172. *The Relative Stabilising Influences of Substituents on Free Alkyl Radicals. Part IV.*[1] *Selective Hydrogen-abstraction by Free* tert.-*Butoxy-radicals.*

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In the reaction of *tert.*-butoxy-radicals with compounds $X{\cdot}CH_2{\cdot}CH_2{\cdot}Y$ ($X = Ph$; $Y = CO_2Et$, COMe, COPh, CO_2H, CN, Cl, and p-$Cl{\cdot}C_6H_4$) a 50% or higher yield of the " dimer " $[{\cdot}CHX{\cdot}CH_2Y]_2$ was obtained in the first three cases, indicating that hydrogen abstraction occurred selectively to give the radical ${\cdot}CHX{\cdot}CH_2Y$ and hence that X is more stabilising than Y on the intermediate alkyl radical (*i.e.*, Ph > CO_2Et, COMe, or COPh). In the other cases, the yields of " dimers " were small, rendering comparison impracticable.

A characteristic reaction of free alkyl or alkoxy-radicals in solution is the abstraction of hydrogen atoms from the hydrocarbon chain of the solvent. This occurs particularly readily when the solvent molecule contains a substituent group capable of stabilising, by resonance, the radical so produced. Action of the attacking radical then becomes highly specific, and hydrogen abstraction occurs invariably from the carbon atom adjacent to such a substituent, which may be phenyl, carbonyl, or other unsaturated group; the fate of the radical is usually dimerisation.[2, 3] Examples are ethylbenzene and butanone, which with free methyl [2] or *tert.*-butoxy-radicals [3] give, *via* the radicals (I) and (III), the diphenylbutane (II) and the 1 : 4-diketone (IV), respectively:

$$R{\cdot} + Ph{\cdot}CH_2Me \longrightarrow RH + Ph{\cdot}CHMe{\cdot}\ \text{(I)};\ 2\text{(I)} \longrightarrow (CHPhMe)_2\ \text{(II)}$$

$$R{\cdot} + Me{\cdot}CO{\cdot}CH_2Me \longrightarrow RH + Me{\cdot}CO{\cdot}CHMe{\cdot}\ \text{(III)};\ 2\text{(III)} \longrightarrow (CHMe{\cdot}COMe)_2\ \text{(IV)}$$

In a substance $X{\cdot}CH_2{\cdot}CH_2{\cdot}Y$ in which both X and Y are unsaturated groups, both methylene groups would be open to attack by the free radical and, provided that there is no orientating effect of steric origin, the course of the reaction would be governed by the relative stability of the intermediate radical.[4] Thus, the radical ${\cdot}CHX{\cdot}CH_2Y$ would be formed in preference to $X{\cdot}CH_2{\cdot}CHY{\cdot}$ if X stabilises the intermediate alkyl radical more effectively than Y. Selective hydrogen-abstraction by a radical, the course of which can be unambiguously established by identification of the dimeric product, therefore provides a means by which the relative stabilising influences of X and Y can be compared. In this work we have studied the selective hydrogen-abstraction by *tert.*-butoxy-radicals (generated from *tert.*-butyl peroxide by thermolysis) of seven substances of the type indicated above, in which X is Ph and Y is CO_2Et, CO_2H, CN, Cl, COMe, COPh, or p-$Cl{\cdot}C_6H_4$. A yield of 50% or higher of the " dimer " $({\cdot}CHX{\cdot}CH_2Y)_2$ was obtained when Y was CO_2Et,

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[1] Part III, Huang and Si-Hoe, *J.*, 1957, 3988.

[2] Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, (*a*) 394, (*b*) 401; (*c*) *J. Amer. Chem. Soc.*, 1948, **70**, 1269.

[3] (*a*) Farmer and Moore, *J.*, 1951, 131; (*b*) Moore, *J.*, 1951, 236; Huang and Kum-Tatt, *J.*, (*c*) **1954**, 2570; (*d*) 1955, 4229.

[4] See Huang, *J.*, 1954, 3084.

COMe, and COPh, providing conclusive evidence for the greater stabilising effect of the phenyl group over these substituents. In the other cases, only small yields of dimeric products were obtained and no comparison could be made.

Reaction of ethyl β-phenylpropionate with *tert.*-butyl peroxide at 120° gave a 50% yield of diethyl *meso*-ββ′-diphenyladipate (V), which on hydrolysis furnished the *meso*-acid. The *meso*- and the racemic forms of the acid and the methyl ester, as well as the ethyl *meso*-ester, are known and their structures have received further confirmation by the conversion of the acids into chrysene derivatives.[5] The preferential formation of one stereomodification by the above radical reaction, though uncommon, has analogies in the dimerisation of the radicals derived from dimethyl succinate [2b] and *p*-methoxyphenylacetic acid,[3d] and is explicable in terms of the conformational aspects of the system concerned. Thus in the *meso*-adipate above, the gauche repulsions in the most favoured staggered conformation are Ph : $CH_2\cdot CO_2Et$, whereas in the diastereoisomer they are Ph : Ph and $CH_2\cdot CO_2Et$: $CH_2\cdot CO_2Et$.[6] Hydrogen abstraction by *tert.*-butoxy-radicals from ethyl β-phenylpropionate therefore occurred with preferential formation of the radical (VI), rather than (VII), and it follows that the phenyl group is more stabilising than ethoxycarbonyl, confirming the results found in Part I [7] concerning these substituents.

β-Phenylpropionic acid by contrast gave a poor yield of *meso*-diphenyladipic acid, together with much polymeric material. No conclusion can be drawn concerning the phenyl and the carboxyl group.

β-Phenylpropionitrile by the same treatment afforded, also in modest yields, two isomers, m. p. 215° and 165°, and large quantities of polymers. The higher-melting isomer, obtained in higher yield, was very probably the (*meso*-)adiponitrile [8] (VIII), m. p. 212°. The lower-melting isomer was probably the previously unknown racemic form, or possibly the succinonitrile (IX). Again, on account of the low yields, no comparison of the substituent groups could be made.

$(\cdot CHPh\cdot CH_2\cdot CO_2Et)_2$ (V)
$\cdot CHPh\cdot CH_2\cdot CO_2Et$ (VI)
$Ph\cdot CH_2\cdot \dot{C}H\cdot CO_2Et$ (VII)
$(\cdot CHPh\cdot CH_2\cdot CN)_2$ (VIII)
$(CH_2Ph\cdot \dot{C}H\cdot CN)_2$ (IX)
$(\cdot CHPh\cdot CH_2\cdot COMe)_2$ (X)
$(\cdot CHPh\cdot CH_2\cdot COPh)_2$ (XI)
$\cdot CHPh\cdot CH_2\cdot CO\cdot Ph$ (XII)
$(\cdot CHPh\cdot CH_2Cl)_2$ (XIII)
$(\cdot CHAr\cdot CH_2Ph)_2$ (XIV): Ar = Ph
(XVI): $Ar = p\text{-}Cl\cdot C_6H_4$
$(\cdot CPh{:}CH\cdot Ph)_2$ (XV)

From 4-phenylbutan-2-one and *tert.*-butyl peroxide was obtained, in a 57% yield, the 1 : 6-diketone (X) which Dippy and Lewis [9] had prepared, in one stereomodification only, by an unambiguous method. The phenyl group thus has a greater stabilising influence than an isolated ketonic group (acetyl). This is the first direct comparison of these substituents, and the result is in agreement with the relation deduced for them in Part II.[10]

β-Phenylpropiophenone gave, by the same reaction, the *meso*-form of the diketone (XI), which had previously been synthesised, in both the *meso*- and the racemic form, from benzylideneacetophenone by reduction [11] and by a cobaltous chloride-catalysed Grignard reaction,[12] and from ββ′-diphenyladipoyl dichloride and diphenylcadmium.[11] Although the yield of the diketone (XI) in the radical reaction was low, the high recovery of the

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[5] Oommen and Vogel, *J.*, 1930, 2148; Ramage and Robinson, *J.*, 1933, 607; Wilds and Sutton, *J. Org. Chem.*, 1951, **16**, 1371.

[6] Cf. Newman: "Steric Effects in Organic Chemistry," Wiley & Sons, New York, 1956, p. 147. We thank a Referee for drawing our attention to this point.

[7] Huang, *J.*, 1956, 1749.

[8] Baker and Lapworth, *J.*, 1924, 2333.

[9] Dippy and Lewis, *Rec. Trav. chim.*, 1937, **56**, 1000.

[10] Huang, *J.*, 1957, 1342.

[11] Finch and White, *J.*, 1950, 3367.

[12] Kharasch and Sayles, *J. Amer. Chem. Soc.*, 1942, **64**, 2972.

starting material, together with the fact that little or no by-product was formed, leaves little doubt that the main course of the reaction was the generation of the radical (XII), indicating that the benzene ring is more stabilising than the benzoyl group. This has been confirmed in a study of the selective bromination by *N*-bromosuccinimide.[13]

In an attempt to compare the phenyl group with the chlorine atom, phenethyl chloride was treated with *tert.*-butyl peroxide in the usual manner. Only a 16% yield was obtained of a substance which may have structure (XIII), but no degradative studies were carried out. Another attempt to compare these substituents was made by the homolytic addition of bromotrichloromethane to ω-chlorostyrene, as described in Part I.[7] This gave mainly polymeric products, together with some 1 : 1 adduct which could not be purified.

The relative stabilising influences are thus: Ph > CO_2Et, COMe, COPh.

By using substituted dibenzyls, this method could be extended to a comparison of the stabilising effects of aryl groups, and thus provide a parallel approach to that involving the cleavage of dibenzyl ethers (Part III [1]). Dimerisation of the radical derived from a dibenzyl would give a 1 : 2 : 3 : 4-tetra-arylbutane which, if unknown, could be identified by degradation, for example, by bromination followed by dehydrobromination and oxidation. A case studied was that of 4-chlorodibenzyl, in a comparison of the stabilising capacities of the phenyl and the *p*-chlorophenyl group. As a model experiment, dibenzyl itself was treated with *tert.*-butyl peroxide; it gave a 38% yield of the tetraphenylbutane [14] (XIV). Model degradations were then carried out on this tetraphenyl homologue. *N*-Bromosuccinimide under various conditions led to three dibromo-derivatives, m. p. 163°, 181°, and 201°. The highest-melting isomer (obtained in a 35% yield), on dehydrobromination with dimethylaniline, afforded only small quantities of the known tetraphenylbutadiene (XV), while the isomer of m. p. 181° (42% yield) gave only intractable oils; the third isomer being obtained in low yields was not degraded. It appears therefore that degradation of unknown tetra-arylbutanes by this route (bromination, dehydrobromination, then oxidation) is not promising. Further, when 4-chlorodibenzyl reacted with *tert.*-butyl peroxide, only traces of a tetra-arylbutane, presumably (XVI) (since *p*-chlorophenyl has been found to be more stabilising on alkyl radicals than phenyl [1]), were formed, together with polymeric products. This project was therefore abandoned.

EXPERIMENTAL

Unless otherwise stated, experiments with *tert.*-butyl peroxide were carried out under nitrogen in a sealed tube heated at 120° for 48 hr., 0·5 mole of the peroxide being used per mole of the substance studied.

Ethyl β-Phenylpropionate.—The ester (15 g., 0·084 mole; b. p. 72°/1 mm., n_D^{24} 1·4930) and *tert.*-butyl peroxide (8·6 g., 0·058 mole) after 48 hr. at 120° gave, on distillation, (i) volatile material, (ii) unchanged ester (7·4 g.), and (iii) a viscous liquid (7·6 g.). A portion of this (1·2 g.) was evaporatively distilled, giving three fractions (bath-temp., *ca.* 200°/0·5 mm.) all crystallising and affording diethyl *meso*-ββ′-diphenyladipate (0·6 g.), needles (from ethanol), m. p. 113° (Found: C, 74·9; H, 7·4. Calc. for $C_{22}H_{26}O_4$: C, 74·6; H, 7·3%). There was an undistillable residue (0·6 g.). The adipate on hydrolysis with aqueous ethanolic potassium hydroxide gave the acid, needles (from ethanol), m. p. 269°. Oommen and Vogel [5] record m. p.s 114° and 270—271°, respectively.

β-Phenylpropionic Acid.—The product from this acid (10 g.) and *tert.*-butyl peroxide, after removal of volatile fractions and unchanged acid (b. p. 110—114°/0·7 mm.; 5·2 g.), gave on treatment with ether small quantities of *meso*-ββ′-diphenyladipic acid, m. p. and mixed m. p. 269° (*ca.* 0·15 g.), no other crystalline material being isolated. The bulk of the product was then esterified with ethanol (sulphuric acid) and evaporatively distilled, giving three fractions (bath at 170°, 210—220° and 240—250° respectively, at 0·7 mm.), none of which crystallised. When heated with the peroxide at 90° for 6 days, β-phenylpropionic acid (10 g.) gave unchanged material (7·8 g.), the above adipic acid (0·35 g.), and intractable oils.

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[13] Huang and Williams, unpublished work.

[14] Smith and Hoehn, *J. Amer. Chem. Soc.*, 1941, **63**, 1184.

β-*Phenylpropionitrile.*—The nitrile was prepared (*a*) by dehydration of the amide with phosphoric anhydride at 130—150° for 40 min., followed by extraction with benzene (57% yield) and (*b*) by benzylation of acetonitrile [15] by sodamide and benzyl chloride (20% yield). It had b. p. 74—76°/1 mm., n_D^{22} 1·5220 (Found: C, 82·7; H, 6·9. Calc. for C_9H_9N: C, 82·45; H, 6·9%). The product from this nitrile (11·0 g.) and the peroxide, after recovery of unchanged nitrile (5·4 g.) by distillation, was dissolved in benzene and adsorbed on alumina, and eluted by benzene followed by benzene–acetone (20 : 1), to give the following: (*a*) ββ'-diphenyladiponitrile, which crystallised from benzene in needles, m. p. 215° (0·25 g.) (Found: C, 83·1; H, 6·2. Calc. for $C_{18}H_{16}N_2$: C, 83·1; H, 6·15%); (*b*) an *isomer*, prisms (from benzene), m. p. 165° (0·10 g.) (Found: C, 83·25; H, 6·1. $C_{18}H_{16}N_2$ requires C, 83·1; H, 6·15%); and (*c*) intractable oils which appeared polymeric. Baker and Lapworth [8] report m. p. 212° for the adiponitrile. When the proportion of the peroxide was increased (to 1 : 1), there was a 20% recovery of nitrile and a small yield of the above adiponitrile of m. p. 215°, together with large quantities of polymer.

4-*Phenylbutan*-2-*one.*—The mixture from 4-phenylbutan-2-one (8·0 g.; prepared from ethyl α-benzylacetoacetate,[16] b. p. 66—68°/1 mm., n_D^{22} 1·5109) and *tert.*-butyl peroxide on cooling deposited 4 : 5-diphenyloctane-2 : 7-dione (0·7 g.) which was filtered off and after two recrystallisations from methanol melted at 160° (Found: C, 81·0; H, 7·5. Calc. for $C_{20}H_{22}O_2$: C, 81·6; H, 7·5%) (Dippy and Lewis [9] report m. p. 161°). The filtrate was distilled, giving volatile material, unchanged ketone (3·6 g.), and a viscous residue (3·7 g.). This residue on evaporative distillation afforded a fraction, b. p. 170—180° (bath)/0·7 mm., which in contact with methanol crystallised to give more of the dione, m. p. 160° (1·9 g.). The dione (0·13 g.), when refluxed with hydroxylamine hydrochloride (0·6 g.) in pyridine (4 c.c.) and ethanol (20 c.c.) for 4·5 hr., furnished the dioxime, m. p. 232° (from ethanol). Harries and Eschenbach [17] report m. p. 235—237°.

β-*Phenylpropiophenone.*—The mixture from this ketone (15 g.; m. p. 72°; prepared from benzylideneacetophenone by hydrogenation) and the peroxide was extracted with boiling ethanol. The solid which survived extraction was *meso*-1 : 3 : 4 : 6-tetraphenylhexane-1 : 6-dione (0·57 g.) and crystallised from benzene as needles, m. p. 269°, alone or mixed with a sample prepared by Finch and White's method [11] (Found: C, 86·6; H, 6·3. Calc. for $C_{30}H_{26}O_2$: C, 86·1; H, 6·2%) (lit., m. p. 269°,[11] 276° [12]). The ethanolic extract was concentrated in stages, and the solids which separated were collected, giving five crops of unchanged ketone (11·5 g.). Small quantities of a brown oil accompanied the fifth crop.

In another experiment in which more peroxide was used (1 : 1), β-phenylpropiophenone (18 g.) gave (after chromatography on alumina): unchanged ketone (4·1 g.), the 1 : 6-dione (0·4 g.), and polymer (13·6 g.).

Phenethyl Chloride.—The product from this chloride [18] (9·1 g.; b. p. 34°/1 mm., n_D^{23} 1·5285) and *tert.*-butyl peroxide, after removal of volatile material and unchanged chloride (5·0 g.), was a viscous liquid (4·1 g.) which in contact with benzene deposited crystals, probably 1 : 4-*dichloro*-2 : 3-*diphenylbutane*, m. p. 140—150° (0·4 g.) raised to 180° on recrystallisation from the same solvent from which it separated in stout needles (Found: C, 69·0; H, 5·7. $C_{16}H_{16}Cl_2$ requires C, 68·8; H, 5·7%). Chromatography of the filtrate yielded a further crop of the butane (0·26 g.). With less peroxide (10·4 g.) the same chloride (40 g.) after 24 hours' heating gave much unchanged material (32 g.) and a 13% yield of the butane derivative (m. p. 180°).

Dibenzyl.—The product from dibenzyl (10·0 g.) and *tert.*-butyl peroxide after removal, by distillation, of volatile material and unchanged dibenzyl (b. p. 82—84/0·5 mm.; 4·4 g.), gave a viscous liquid (5·6 g.) which, on dissolution in benzene–*cyclo*hexane and storage, deposited 1 : 2 : 3 : 4-tetraphenylbutane (2·1 g.). This crystallised from the above solvent mixture in needles, m. p. 179° (Found: C, 92·6; H, 7·2. Calc. for $C_{28}H_{26}$: C, 92·8; H, 7·2%). Smith and Hoehn [14] report m. p. 179—180°. The yield of tetraphenylbutane dropped when more peroxide was used.

Wohl–Ziegler Bromination of 1 : 2 : 3 : 4-*Tetraphenylbutane.*—The butane (0·5 g.) and *N*-bromosuccinimide in pure carbon tetrachloride (20 c.c.) were irradiated with a 100 w incandescent lamp under nitrogen until reaction was complete (30—40 min.). Succinimide

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[15] Chen and Barthel, *J. Amer. Chem. Soc.*, 1953, **75**, 4287.

[16] Bergström and Agostinho, *ibid.*, 1945, **67**, 2152.

[17] Harries and Eschenbach, *Ber.*, 1896, **29**, 380.

[18] Norris and Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 753.

was filtered off and the filtrate concentrated under partially reduced pressure, and the dibromo-compound which separated crystallised from *cyclo*hexane. Four such bromination experiments were carried out, as summarised in the annexed Table.

Mole of *N*-bromosuccimide used per mole of hydrocarbon	Irradiation (min.)	M. p. of dibromide obtained	Yield (%)	Found (%) * C	H	Br
1·5	30	181°	24	65·1	4·6	—
2	30	162—163,	36	—	—	30·0
		181	1	—	—	—
3	40	181	42	—	—	—
3	40	201	35	—	—	30·4

* $C_{28}H_{24}Br_2$ requires C, 64·6; H, 4·6; Br, 30·8%.

Dehydrobromination. The dibromide of m. p. 201° (0·3 g.) was refluxed with dimethylaniline for 15 min. under nitrogen. The mixture was poured into an excess of dilute hydrochloric acid, and the product taken up in ether, washed with aqueous sodium hydrogen carbonate, dried, and concentrated, to give small quantities of, probably, 1 : 2 : 3 : 4-tetraphenylbuta-1 : 3-diene which after one crystallisation from light petroleum had m. p. 177° (needles). Smith and Hoehn [14] record m. p. 182·5—183°. The dibromide of m. p. 181° on similar treatment gave an oil.

4-*Chlorodibenzyl.*—The mixture from 4-chlorodibenzyl [19] (25 g., m. p. 49°) and the peroxide in contact with light petroleum deposited, probably, 2 : 3-*di*-p-*chlorophenyl*-1 : 4-*diphenylbutane*, which was filtered off and crystallised from benzene in needles, m. p. 191° (0·12 g.) (Found: C, 77·8; H, 5·7. $C_{28}H_{24}Cl_2$ requires C, 77·9; H, 5·6%). The filtrate was concentrated, then adsorbed on alumina, and eluted with light petroleum, then light petroleum–benzene (35 fractions being collected), to give unchanged dibenzyl (10·5 g.), traces of the above butane, and intractable oils.

Microanalyses by Dr. W. Zimmermann, Melbourne.

University of Malaya, Singapore. [*Received, October* 14*th*, 1957.]

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[19] Bergman, Weizmann, and Shapiro, *J. Org. Chem.*, 1944, **9**, 408.