	‡	9·09, 9·07, 9·11 §
7	1-Benzoyl-3,3-dimethyl-pentane semicarbazone	9·07s ¶	—	7·97m (A_2B_2)	1·17 (N·NH), 3·85 ($CONH_2$)
8	Methyl 6-methylhept-anoate	9·12d	—	7·73t ¶ (α-CH_2−)	6·39 (OCH_3)
9	6-Methylheptanamide	9·15d	—	7·78t ¶ (α-CH_2−)	
10	1-Benzoyl-5-methylhexane	9·12d	—	7·72t (−CH_2−)	2·02 (Ph),[34] AB_2C_2 [35]
11	semicarbazone	9·15d	—	†	0·48 (N·NH), 3·60 ($CONH_2$)
12	γ-Cyano-$\alpha\alpha$-diethylbutyr-aldehyde	9·17t ¶	8·45q ¶	7·97m (A_2B_2)	
13	$\alpha\alpha$-Diethylglutaric an-hydride	9·08t	8·33q	8·20t, 7·30t (A_2X_2)	
14	Dimethyl $\alpha\alpha$-diethyl-glutarate	9·16t	8·40q	8·00m (A_2B_2)	3·65, 3·63 ¶ (CO_2Me)
15	γ-p-Anisoyl-$\alpha\alpha$-diethyl-butyric acid	9·09t	8·30q	7·97t, 7·15t (A_2X_2)	1·43 (CO_2H) ‖
16	methyl ester	9·19t	8·20q	7·84s (A_4)	6·38 (CO_2Me), 6·17 (COMe) ‖
17	4-Ethyl-4-phenylhexanoyl chloride	9·30t	8·30q	7·67m (A_2B_2)	
18	4,4-Diethyltetralone	9·17t	?	7·65m (A_2B_2)	
19	4,4-Dimethylbenzocyclo-heptenone	9·05s	—	8·72t, 7·25t ¶ (A_2X_2)	7·54s (5-CH_2), $\sim$2·7 ** (C_6H_4)

* $J = 7·05$ c./sec. † Not resolved. ‡ Reduced intensity. § New signals. ¶ Considerable splitting of the main absorptions was observed. ‖ 2·05, 3·08 (C_6H_4) $(AB)_2$. $J_{AB} = 8·50$ c./sec. ** 14 signals.

procedure described by Pople, Schneider, and Bernstein [37] were made. Using their Tables 6—20 and 6—21, possible values of the chemical shifts and of the coupling constant J_{AB} were evaluated. A rough estimate of the intensities of the signals showed them to be in the correct order.

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[34] Ref. 20, vol. 1, No. 192.
[35] Ref. 35, p. 259.
[36] Ref. 20, vol. 1, No. 142.
[37] J. A. Pople, W. G. Schneider, and H. J. Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw Hill, New York, 1959, p. 144.