1248. *The Addition of Benzyl Radicals to Olefinic Systems*

By R. L. Huang, H. H. Lee, and (Miss) Lai-Yoong Wong

The addition of benzyl radicals at 140° to dec-1-ene, methyl crotonate, methyl ββ-dimethylacrylate, ethyl β-acetoacrylate, and methyl cinnamate gives the 1 : 1 adducts in yields of 37, 59, ~90, 16, and 10%, respectively, accompanied by telomers. *p*-Methylbenzyl radicals give similar results with dec-1-ene, and a 30% yield of the 1 : 1 adduct and its dehydrohalogeno-products with β-chlorostyrene. The orientation in each addition reaction is discussed in terms of (*a*) the relative stability of the intermediate radical, and (*b*) possible participation of a polar effect. Of these, the former appears to dominate.

Among addition reactions of radicals to olefinic double bonds, those involving benzyl radicals have hitherto received little attention. The few reports on this subject concern addition to alkenes,[1] chloroethylenes,[2] and maleic anhydride,[3] giving widely different yields of the 1 : 1 adducts. This work is a study of the addition of benzyl and/or *p*-methylbenzyl radicals to isolated as well as conjugated olefinic systems, including dec-1-ene, methyl crotonate, methyl ββ-dimethylacrylate, ethyl β-acetoacrylate, methyl cinnamate, and β-chlorostyrene. The results are summarised in the Table.

Addition of benzyl radicals to olefins

	Reactants in moles				Products in mmoles (% yield) *						
		Olefin							Dimers		
Olefin	Addend toluene	Initial	Con-sumed	Per-oxide	1 : 1 Adduct	2 : 1 Adduct	3 : 1 Adduct	Others	From addend (bibenzyl)	From 1 : 1 adduct (2 : 2 adduct)	Polymeric material (g.)
Dec-1-ene	1·4	0·24	0·052	0·026	16·6(33)	4·7(19)	2·5(15) † 6·9(42)		‡		3·0
	1·6	0·28	0·042	0·030	15·8(37)	5·6(27)	5·1(36) †		2·7		7·8
Methyl crotonate	2·7	0·35	0·12	0·027	23·8(20)	5·0(8)		3 : 2 Adduct 4·5(11)	Nil	9·3(16)	3
	3·8	0·076	0·035	0·0096	20·7(59)	1·7(10)				3·9(22)	0·5
Methyl ββ-dimethylacrylate	9·1	0·18	0·01	0·023	7 2 †				16		0·7
Ethyl β-acetoacrylate	3·9	0·078	0·078	0·0098	12·6(16)		5·7(22)	Ethyl cinnamate 6·6(8) Ethyl lævulate 10·9(14)	Nil		3·7
Methyl cinnamate	4·7	0·094	0·027	0·012	2·6(10)			1 : 2 Adduct 10·9(40) Stilbene 1·4(5·3)		0·6(4)	0·6
	Addend *p*-xylene								1,2-Di-(*p*-tolyl)ethane		
Dec-1-ene	1·1	0·18	‡	0·020	11·2	3·8	5·3 †		5·5		1·4
β-Chlorostyrene	1·1	0·19	0·14	0·020	5·7(5·5) 24·5(24) §					5·8(11)	4·0

* % Yield of crude based on olefin consumed. † Dehydro-product. ‡ Quantitative estimation not attempted. § Dehydrohalo-product.

Addition of benzyl radicals (from toluene and di-t-butyl peroxide at 140°) to dec-1-ene gave the 1 : 1 adduct (I) in 37% yield, as well as the telomeric 2 : 1 and 3 : 1 adducts (II) and (III), and/or their dehydro-derivatives, in comparable quantities (see Table), indicating a relatively inefficient transfer step. That the addition step was similarly not easy is shown by the isolation of bibenzyl. Addition of *p*-methylbenzyl radicals (from *p*-xylene and the peroxide) to the same olefin afforded the corresponding 1 : 1, 2 : 1, and 3 : 1 adducts in much the same molar ratio. More of the dimer, di-(*p*-tolyl)ethane, however, was formed, probably because of increased stability, and hence diminished additive capacity, of the radical.

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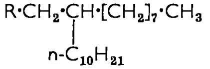
[1] G. I. Nikishin, V. D. Vorb'ev, and A. D. Petrov, *Doklady Akad. Nauk S.S.S.R.*, 1960, **130**, 1256.
[2] L. Schmerling and J. P. West, *J. Amer. Chem. Soc.*, 1953, **75**, 6216.
[3] H. Shechter and H. C. Barker, *J. Org. Chem.*, 1956, **21**, 1473.

Methyl crotonate gave a much higher yield (59%) of the 1 : 1 adduct (IV) accompanied by considerably less telomers, and no bibenzyl. The formation of the 2 : 2 adduct (V) (the structure of which is based on physical properties and elemental analysis), is of interest, as it suggests that the intermediate radical (VI), compared with the corresponding radical from dec-1-ene, is less inclined, probably owing to steric reasons, to add to another molecule of the olefin, but prefers to dimerise. That the 1 : 1 adduct (IV) was not contaminated by the isomeric ester (VII) was established as follows: The adduct was hydrolysed to the acid, which was purified through its amide, and reconverted into the ester with diazomethane. The purified acid, as well as the ester derived from it, had infrared absorption identical with that of the 1 : 1 adduct and that of the acid obtained therefrom. The isomeric ester (VII) was then synthesised by standard methods, and found to possess an infrared spectrum distinctly different from that of the adduct. It is therefore concluded that addition of the benzyl radical to methyl crotonate proceeded predominantly, if not entirely, by attack on the β-carbon atom to generate the radical (VI).

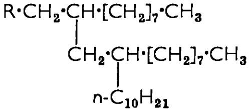
$\mathrm{R{\cdot}CH_2{\cdot}CH_2{\cdot}[CH_2]_7{\cdot}CH_3}$

(I)



$\mathrm{R{\cdot}CH_2{\cdot}\underset{n\text{-}C_{10}H_{21}}{\underset{|}{C}H}{\cdot}[CH_2]_7{\cdot}CH_3}$

(II)



$\mathrm{R{\cdot}CH_2{\cdot}\underset{CH_2{\cdot}\underset{n\text{-}C_{10}H_{21}}{\underset{|}{C}H}{\cdot}[CH_2]_7{\cdot}CH_3}{\underset{|}{C}H}{\cdot}[CH_2]_7{\cdot}CH_3}$

(III)

$\mathrm{CH_3{\cdot}CHR{\cdot}CH_2{\cdot}CO_2Me}$

(IV)

$\mathrm{[CH{\cdot}_3\overset{|}{C}HR{\cdot}CH{\cdot}CO_2Me]_2}$

(V)

$\mathrm{CH_3{\cdot}CHR{\cdot}\dot{C}H{\cdot}CO_2Me}$

(VI)

$\mathrm{CH_3{\cdot}CH_2{\cdot}CHR{\cdot}CO_2Me}$

(VII)

$\mathrm{Me_2CH{\cdot}CHR{\cdot}CO_2Me}$

(VIII)

$\mathrm{Me_2C{=}CHR{\cdot}CO_2Me}$

(IX)

$\mathrm{Me_2\dot{C}{\cdot}CHR{\cdot}CO_2Me}$

(X)

$\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CHR{\cdot}CO_2Et}$

(XI)

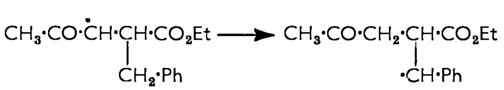
$\mathrm{CH_3{\cdot}CO{\cdot}CHR{\cdot}CH_2{\cdot}CO_2Et}$

(XII)

$\mathrm{R = Ph{\cdot}CH_2}$

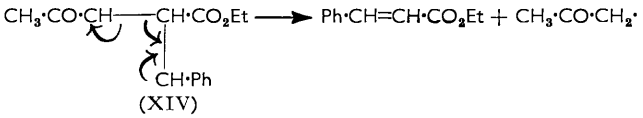
Addition of free benzyl to methyl ββ-dimethylacrylate proceeded very sluggishly, as evidenced by a recovery of over 95% of the acrylate and isolation of large quantities of bibenzyl. The product consisted of the adduct (VIII) and its dehydro-derivative (IX), which arose probably through disproportionation of the intermediate radical (X), the inadequacy of which in abstracting α-hydrogen atoms from toluene is understandable. The addition to the α-carbon atom here, in contrast with the orientation in methyl crotonate, seems best explained on steric grounds.

Ethyl β-acetoacrylate was, among the olefins studied, the only one which was completely consumed in the reaction, no trace of bibenzyl being found. The 1 : 1 adduct, however, was isolated only in 16% yield, and appeared to be mainly compound (XI), possibly admixed with a little of the isomeric (XII). Telomeric products were formed to a very large extent, including what is probably a 3 : 1 adduct (22%). A product of interest is ethyl cinnamate, the formation of which might have arisen by an intramolecular hydrogen abstraction in the radical (XIII), followed by disproportionation, as follows:



$$\mathrm{CH_3{\cdot}CO{\cdot}\dot{C}H{\cdot}\underset{CH_2{\cdot}Ph}{\underset{|}{C}H}{\cdot}CO_2Et \longrightarrow CH_3{\cdot}CO{\cdot}CH_2{\cdot}\underset{\dot{C}H{\cdot}Ph}{\underset{|}{C}H}{\cdot}CO_2Et}$$

(XIII) (XIV)



$$\mathrm{CH_3{\cdot}CO{\cdot}CH{-}\underset{\dot{C}H{\cdot}Ph}{\underset{|}{C}H}{\cdot}CO_2Et \longrightarrow Ph{\cdot}CH{=}CH{\cdot}CO_2Et + CH_3{\cdot}CO{\cdot}CH_2{\cdot}}$$

(XIV)

From the addition to methyl cinnamate the major product (40% yield) was the 1 : 2 adduct (XV), the 1 : 1 adduct (XVI) being formed to the extent of 10% only. Also isolated was a 2 : 2 adduct (4%), considered to be the adipate (XVII), and stilbene. The latter is probably derived in part at least, from bibenzyl since it has been shown that stilbene is formed when (*a*) benzyl radicals are generated in the presence of bibenzyl,[4] and (*b*) bibenzyl is heated with di-t-butyl peroxide under the same conditions (stilbene being detected spectroscopically). The complete absence of the isomeric 1 : 1 adduct (XVIII) constitutes strong evidence for the addition having taken place predominantly, if not solely, *via* the radical intermediate (XIX), and hence also support for the structure assigned to the 2 : 2 adduct above. The relatively high yield of the 1 : 2 adduct (XV), no doubt resulting from combination of the radical (XIX) with a benzyl radical, strongly suggests that both these radicals were present in considerable concentration, and this in turn indicates that both (*a*) the addition of free benzyl to the cinnamate, and (*b*) abstraction of hydrogen atoms from toluene by the radical (XIX), were relatively inefficient processes.

$\mathrm{Ph{\cdot}CHR{\cdot}CHR{\cdot}CO_2Me}$
(XV)

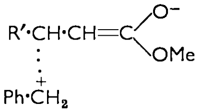
$\mathrm{Ph{\cdot}CH_2{\cdot}CHR{\cdot}CO_2Me}$
(XVI)

$\mathrm{[Ph{\cdot}\overset{|}{C}H{\cdot}CHR{\cdot}CO_2Me]_2}$
(XVII)

$\mathrm{Ph{\cdot}CHR{\cdot}CH_2{\cdot}CO_2Me}$
(XVIII)

$\mathrm{Ph{\cdot}\dot{C}H{\cdot}CHR{\cdot}CO_2Me}$
(XIX)

The addition of aldehydes and bromotrichloromethane to the above, and other olefinic systems, has been investigated by one of us, who, on the assumption that the predominant factor controlling the course of the reaction is the relative stability of the radical intermediate, arrived at a scale of relative stabilising capacities of substituent groups as follows: $\mathrm{Ph > CO \sim CN > CO_2Et \sim CO_2H > Me > H}$.[5] The results now obtained appear consistent with this scale. Although the above assumption finds support in a recent study on the addition of bromotrichloromethane to stilbene,[6] the participation of polar transition states has, in the case of the addition of aliphatic aldehydes and alcohols, been invoked to explain the superior yields with conjugated, as compared with isolated, olefinic double bonds.[7] A similar polar effect would account for the addition of benzyl radicals (which may also be considered electrondonating) [8] being more readily achieved with the chloroethylenes and maleic anhydride than with dec-1-ene and hex-1-ene. The relative facility with which methyl crotonate adds could then be due to polar transition states such as (XX) reinforcing the overall directive effect due to the stabilising influence of the ester group (since $\mathrm{CO_2Et > Me}$). In methyl cinnamate, however, these effects are in opposition, the stabilising factor favouring addition at the α-carbon atom (since $\mathrm{Ph > CO_2Et}$), while transition states such as (XXI) are activating the β-carbon atom. The result of the addition shows that here the former factor predominates. The question thus arose as to whether, in a system in which polar effects are intensified, the situation might be reversed. One such system chosen for study was the addition of *p*-methylbenzyl radicals to β-chlorostyrene. This was found to proceed, with evolution of much hydrogen chloride and formation of


(XX) R′ = Me
(XXI) R′ = Ph

$\mathrm{Ph{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}Ar}$
(XXII)

$\mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}Ar}$
(XXIII)

($\mathrm{Ar} = p\text{-}\mathrm{Me{\cdot}C_6H_4}$)

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[4] R. L. Huang, H. H. Lee, and M. S. Malhotra, *J.*, 1964, 5951.
[5] R. L. Huang, *J.*, (*a*) 1956, 1749; (*b*) 1957, 1342.
[6] J. I. G. Cadogam, E. G. Duell, and P. W. Inward, *J.*, 1962, 4164.
[7] T. M. Patrick, jun., *J. Org. Chem.*, 1952, **17**, 1009, 1269; J. D. LaZerte and R. J. Moshar, *J. Amer. Chem. Soc.*, 1955, **77**, 910.
[8] Cf. R. L. Huang and H. H. Lee, *J.*, 1964, 2500.

polymer, to give a mixture consisting of the 1 : 1-adduct (XXII) and its dehydrochlorinated products (30% yield) as indicated by ultraviolet spectroscopy, and by its oxidation to benzoic and toluic acids, and conversion in two steps into the straight-chain hydrocarbon (XXIII), identified by comparison of infrared absorption with that of a specimen synthesised by standard methods. It is believed that the evolution of hydrogen chloride arose, in part at least, from the occurrence of a chain reaction involving atomic chlorine, generated from the intermediate radical (XXV) in a manner for which analogies [9] are known:

$$\underset{\text{(XXV)}}{\text{Ph}\cdot\dot{\text{C}}\text{H}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{Ar}} \longrightarrow \text{Ph}\cdot\text{CH}{=}\text{CH}\cdot\text{CH}_2\cdot\text{Ar} + \text{Cl}\cdot$$

$$\text{Ar}\cdot\text{CH}_3 + \text{Cl}\cdot \longrightarrow \text{Ar}\cdot\text{CH}_2\cdot + \text{HCl}$$

EXPERIMENTAL

Melting points were taken on a Kofler micro-hot stage apparatus. Infrared spectra were determined in carbon tetrachloride solution with a Hilger and Watts model H 800 spectrophotometer and ultraviolet spectra in ethanolic solution with a Hilger and Watts " Uvispek." Petroleum refers to a fraction of b. p. 60—80°. Microanalyses were carried out by Dr. W. Zimmermann (Melbourne) and Mrs. H. K. Tong (Singapore).

General Procedure.—A solution of the olefin and di-t-butyl peroxide in the addend was sealed under pure nitrogen in 4—7 Carius tubes and heated at 140° ± 2° for 16 hr. In one of the experiments (addition of *p*-xylene to dec-1-ene) quantitative estimation by infrared spectroscopy of the acetone and t-butyl alcohol produced indicated complete decomposition of the peroxide.

Addition of Toluene to Dec-1-*ene.*—(*a*) The reaction mixture from dec-1-ene (33·8 g., 0·24 mole) and di-t-butyl peroxide (3·84 g., 0·026 mole), in toluene (129 g., 1·4 mole), after removal of volatile products and unreacted olefin (b. p. 64°/30 mm.—55°/0·25 mm., found by infrared spectroscopy to contain 0·19 mole of dec-1-ene) was fractionated, giving the following: (i) 1-*phenylundecane* (3·85 g.) which after redistillation had b. p. 95—100° (bath)/0·02 mm., (1·7 g.), n_D^{23} 1·4783, $\nu_{max.}$ 693 cm.$^{-1}$ [Found: C, 87·55; H, 12·3%; *M* (Rast), 259. $C_{17}H_{28}$ requires C, 87·9; H, 12·1%; *M*, 232]; (ii) 9-*phenethylnonadecane* (1·76 g.) which after redistillation had b. p. 120° (bath)/0·02 mm. (1·4 g.), n_D^{22} 1·4544, $\nu_{max.}$ 693 cm.$^{-1}$ [Found: C, 86·9; H, 13·8%; *M* (Rast), 349. $C_{27}H_{48}$ requires C, 87·0; H, 13·0%; *M*, 373]; (iii) 11-*n-octyl*-13-*phenethylheneicosene* (1·26 g.) which, redistilled, had b. p. 190° (bath)/0·02 mm., and $n_D^{22\cdot4}$ 1·4794 [Found: C, 87·3; H, 13·05%; *M* (Rast), 479. $C_{37}H_{66}$ requires C, 87·0; H, 13·0%; *M*, 511]; (iv) 11-*n-octyl*-9-*phenethylheneicosane* (3·52 g.), which after purification by distillation boiled at 210° (bath)/0·02 mm. (3·0 g.), and had n_D^{22} 1·4846 [Found: C, 86·5; H, 13·1%; *M* (Rast) 589. $C_{37}H_{68}$ requires C, 86·6; H, 13·4%; *M*, 513]; and (v) a viscous yellow residue (3·03 g.), n_D^{22} 1·4854.

(*b*) In a second experiment the products were fractionated using a 12 in. Nester–Faust spinning-band column, bibenzyl (0·48 g.) being isolated in addition to the products named above (see Table).

Addition of p-*Xylene to Dec*-1-*ene.*—The products from dec-1-ene (25·0 g.), *p*-xylene (113 g.) and di-t-butyl peroxide (2·9 g.) were (i) 1,2-di(*p*-tolyl)ethane, b. p. 134—140°/0·6 mm. (2·56 g.), m. p. 80—83° alone or mixed with an authentic sample prepared by the method of Cram and Steinburg,[10] which also showed an identical infrared spectrum; (ii) 1-(p-*tolyl*)*undecane* (2·8 g.) which after redistillation possessed b. p. 95—100°/0·02 mm., $n_D^{22\cdot5}$ 1·4837, $\nu_{max.}$ 710 cm.$^{-1}$ [Found: C, 88·0; H, 12·4%; *M* (Rast), 281. $C_{18}H_{30}$ requires C, 87·7; H, 12·3%; *M*, 246]; (iii) 11-(p-*methylphenethyl*)*nonadecene* (1·45 g.) which, redistilled, had b. p. 185—190°/0·02 mm. (1·0 g.), n_D^{22} 1·4912, $\nu_{max.}$ 1619 and 711 cm.$^{-1}$ [Found: C, 87·4; H, 12·5%; *M* (Rast), 436. $C_{28}H_{48}$ requires C, 87·4; H, 12·6%; *M*, 385. $C_{28}H_{50}$ requires C, 87·0; H, 13·0%; *M*, 387]; (iv) 13-(p-*methylphenethyl*)-11-(*n-octyl*)*heneicosene* (2·6 g.) which, redistilled, boiled at 200—210°/0·02 mm. (2·0 g.) n_D^{22} 1·4936, $\nu_{max.}$ 1619 and 714 cm.$^{-1}$ [Found: C, 87·4; H, 12·4%; *M* (Rast), 517.

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[9] *Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, 199; F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, 1941, **6**, 479; see *Quart. Rev.*, 1956, **10**, 330.

[10] D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, 1951, **73**, 5691.

$C_{38}H_{68}$ requires C, 86·9; H, 13·1%; *M*, 525. $C_{38}H_{66}$ requires C, 87·3; H, 12·7%; *M*, 523]; and (v) a glassy residue (1·35 g.).

Addition of Toluene to Methyl Crotonate.—The reaction mixture from the ester (35·1 g.), toluene (253 g.), and the peroxide (4·0 g.), after removal of volatile material, was fractionated through a 12 in. Nester–Faust spinning-band column to give unchanged crotonate (0·23 mole, by infrared spectroscopy) and the following liquid fractions: (i) b. p. 47—57°/0·3 mm., (0·80 g.), (ii) b. p. 60—69·5°/0·2 mm., (4·50 g.), (iii) b. p. 75—85°/0·2 mm. (1·03 g.), (iv) b. p. 80—97°/0·15 mm. (1·47 g.), (v) b. p. *ca.* 200°/0·15 mm. (5·72 g.), and (vi) a residue (3 g.).

Fraction (i) was shown by infrared spectroscopy to be largely methyl 3-benzyl-n-butyrate, as in (ii). Fraction (ii) was shown to be almost pure methyl 3-benzyl-n-butyrate (uncontaminated by the isomeric 2-benzyl-n-butyrate or by dibenzyl) as follows: A portion (1·5 g., n_D^{21} 1·4891) was saponified with 10% methanolic sodium hydroxide and the acid so obtained purified by distillation, b. p. 110° (bath)/0·35 mm. (0·85 g.), n_D^{21} 1·5104 (lit.,[11] b. p. 152—153/5 mm., n_D^{25} 1·5106), $\nu_{max.}$ 3050, 2955, 2660, 1708, 1379, 694 cm.$^{-1}$, and identified through the amide, m. p. 80—81° (lit.,[12] 83°), and the anilide, m. p. 102—103° (Found: C, 80·3; H, 7·6. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·6%). Its infrared spectrum, compared with that of the isomeric 2-benzyl-n-butyric acid (prepared as described below), indicated complete freedom from contamination by the latter acid. A mixture of the anilides of the two acids melted at 69—76°. A pure sample of 3-benzyl-n-butyric acid was then prepared by alkaline hydrolysis of the amide obtained as described above. This showed infrared absorption identical with that of the material obtained earlier by saponification of the ester in fraction (ii), and when esterified with diazomethane gave a methyl ester, b. p. 75° (bath)/0·3 mm. n_D^{23} 1·4936 (lit.,[11] b. p. 255—257°, n_D^{25} 1·4935), $\nu_{max.}$ 1735, 1370, and 693 cm.$^{-1}$ (Found: C, 74·75; H, 8·5. Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·4%), the infrared absorption of which was identical with that of fraction (ii) but distinctly different, especially in the 1400—900 cm.$^{-1}$ region, from that of the isomeric methyl 2-benzyl-n-butyrate (prepared as described below).

Redistillation of fraction (iii) gave a sample, b. p. 70—75° (bath)/0·3 mm., n_D^{22} 1·4905, which based on its infrared spectrum was methyl 3-benzyl-n-butyrate contaminated with an unknown unsaturated ester, $\nu_{max.}$ 1737, 1660, 1369, and 693 cm.$^{-1}$. Fraction (iv) on redistillation afforded *dimethyl* 4-*benzyl*-2-*methylpentane*-1,3-*dicarboxylate* in the form of a very viscous liquid, b. p. 170—175° (bath)/0·3 mm., n_D^{22} 1·5073, $\nu_{max.}$ 1737, 1381, 1363, and 693 cm.$^{-1}$ [Found: C, 69·0; H, 8·2%; *M* (Rast), 241. $C_{17}H_{24}O_4$ requires C, 69·8; H, 8·3%; *M*, 292]. Fraction (v) was separated by redistillation into two fractions (*a*) b. p. 200° (bath)/0·15 mm. (3·55 g.), $n_D^{22·5}$ 1·5173, and (*b*) b. p. 210° (bath)/0·15 mm. (2·17 g.) $n_D^{22·5}$ 1·5188. Distillation of (*a*) gave *dimethyl* 1,4-*dibenzyl*-2-*methylpentane*-1,3-*dicarboxylate* (or an isomer thereof), b. p. 190° (bath)/0·2 mm. (Found: C, 75·1; H, 8·1. $C_{24}H_{30}O_4$ requires C, 75·4; H, 7·9%). A portion of (*a*) was saponified to the *acid*, b. p. 190—200° (bath)/0·3 mm., $\nu_{max.}$ 2963, 2652, 1707, and 694 cm.$^{-1}$. [Found: C, 74·8; H, 7·3%; *M* (Rast), 368. $C_{22}H_{26}O_4$ requires C, 74·55; H, 7·4%; *M*, 354]. Distillation of (*b*) gave *trimethyl* 1,6-*dibenzyl*-2,4-*dimethylheptane*-1,3,5-*tricarboxylate* (or an isomer thereof), b. p. 195° (bath)/0·2 mm., $n_D^{22·5}$ 1·5172 [Found: C, 72·3; H, 8·3%; *M* (Rast), 475. $C_{29}H_{38}O_6$ requires C, 72·2; H, 7·9%; *M*, 483].

In another experiment using a 50-mole excess of toluene over the crotonate, a 59% yield of methyl 3-benzyl-n-butyrate was realised (see Table).

Preparation of 2-Benzyl-n-butyric Acid.—α-Ethylcinnamic acid prepared in 34% yield by heating benzaldehyde (26·5 g.), n-butyric anhydride (47·5 g.), and fused sodium butyrate (27·5 g.)[13] at 130—135° for 40 hr. (m. p. 105—106°, $\nu_{max.}$ 2978, 2622, 1681, 1626, and 689 cm.$^{-1}$), was hydrogenated in ethanol over platinum oxide to give the required acid, b. p. 100—105° (bath)/0·25 mm., n_D^{23} 1·5082, $\nu_{max.}$ 3040, 2965, 2660, 1707, and 693 cm.$^{-1}$. The anilide had m. p. 89·5—91° (lit.,[14] b. p. for acid: 180°/8 mm., m. p. for anilide 89°, 90°). Treatment with diazomethane gave the methyl ester, b. p. 80—85° (bath)/0·3 mm., n_D^{23} 1·4902, $\nu_{max.}$ 1735, 1360, 1008, and 693 cm.$^{-1}$ (Found: C, 74·6; H, 8·8. Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·4%).

Addition of Toluene to Methyl ββ-*Dimethylacrylate.*—The product from the acrylate (20·5 g.), peroxide (3·3 g.), and toluene (834 g.), after removal of volatile fractions and unchanged acrylate

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[11] K. B. Wiberg and T. W. Hutton, *J. Amer. Chem. Soc.*, 1956, **78**, 1640.

[12] J. F. Lane, J. Willenz, A. Weissberger, and E. S. Wallis, *J. Org. Chem.*, 1940, **5**, 276.

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($\nu_{max.}$ 1146 cm.$^{-1}$, ε 763), was distilled to give the following fractions: (i) b. p. 81—84°/0·4 mm. (2·86 g.); (ii) b. p. 84—85°/0·4 mm. (0·89 g.); (iii) b. p. 85—89°/0·4 mm. (1·19 g.); and (iv) a residue (0·66 g.). Each of these was hydrolysed with 10% methanolic sodium hydroxide giving a neutral and an acidic component. The neutral material was in each case bibenzyl (m. p. and mixed m. p.), whilst the acidic component was α-isopropylhydrocinnamic acid in fraction (i), a mixture of this acid and α-isopropylidenehydrocinnamic acid in (ii), α-isopropylidenehydrocinnamic acid in (iii), and a high-boiling acid in (iv). The total yields of these products are given in the Table. Characterisation of the acids was carried out as follows:

(*a*) α-Isopropylhydrocinnamic acid had b. p. 107—110°/0·3 mm., n_D^{23} 1·5078 (lit.,[15] b. p. 117—120°/0·1 mm., n_D^{22} 1·5052), $\nu_{max.}$ 3037, 2963, 2667, 1707, and 693 cm.$^{-1}$ (Found: C, 75·2; H, 8·45. Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·4%). Its amide had m. p. 94·5—95·5° (lit.,[16] 94—95°; reported [17] for the isomeric β-benzylisobutyric acid amide, m. p. 117°) (Found: C, 75·5; H, 8·8. Calc. for $C_{12}H_{17}ON$: C, 75·35; H, 9·0%). Treatment with diazomethane gave the methyl ester, b. p. 65—70°/0·3 mm., $n_D^{22\cdot5}$ 1·4924, $\nu_{max.}$ 1734 (ε 402), 1369, 1152, and 693 cm.$^{-1}$ (Found: C, 75·75; H, 8·9. Calc. for $C_{13}H_{18}O_2$: C, 75·7; H, 8·8%).

(*b*) α-Isopropylidenehydrocinnamic acid, b. p. 125—130°/0·3 mm., $n_D^{21\cdot5}$ 1·5312, $\nu_{max.}$ 3022, 2956, 2652, 1700, and 1641 cm.$^{-1}$. $\lambda_{max.}$ 208—209 mμ (log ε 4·15), was hydrogenated in presence of 30% palladised charcoal to the saturated acid, identical in infrared absorption with the acid in (*a*) above. Ultraviolet absorption reported for crotonic acid,[18] $\lambda_{max.}$ 204 mμ, log ε 4·07, and for cinnamic acid,[19] $\lambda_{max.}$ 273 mμ, log ε 4·32.)

Addition of Toluene to Ethyl β-*Acetoacrylate*.—The acrylate, prepared [5a] by bromination of ethyl laevulate (1 mole) with bromine (1 mole) at 0° in ether, followed by dehydrobromination with potassium acetate in acetic acid at 100°, had b. p. 49—52°/0·3 mm., $n_D^{21\cdot5}$ 1·4473, $\lambda_{max.}$ 221 mμ (log ε 4·10). (It is not known whether this product contained any unchanged laevulate, as the ultraviolet absorption of the pure acrylate has not been reported, although another preparation using a 25% excess of bromine gave a product with exactly the same physical properties. The isolation of ethyl laevulate in the products of the addition reaction, however, suggests that the acrylate contained about 11% of the laevulate.) The reaction mixture from the acrylate (11·1 g.), toluene (361 g.), and peroxide (1·43 g.) was fractionated to give the following products (no acrylate being recovered). (i) Ethyl laevulate, b. p. 115—121°/30 mm., $n_D^{21\cdot5}$ 1·4222, identified by comparison of its infrared absorption ($\nu_{max.}$ 1726 and 1373 cm.$^{-1}$) with that of an authentic sample. (ii) Ethyl cinnamate, b. p. 80° (bath)/0·03 mm., identified by comparison of its infrared and ultraviolet spectra ($\nu_{max.}$ 1718, 1640, 986, 979, and 706 cm.$^{-1}$, and $\lambda_{max.}$ 277, log ε 4·30) with those of an authentic sample, and by alkaline hydrolysis to cinnamic acid (m. p. and mixed m. p., and infrared absorption). (iii) A 1 : 1 adduct, composed mainly of ethyl α-benzyl-laevulate, b. p. 106—107° (bath)/0·02 mm., n_D^{22} 1·4970, $\nu_{max.}$ 1725, 1376, 1367, 1354, and 695 cm.$^{-1}$ (Found: C, 71·8; H, 7·8. Calc. for $C_{14}H_{18}O_3$: C, 71·8; H, 7·7%). Saponification with 7% ethanolic sodium hydroxide gave α-benzyl-laevulic acid, b. p. 120—123° (bath)/0·02 mm., which, after sublimation and crystallisation, had m. p. 52—92°, and infrared spectrum identical with that of an authentic sample (see below) except for the relative intensities of some weak bands. The phenylhydrazone of the acid, after eight recrystallisations, had m. p. and mixed m. p. 136—139° (Found: C, 72·6; H, 6·65; N, 9·4. Calc. for $C_{18}H_{20}N_2O_2$: C, 72·95; H, 6·8; N, 9·45%). (iv) A *triester*, probably a 3 : 1 adduct, b. p. 137—140°/0·02 mm., n_D^{23} 1·4885, $\nu_{max.}$ 1730, 1367, 1355, and 693 cm.$^{-1}$ (Found: C, 64·4; H, 7·5. $C_{28}H_{38}O_9$ requires C, 64·85; H, 7·4%), which appears to undergo partial decomposition on distillation. No bibenzyl could be detected (spectroscopically) among the reaction products. The authentic sample of α-benzyl-laevulic acid was prepared from 5-benzylbarbituric acid and bromoacetone followed by hydrolysis with sodium hydroxide,[20] m. p. 64·5—66·5°, $\nu_{max.}$ 3040, 2930, 2680, 1711, and 696 cm.$^{-1}$ (Found: C, 69·6; H, 6·9. Calc. for $C_{12}H_{14}O_3$: C, 69·9; H, 6·8%), phenyl hydrazone, m. p. 136—138° (decomp. on standing).

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Addition of Toluene to Methyl Cinnamate.—The reaction mixture from the cinnamate (15·2 g.), toluene (432 g.), and the peroxide (1·71 g.) was distilled to remove unreacted toluene and cinnamate (10·8 g.). Infrared absorption of the latter indicated presence of stilbene ($\nu_{max.}$ 959 cm.$^{-1}$). This was isolated on hydrolysis and removal of cinnamic acid, and identified (12 mg., from a 2·2 g. sample, m. p. and mixed m. p.). The residue from the distillation was triturated with ether, and a white solid (0·34 g.) which precipitated was filtered off (see below). The filtrate was concentrated and distilled, giving the following fractions. (i) A liquid, b. p. 124—162°/0·15 mm. (0·83 g.), $n_D^{23\cdot5}$ 1·5515, $\nu_{max.}$ 1737, 1641, and 693 cm.$^{-1}$, which on hydrolysis with 10% methanolic sodium hydroxide yielded stilbene (35 mg.), and dibenzylacetic acid, b. p. 137—140° (bath)/0·02 mm. (626 mg.), m. p. 85—89°, identified by comparison of its infrared absorption with that of an authentic specimen (synthesised *via* diethyl dibenzylmalonate) [21] and through the amide, m. p. and mixed m. p. 125—128° (Found: C, 80·2; H, 7·35; N, 5·4. Calc. for $C_{16}H_{17}ON$: C, 80·3; H, 7·2; N, 5·85%). Diazomethane converts the acid into the methyl ester, b. p. 125—130° (bath)/0·3 mm., $n_D^{20\cdot5}$ 1·5468 (Found: C, 80·0; H, 7·1. Calc. for $C_{17}H_{18}O_2$: C, 80·3; H, 7·1%) which has an infrared spectrum identical with that of a synthetic sample. (ii) A liquid b. p. 162—200°/0·15 mm. (4·04 g.), $\nu_{max.}$ 1739 and 693 cm.$^{-1}$, which on hydrolysis afforded stilbene (164 mg.), and αβ-*dibenzylhydrocinnamic acid* (3·64 g., in the form of a glass. Repeated precipitation from a dilute alkaline solution with hydrochloric acid gave the acid as an amorphous powder, m. p. 99—102°, $\nu_{max.}$ 3022, 2939, 2652) 1705, and 693 cm.$^{-1}$ (Found: C, 79·2, 79·2; H, 6·5, 6·7%; Equiv. 379, 378. $C_{23}H_{22}O_2,H_2O$ requires C, 79·3; H, 6·9%; *M*, 348). (iii) A viscous residue (0·6 g.).

The white solid obtained as described above was recrystallised from ethanol-benzene, giving *dimethyl* 2,5-*dibenzyl*-3,4-*diphenyladipate*, m. p. 257—258°, $\nu_{max.}$ 1737 cm.$^{-1}$ (Found: C, 80·7; H, 6·9. $C_{34}H_{34}O_4$ requires C, 80·6; H, 6·8%). Saponification gave the adipic acid which was amorphous and insoluble in the usual solvents, and was purified by repeated precipitation from an alkaline solution, m. p. 353—357° (Found: C, 78·8; 78·6; H, 6·5, 6·6. Calc. for $C_{32}H_{30}O_4,\frac{1}{2}H_2O$; C, 78·5; H, 6·8%). In another addition experiment in which the addend : olefin ratio was reduced to 10 : 1 a lower yield of the 1 : 1 adduct (4%) was obtained.

Addition of p-*Xylene to* β-*Chlorostyrene.*—A mixture of β-chlorostyrene (25·9 g.), di-t-butyl peroxide (2·86 g.), and *p*-xylene (112 g.) was refluxed (138—143°) for 16 hr., hydrogen chloride being evolved during this period. Fractional distillation removed unreacted xylene and chlorostyrene (11·5 g.) and gave the following fractions. (1) A liquid, b. p. 140°/0·2 mm. (6·4 g.) $\nu_{max.}$ 1648, 962, 686 cm.$^{-1}$, $\lambda_{max.}$ 254 mμ ($\varepsilon^{1\%}_{1\,cm.}$ 850) (Found: C, 89·9; H, 7·4; Cl, 2·9. Calc. for $C_{16}H_{17}Cl$: C, 78·5; H, 7·0; Cl, 14·5%. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7; Cl, 0%), which as shown by the chlorine content and the degradative studies described below, consists of approx. 20% of 2-chloro-1-phenyl-3-(*p*-tolyl)propane and 80% of 3-phenyl-1-(*p*-tolyl)prop-1-ene and/or 1-phenyl-3-(*p*-tolyl)prop-1-ene. (ii) A viscous liquid, b. p. 180°/0·55 mm. (2·4 g.), $\nu_{max.}$ 962 and 686 cm.$^{-1}$, which liberates hydrogen chloride on standing. (iii) A residue (4 g.).

A portion of fraction (i) (above) (0·23 g.) in pyridine (5 c.c.) was added to an aqueous pyridine solution (80 c.c.) containing sodium metaperiodate and potassium permanganate [22] and the mixture set aside at room temperature (28°) for 48 hr. with occasional shaking. Continual extraction with ether (100 c.c.) for 20 hr., followed by isolation with aqueous sodium hydrogen carbonate, then afforded (*a*) starting material (identified by infrared spectrum), (*b*) benzoic acid, m. p. and mixed m. p. 118—120°, and (*c*) *p*-toluic acid, m. p. and mixed m. p. 177°, the acids being separated by recrystallisation from water. Another portion (0·52 g.) of (i) on hydrogenation over 30% palladised charcoal gave a product (0·4 g.) which contained chlorine (1·2%) and was treated with a solution of sodium (0·5 g.) in ethanol (20 c.c.) at room temperature (40 hr. standing). The product so obtained was then hydrogenated, giving 1-phenyl-3-(*p*-tolyl)propane, b. p. 95° (bath)/0·35 mm., n_D^{22} 1·5508 [Found: C, 91·3; H, 8·7%; *M* (Rast), 196. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%; *M*, 210], the infrared absorption of which ($\nu_{max.}$ 2920, 2865, 1605, 695 cm.$^{-1}$) was identical with that of an authentic sample (see below).

A portion (0·5 g.) of fractions (ii), after treatment with sodium ethoxide and hydrogenation as above, gave a glassy product, probably 3,4-diphenyl-1,6-di-(*p*-tolyl)hexane or an isomer thereof, b. p. 140° (bath)/0·35 mm., $\nu_{max.}$ 686 cm.$^{-1}$ [Found: C, 91·05; H, 8·2%; *M* (Rast), 422. Calc. for $C_{32}H_{34}$. C, 91·8; H, 8·2%; *M*, 419].

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Preparation of 1-*phenyl*-3-(p-*tolyl*)*propane*.[23]—4′-Methylchalcone (prepared from tolualdehyde and acetophenone), m. p. 94—95°, $\nu_{max.}$ 1666 and 982 cm.$^{-1}$, was reduced with sodium borohydride to give 3-phenyl-1-(*p*-tolyl)prop-1-en-3-ol, b. p. 158°/0·6 mm., n_D^{22} 1·5573, $\nu_{max.}$ 3414, 1648, and 970 cm.$^{-1}$, which was then hydrogenated over platinum oxide to 1-phenyl-3-(*p*-tolyl)propan-1-ol,[24] b. p. 130°/0·6 mm. $\nu_{max.}$ 3400 cm.$^{-1}$. Dehydration of this alcohol with phosphoric acid [23] gave a product, b. p. 140° (bath)/0·2 mm., $n_D^{21\cdot5}$ 1·5844, the infrared absorption of which was identical with that of fraction (i) above, except for differences in the intensities of some bands. Hydrogenation over palladised charcoal then afforded 1-phenyl-3-(*p*-tolyl)-propane, b. p. 95—100° (bath)/0·2 mm., $n_D^{21\cdot5}$ 1·5554 (lit.,[24] b. p. 130—131°/1 mm., n_D^{20} 1·5509), with infrared absorption identical with that of the product obtained from fraction (i).

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