752. 1,2-*Homolytic Rearrangements.*

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The thermal decomposition of nitrosamines and of diacyl peroxides has been examined. In the latter series there is evidence of radical rearrangements of the type $(Ar{\cdot}CR_2{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot})_2 \longrightarrow Ar{\cdot}CR_2{\cdot}CH_2{\cdot} \longrightarrow {\cdot}CR_2{\cdot}CH_2Ar \longrightarrow$ (Products).

HOMOLYTIC molecular rearrangements, as counterparts of nucleophilic and electrophilic changes, have not been studied extensively; significant examples are the peroxide-promoted decomposition of aldehydes:[1,2] $R_3C{\cdot}CH_2{\cdot}CHO \longrightarrow R_3C{\cdot}CH_2{\cdot}CO{\cdot} \longrightarrow CO + R_3C{\cdot}CH_2{\cdot} \longrightarrow {\cdot}CR_2{\cdot}CH_2R \longrightarrow$ Products, and the pyrolysis of triarylmethyl peroxides,[3] $Ar_3C{\cdot}CO{\cdot}OR \longrightarrow$ Products derivable from ${\cdot}CAr_2{\cdot}OR$. The former case involves migration from carbon to carbon, the latter from carbon to oxygen. This paper records experiments with nitrosamines, and with diacyl peroxides.

Many nitrosamines are decomposed thermally[4] or by irradiation,[5] with production of

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[1] Curtin and Hurwitz, *J. Amer. Chem. Soc.*, 1952, **74**, 5381.

[2] Seubold, *J. Amer. Chem. Soc.*, 1953, **75**, 2532.

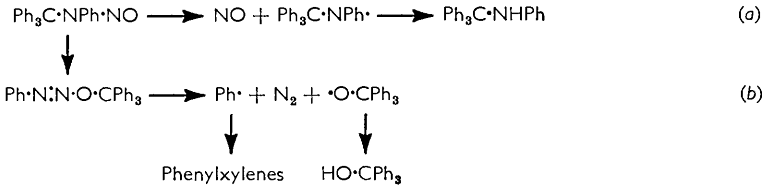
[3] Wieland, *Ber.*, 1911, **44**, 2550; Kharasch, Poshkus, Fono, and Nudenberg, *J. Org. Chem.*, 1951, **16**, 1458.

[4] Wieland and Lecher, *Annalen*, 1912, **392**, 164.

[5] Bamford, *J.*, 1939, 12.

nitric oxide and, no doubt, a radical RR'N·. We have examined four cases, seeking products formed by rearrangement of the free radical, CHRR'·NR''· ⟶ ·CHR·NR'R'', etc., without finding evidence of a change of this kind. The observations are summarised in Table 1, in which the yields are moles %.

The decomposition of nitrosamine 1 is plausibly formulated:



The alternative (*b*) appears to demand the presence of the very mobile triphenylmethyl group, while (*a*) is favoured by an *N*-aryl radical. It is thus understandable that cases 1—4 exhibit, respectively, processes (*a* + *b*), (*b*), (*a*), and (*a*). The formation of Schiff bases in cases 3 and 4 (along with secondary amine) suggests disproportionation of the unrearranged free radical, but in the photolysis of *C*-nitroso-compounds there is evidence of the formation of olefins by elimination of HNO (≡ hyponitrous acid).[6]

TABLE 1.

Decomposition of nitrosamines.

Case	Nitrosamine	Conditions	Products
1	$Ph_3C\cdot NPh\cdot NO$	Boiling xylene	NO (20—25%); $Ph_3C\cdot OH$ (32%); $Ph_3C\cdot NHPh$ (21%); phenylxylenes (?) (12%); $NO_2\cdot C_6H_4\cdot NH\cdot CPh_3$ (11%); high-boiling oil
2	$Ph_3C\cdot NMe\cdot NO$	240°	No NO; $Ph_3C\cdot OH$ (70%); Ph_3CH (0·5%); Ph_2CO (0·3%)
3	$Ph_2CH\cdot NMe\cdot NO$	240°	NO (20—25%); $Ph_2CH\cdot CHPh_2$ (6%); Ph_2CO (19%); ($Ph_2CH\cdot NHMe$ + $Ph_2C{=}NMe$) (58%); NH_2Me (?)
4	$p\text{-MeO}\cdot C_6H_4\cdot\underset{\displaystyle CH_2Ph}{\underset{\vert}{N}}\cdot NO$	190°	NO (73%); $MeO\cdot C_6H_4\cdot N{=}CHPh$ (35%); $MeO\cdot C_6H_4\cdot NH\cdot CH_2Ph$

Diacyl peroxides undergo thermal decomposition, partly by the sequence, R·CO·O·O·CO·R ⟶ R·CO·O· + ·O·CO·R; R·CO·O· ⟶ R· + CO_2, and partly by simultaneous fission at more than one point, some carbon dioxide being produced otherwise than through R·CO·O·.[7] Six peroxides of the type $(Ar\cdot CR_2\cdot CH_2\cdot CO)_2O_2$ have now been pyrolysed, usually in benzene or chlorobenzene, and in several cases products have been recognised in which Ar has migrated to the adjacent carbon atom: $(Ar\cdot CR_2\cdot CH_2\cdot CO)_2O_2 \longrightarrow Ar\cdot CR_2\cdot CH_2\cdot \longrightarrow \cdot CR_2\cdot CH_2Ar \longrightarrow CHR_2\cdot CH_2Ar$ and/or $CR_2{=}CHAr$.

Bis-βββ-triphenylpropionyl peroxide was decomposed in boiling chlorobenzene, giving the products set out in Table 2; these account satisfactorily for the initial material in respect both of the benzene nuclei and of the carbonyl-carbon atoms; there is a substantial deficiency in hydrogen. The only simple representative of the liberated triphenylethyl radical is triphenylethylene, produced by rearrangement and a dehydrogenation which no doubt accounts for part of the triphenylpropionic acid produced. The unrearranged radical is represented by more complicated products attributable to "solvent cage" processes taking place before the radical becomes kinetically free. These are the dimer, $Ph_3C\cdot CH_2\cdot CH_2\cdot CPh_3$, and the alcohol, $Ph_3C\cdot CH_2\cdot OH$. This alcohol, and part of the triphenylpropionic acid recorded, are probably formed by saponification (a stage in the process of working up) of the ester $Ph_3C\cdot CH_2\cdot CO\cdot O\cdot CH_2\cdot CPh_3$, resulting from the combination of $Ph_3C\cdot CH_2\cdot CO\cdot O\cdot$ and $\cdot CH_2\cdot CPh_3$.

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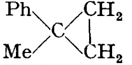
[6] Anderson, Crumpler, and Hammick, *J.*, 1935, 1679.

[7] Hammond and Soffer, *J. Amer. Chem. Soc.*, 1950, **72**, 4711; DeTar and Lamb, *ibid.*, 1959, **81**, 122.

TABLE 2.

Decomposition of peroxides (yields are moles %).

(*A*) $(Ph_3C{\cdot}CH_2{\cdot}CO)_2O_2$		
CO_2	(1) 72	(2) 76
$Ph_3C{\cdot}CH_2{\cdot}CO_2H$	64	68
$Ph_2C{:}CH{\cdot}CO_2H$	(64)	(54)
$Ph{\cdot}OH$	64	54
$Ph_3C{\cdot}CH_2{\cdot}OH$	4	6
$Ph_2C{:}CHPh$	51	40
$Ph_3C{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_3$ (?)	3	9
(*B*) $[(NO_2{\cdot}C_6H_4)_3C{\cdot}CH_2{\cdot}CO]_2O_2$		
CO_2	131	
(*C*) $(Ph_2CH{\cdot}CH_2{\cdot}CO)_2O_2$		
CO_2	146	
$Ph_2CH{\cdot}CH_2{\cdot}CO_2H$	44	
Alcohols (?)	18	
$Ph{\cdot}CH{:}CHPh$	22	
$Ph_2C{:}CH_2$	3	
$Ph{\cdot}CH_2{\cdot}CH_2Ph$	9	
Ph_2CHMe	15	
" Dimers," $C_{28}H_{26}$	37	

(*D*) $(Ph{\cdot}CMe_2{\cdot}CH_2{\cdot}CO)_2O_2$	
CO_2	154
$Ph{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$	57
Alcohols (?)	12
$Ph{\cdot}CH_2{\cdot}CMe{:}CH_2$	1
$Ph{\cdot}CH{:}CMe_2$	3
	21
$Ph{\cdot}CMe_3$	2
$Ph{\cdot}CH_2{\cdot}CHMe_2$	18
" Dimers," $C_{20}H_{26}$	36
(*E*) $(NO_2{\cdot}C_6H_4{\cdot}CMe_2{\cdot}CH_2{\cdot}CO)_2O_2$	
CO_2	166
(*F*) $(Ph{\cdot}CHMe{\cdot}CH_2{\cdot}CO)_2O_2$	
CO_2	158
$Ph{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$	27
Alcohols (?)	15
$Ph{\cdot}CH{:}CHMe$	4
$Ph{\cdot}CH_2{\cdot}CH_2Me$	8
$Ph{\cdot}CHMe_2$	19
" Dimers," $C_{18}H_{22}$	23

Diphenylacrylic acid and phenol are considered to be produced by hydrolysis of the ester $Ph_2C{:}CH{\cdot}CO_2Ph$ formed by 1,4-migration of phenyl: $Ph_3C{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot} \longrightarrow {\cdot}CPh_2{\cdot}CH_2{\cdot}CO_2Ph \xrightarrow{-H\cdot} Ph_2C{:}C{\cdot}CO_2Ph$. Somewhat similar rearrangements are recorded (i) in the Hunsdiecker reaction [8] between bromine and silver βββ-triphenylpropionate, which gave phenyl ββ-diphenylacrylate, and (ii) in the electrolysis [9] of sodium triphenylpropionate which afforded the ester $MeO{\cdot}CPh_2{\cdot}CH_2{\cdot}CO_2Ph$.

Pyrolysis of a more concentrated solution gave very similar results, but with a significant increase in the production of the dimer hexaphenylbutane and a fall in that of triphenylethylene.

Dry decomposition of the very insoluble bis-βββ-tri-*p*-nitrophenylpropionyl peroxide gave much more carbon dioxide, and highly insoluble material from which nothing could be isolated.

Bis-ββ-diphenylpropionyl peroxide, decomposed in benzene, gave much carbon dioxide and no products attributable to 1,4-migration of phenyl. The C_{14} hydrocarbons included rearranged and unrearranged structures, saturated and unsaturated. Rearranged (1,2,3,4-) and unrearranged (1,1,4,4-)tetraphenylbutanes were also isolated.

In the same way, bis-β-phenylbutyryl peroxide gave β-methylstyrene with propyl- and isopropyl-benzene, the first two involving rearrangement. The homologous bis-β-methyl-β-phenylbutyryl peroxide yielded several C_{10} hydrocarbons, rearranged and otherwise, including methylphenylcyclopropane. The last hydrocarbon was not observed (and would not have been overlooked) by Urry and Kharasch [10] in their study of the fate of neophyl radicals ($Ph{\cdot}CMe_2{\cdot}CH_2{\cdot}$) from the action of cobalt chloride and phenylmagnesium bromide on neophyl chloride. On the other hand, neophyl chloride with ethylsodium gives 61% of methylphenylcyclopropane.[11] The peroxide also afforded the " rearranged dimer " $(Ph{\cdot}CH_2{\cdot}CMe_2{\cdot})_2$. Heated in chlorobenzene, bis-β-methyl-β-*p*-nitrophenylbutyryl peroxide gave a little of the parent acid and no other definable product; there was evidence for the production of an olefinic C_{10} nitro-compound, which would involve skeletal rearrangement.

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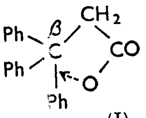
[8] Wilt and Oathoudt, *J. Org. Chem.*, 1958, **23**, 218.
[9] Breederveld and Kooyman, *Rec. Trav. chim.*, 1957, **76**, 297.
[10] Urry and Kharasch, *J. Amer. Chem. Soc.*, 1944, **66**, 1438.
[11] Whitmore, Weisgerber, and Shabica, *J. Amer. Chem. Soc.*, 1943, **65**, 1469.

Since it is very likely that the alcohols are produced by a " cage " reaction, and this may well apply to the " dimers " also, our best resource for purposes of comparison is to consider the products, arising from each postulated free-radical intermediate $R_3C{\cdot}CH_2{\cdot}$ by gain or loss of hydrogen, as indicating the incidence in the several cases of the rearrangement under investigation. The proportion of these products attributable to migration of phenyl in each case is: $Ph_3C{\cdot}CH_2{\cdot}$, 100; $Ph_2CH{\cdot}CH_2{\cdot}$, 63; $Ph{\cdot}CMe_2{\cdot}CH_2$, 49; $Ph{\cdot}CHMe{\cdot}CH_2{\cdot}$, 39%. The last value is probably too high, since 2-phenylpropene (unrearranged), known[12] to be more easily polymerised than its isomer, was not recognised though no doubt initially formed. The sequence is that to be expected if (*a*) the driving force of the rearrangement is the tendency to site the unpaired electron in a more favourable position, and (*b*) phenyl migrates more readily than methyl or hydrogen. The occurrence of 1,4-migration in case (*A*) (Table 2) only, giving phenyl diphenylacrylate, can be attributed to the favourable presentation of phenyl radicals for attack by the reactive oxygen atom (I), combined again with the ability of the arylated C_β to assume the radical character.



(I)

Curtin and Hurwitz[1] decomposed βββ-triphenylpropionaldehyde in presence of di-t-butyl peroxide, giving the same radical ($Ph_3C{\cdot}CH_2{\cdot}CHO - H \longrightarrow Ph_3C{\cdot}CH_2{\cdot} + CO$) as in case (*A*), and observed substantially complete production of the saturated rearranged hydrocarbon, $Ph_2CH{\cdot}CH_2Ph$. From β-methoxyphenyl-β-phenylpropionaldehyde they obtained a diarylethane fraction containing $\not<$85% of 1-*p*-methoxyphenyl-1-phenylethane (compare our case *C*). Seubold[2] observed the formation of both isobutylbenzene and t-butylbenzene in the peroxide-catalysed decomposition of the aldehyde $Ph{\cdot}CMe_2{\cdot}CH_2{\cdot}CHO$ (compare case *D*) and noted the absence of migration of methyl.

EXPERIMENTAL

Nitrosamines.—*N*-Methyldiphenylmethylamine was prepared by refluxing benzophenone methylimine[13] with an excess of sodium amalgam in ethanol for 15 hr. The base, purified by precipitation of the hydrochloride from ether by dry hydrogen chloride, had the properties recorded by Busch and Leefhelm.[14] Addition of sodium nitrite to a solution of the base in dilute hydrochloric acid at 0° gave the nitrosamine (3). Nitrosamine (4) was prepared from the secondary amine[15] in the same way, but in case (2) this procedure gave triphenylmethanol. *N*-Methyltriphenylmethylamine[16] was dissolved in acetic acid–acetic anhydride at 0° and powdered sodium nitrite added; after dilution with water, benzene extracted the nitrosamine. The products are recorded in Table 3.

TABLE 3.

Nitrosamines.

				Found (%)				Required (%)		
Case	M. p.	$\lambda_{max.}$	$Log_{10}\ \varepsilon$	C	H	N	Formula	C	H	N
1[17]	156°	3910	4·75	—	—	—	—	—	—	—
2 *	188	3700	4·98	79·1	6·0	9·6	$C_{20}H_{18}N_2O$	79·5	6·0	9·3
3	74	3625	4·40	74·0	6·1	12·2	$C_{14}H_{14}N_2O$	74·3	6·2	12·4
4	80	—	—	68·7	5·9	—	$C_{14}H_{14}N_2O_2$	69·4	5·8	—

* *M*, cryoscopic in benzene, 279, 300. Reqd., *M*, 306.

Decompositions.—*Case* (1). The nitrosamine was refluxed for 3 hr. in xylene under nitrogen. After evaporation of the xylene, benzene and ligroin were added, giving crystalline triphenyl-

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[12] Logemann, Houben-Weyl's "Methoden der organischen Chemie," Georg Thieme, Stuttgart, 4th edn., XIV, p. 839.

[13] Sommelet, *Compt. rend.*, 1927, **184**, 1338.

[14] Busch and Leefhelm, *J. prakt. Chem.*, 1908, **77**, 22.

[15] Fröhlich and Wedekind, *Ber.*, 1907, **40**, 1010.

[16] Vosburgh, *J. Amer. Chem. Soc.*, 1916, **38**, 2090.

[17] Elbs, *Ber.*, 1884, **17**, 704.

methanol. The remaining material was chromatographed on active alumina; ligroin–benzene (9 : 1) eluted an oil, b. p. 280°, possibly phenylxylenes (Found: C, 93·4; H, 7·8. Calc. for $C_{14}H_{14}$: C, 92·3; H, 7·7%); ligroin–benzene (3 : 2) gave a colourless oil, b. p. >250°/10 mm.; ligroin–benzene (2 : 5) eluted triphenylmethylaniline. Finally, elution with benzene gave yellow needles, m. p. 220° (from benzene–ligroin) (Found: C, 79·1; H, 5·4; N, 7·1. $C_{25}H_{20}N_2O_2$ requires C, 78·9; H, 5·3; N, 7·4%). An infrared absorption band at 1307 cm.$^{-1}$ suggests the presence of a nitro-group, and reduction with tin and hydrochloric acid gave triphenylmethane. This material was identical with p-*nitro*-N-*triphenylmethylaniline*, synthesised as follows. Triphenylmethanol (1·5 g.) and *p*-nitroaniline (1·5 g.) were refluxed in acetic acid (6 ml.) for 90 min. and poured into methanol (20 ml.). The solid was crystallised from chloroform–ethanol and from benzene–ligroin.

Case (2). Heated alone under nitrogen, the nitrosamine decomposed vigorously at 240°, and products were separated as in case (1). On chromatography, benzene eluted successively triphenylmethane and benzophenone, and chloroform eluted further triphenylmethanol. By irradiation for 3 days in benzene under nitrogen (mercury lamp; glass vessel; $\lambda > 2800$ Å), the nitrosamine (0·5 g.) gave a smell of formaldehyde; chromatography afforded unchanged material (0·3 g.) and triphenylmethanol (0·05 g.).

Case (3). On pyrolysis (240°; 4 hr.) the nitrosamine gave an odour of methylamine. The residue, by chromatography over alumina, yielded: to benzene–ligroin, *sym*-tetraphenylethane; to benzene, benzophenone; to chloroform, an oil. The oil was nearly all extracted from ether solution by very dilute hydrochloric acid at −5°; warmed with stronger acid, the extract afforded benzophenone (no doubt from hydrolysis of the methylimine) and methyldiphenylmethylamine.

Case (4). Pyrolysis of the nitrosamine at 190° gave as volatile product some benzaldehyde. Repeated crystallisation of the residue yielded benzylidene-*p*-anisidine, and chromatography of the mother-liquors gave *N*-benzyl-*p*-anisidine.

General.—Nitric oxide was recognised by reaction with ferrous sulphate, and measured in a separate experiment in which a stream of carbon dioxide was used. *N*-Methyldiphenylmethylamine was recognised as hydrochloride, benzophenone and benzaldehyde as 2,4-dinitrophenylhydrazones, and other solid products by mixed m. p.s with authentic specimens.

Diacyl Peroxides.—(*A*) To a solution of βββ-triphenylpropionyl chloride [18] (45 g.) in as little toluene as possible were added successively, with stirring, below 5°, 20% hydrogen peroxide (11·25 ml.) and sodium hydroxide (7·2 g. in 9 ml. of water). After 30 min. water was added, and the toluene layer separated, washed, dried (Na_2SO_4), and treated with ligroin (b. p. 40—60°), precipitating the peroxide.

TABLE 4.

Diacyl peroxides, $(R{\cdot}CO)_2O_2$.

			Found (%)					Required (%)			
Case	R	M. p.	C	H	N	O *	Formula	C	H	N	O
A	$Ph_3C{\cdot}CH_2$	138° †	84·0	5·9	—	2·6	$C_{42}H_{34}O_4$	83·7	5·7	—	2·6
B	$(NO_2{\cdot}C_6H_4)_3C{\cdot}CH_2$	165—170 †	57·6	3·9	10·0	—	$C_{42}H_{28}N_6O_{16}$	57·7	3·2	9·6	
C	$Ph_2CH{\cdot}CH_2$	100 †	79·2	5·7	—	3·6 ‡	$C_{30}H_{26}O_4$	79·9	5·8	—	3·6
D	$Ph{\cdot}CMe_2{\cdot}CH_2$	40	74·1	7·2	—	—	$C_{22}H_{26}O_4$	74·0	7·3	—	—
E	$NO_2{\cdot}C_6H_4{\cdot}CMe_2{\cdot}CH_2$	125 †	59·5	5·7	6·3	—	$C_{22}H_{24}N_2O_8$	59·4	5·4	6·3	—
F	$Ph{\cdot}CHMe{\cdot}CH_2$	~0	—	—	—	4·7	$C_{20}H_{22}O_4$	—	—	—	4·9

* Active oxygen (Kokatnur and Jelling, *J. Amer. Chem. Soc.*, 1941, **63**, 1432). † With decomp. ‡ Isopropyl alcohol replaced by acetic anhydride.

(*B*) Crystallised from ethanol, βββ-tri-*p*-nitrophenylpropionic acid had m. p. 265° (lit.,[8] 248—250°); 3 hours' boiling with an excess of thionyl chloride gave the acid chloride, having m. p. 195—200° after crystallisation from chloroform. Pure sodium peroxide (22 g.) was added to a stirred solution of the chloride (48 g.) in methylene chloride (500 ml.) at 0°. After 2 hr. ice–water (100 ml.) was added, and the precipitate was washed successively with water, methylene chloride, and ether, and then dried *in vacuo* over phosphorus pentoxide.

(*C*) ββ-*Diphenylpropionyl chloride* [19] had m. p. 59—60° (Found: C, 73·5; H, 5·6; Cl, 14·7.

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[18] Hellerman, *J. Amer. Chem. Soc.*, 1927, **49**, 1738.

[19] Holmes and Hill, U.S.P. 2,423,025; *Chem. Abs.*, 1947, **41**, 6285.

$C_{15}H_{13}ClO$ requires C, 73·9; H, 5·3; Cl, 14·6%). The peroxide was prepared as in case (*A*), but with ether as solvent. The ether-insoluble peroxide was washed with alkali, water, and ether, dried (P_2O_5), and crystallised from chloroform–ethanol.

(*D*) Treated as in case (*C*), β-methyl-β-phenylbutyryl chloride [20] (from the acid with thionyl chloride) gave an ether-soluble peroxide, which solidified when rubbed with ligroin at −70° and crystallised when ethanol was added to its solution in chloroform.

(*E*) Refluxed for 1 hr. with thionyl chloride, β-methyl-β-*p*-nitrophenylbutyric acid [21] gave an oily acid chloride which could not be distilled. The peroxide was prepared as in case (*B*), with ether as solvent, and purified by precipitation from solution in chloroform by ethanol.

(*F*) β-Phenylbutyric acid [22] gave the chloride [23] and thence as in case (*E*) the peroxide, which could not be purified.

Decomposition of Peroxides.—(*A*) (1) The peroxide (29·4 g.) in chlorobenzene (1100 g.) was heated to boiling in 45 min. in a flask fitted with an efficient upright condenser; a slow stream of nitrogen was passed through the apparatus, then through a calcium chloride tube, three bulbs charged with 30% potassium hydroxide solution, and a calcium chloride guard-tube. Refluxing was continued for 5 hr. Most of the chlorobenzene was removed through an efficient column, no low-boiling product being observed, and the residue was refluxed with 30% ethanolic sodium hydroxide to hydrolyse esters. The solution was diluted with warm water and extracted with warm benzene. The acidified alkaline layer was steam-distilled, giving phenol, m. p. 37° (benzoate, m. p. 69°), and a non-volatile mixture (19·4 g.) of βββ-triphenylpropionic and ββ-diphenylacrylic acid which could be separated partially but not quantitatively by crystallisation or chromatography. Aqueous potassium permanganate (4%) was added to a solution of the mixture in much dilute aqueous sodium carbonate, until the colour persisted for 10 min. The neutral fraction then afforded benzophenone 2,4-dinitrophenylhydrazone (6 g.), and the acid material was triphenylpropionic acid (9·5 g.). The estimate (3·7 g.) of the yield of diphenylacrylic acid based on benzophenone dinitrophenylhydrazone is minimal; the actual quantity produced is probably equivalent to the isolated yield of phenol, *i.e.*, 6·9 g., and this value is entered, in parentheses, in Table 2.

The neutral fraction obtained on saponification was dissolved in a little benzene, and ligroin was added, precipitating a solid which melted at 282° after crystallisation from benzene–ligroin (Found: C, 93·2; H, 6·7%; *M*, 490, 520. Calc. for $C_{40}H_{34}$: C, 93·3; H, 6·7%; *M*, 514). Wieland [24] attributed the formula $Ph_3C{\cdot}CH_2{\cdot}CH_2{\cdot}CPh_3$ to a hydrocarbon, m. p. 271°, which he obtained by treating $Ph_3C{\cdot}CCl_3$ with zinc and acetic acid. The fully rearranged dimer, $Ph{\cdot}CH_2{\cdot}CPh_2{\cdot}CPh{\cdot}_2CH_2Ph$, is known [25] to be unstable. The filtrate from hexaphenylbutane was submitted to chromatography over alumina (150 cm. column). Benzene–ligroin, and benzene, eluted 1,1,2-triphenylethane, m. p. and mixed m. p. 63—64°; chloroform afforded a product, m. p. 107—108° (from ligroin) (Found: C, 87·2; H, 6·6. Calc. for $C_{20}H_{18}O$: C, 87·5; H, 6·6%); the acetyl derivative had m. p. 135°, and the substance is no doubt 2,2,2-triphenylethanol.[26] Further small fractions were not identified.

In run (*A*) (2) 50 g. of peroxide were decomposed in 500 ml. of chlorobenzene and the products isolated as in run (1).

(*B*) The highly insoluble peroxide (20 g.) was mixed with dried, acid-washed sand (60 g.) and decomposed by cautious direct heating. Working up as in case (*A*) gave a little black gummy acid, and neutral material, insoluble in all solvents, which could not be purified.

(*C*) A solution of the peroxide (100 g.) in benzene (1 l.) was refluxed for 8 hr., and the products were worked up as in case (*A*). The only acid material was pure ββ-diphenylpropionic acid. The neutral product, a viscous oil (63 g.), was distilled through an efficient column, giving fractions (i) 20·1 g., b. p. 140—173°/12 mm., (ii) 8·0 g., b. p. 175—195°/12 mm., and (iii) residue (29·7 g.). Fraction (i), which gave benzoic acid and benzophenone on oxidation, was expected to contain 1,1- and 1,2-diphenylethane, and 1,1- and 1,2-diphenylethylene. With synthetic hydrocarbons [27] as reference compounds, the fraction was analysed by vapour-phase

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[20] Winstein and Seubold, *J. Amer. Chem. Soc.*, 1947, **69**, 2917.
[21] Hofmann, *J. Amer. Chem. Soc.*, 1929, **51**, 2545.
[22] Schroeter, *Ber.*, 1907, **40**, 1595.
[23] Steinkopf and Bessaritsch, *Ber.*, 1914, **47**, 2928.
[24] Wieland, *Annalen*, 1934, **514**, 145.
[25] Ziegler and Schnell, *Annalen*, 1924, **437**, 233.
[26] Danilov, *J. Russ. Phys.-Chem. Soc.*, 1919, **51**, 123.
[27] Klages, *Ber.*, 1902, **35**, 2647.

chromatography through a 120 cm. column of Apiezon L on firebrick C22 (John Mansville, 40/60 mesh) at 200°, argon being the carrier gas. Fraction (ii) appeared to contain alcohols (absorption peak at 3600 cm.$^{-1}$) and was not studied in detail. The residue (iii), dissolved in benzene–ligroin and cooled to 0°, afforded a solid mixture, augmented by precipitation with ethanol; chromatography over alumina resolved this into 1,1,4,4-tetraphenylbutane[28] and 1,2,3,4-tetraphenylbutane,[29] identified by mixed m. p. Residues from these operations, by further crystallisation and chromatography, gave a crystalline hydrocarbon, m. p. 85—86°, probably Bergmann's stereoisomeric 1,2,3,4-tetraphenylbutane[30] (Found: C, 92·8; H, 7·5. Calc. for $C_{28}H_{26}$: C, 92·8; H, 7·2%).

(*D*) The peroxide (36·25 g.) was refluxed in benzene (360 ml.) for 6 hr. and worked up as usual. The only acidic product was β-methyl-β-phenylbutyric acid (mixed m. p.). The dark brown, oily, neutral product (19 g.) gave fractions, (i) b. p. 150—186°/760 mm. (5·8 g.), (ii) b. p. 115—125°/12 mm. (1·81 g.), and (iii) residue. Vapour-phase chromatography of (i) over (*a*) silicone grease, and (*b*) Apiezon, at 150°, gave in all six peaks. Peaks 3 and 6 were well-defined in both chromatograms, so that the quantitative results were easily correlated. By experiments with synthetic materials, peaks 3—6 were attributed to, respectively, ββ-dimethylstyrene, 1-methyl-1-phenylcyclopropane, isobutylbenzene, and t-butylbenzene. Peak 5 could alternatively be ascribed to s-butylbenzene, which is not separated from isobutylbenzene under these conditions, but formation of the former hydrocarbon involves migration of methyl in preference to phenyl, unlikely and not observed in other experiments with the neophyl radical.[2] A further sample of material was hydrogenated before chromatography; peaks 2 and 3 were then absent and peak 5 correspondingly augmented. Since 3 is identified, peak 2 must be attributed to the isobutenylbenzene, $Ph\cdot CH_2\cdot CMe{:}CH_2$. The small peak 1 could not be identified. Of the reference materials, isobutylbenzene, prepared by reducing ββ-dimethylstyrene with sodium and ethanol, was characterised as the diacetamido-derivative,[31] m. p. 210°. Ethyl methylphenylmalonate[32] (33 g.) in ether (100 ml.) was reduced with lithium aluminium hydride (12 g.), with stirring for 15 hr., giving 2-methyl-2-phenylpropane-1,3-diol (19 g.); this was converted successively into 1,3-dibromo-2-methyl-2-phenylpropane[33] and methylphenylcyclopropane.[34]

Fraction (ii) was apparently alcoholic (absorption at 3589 cm.$^{-1}$). The residue (iii), in ligroin, was chromatographed on active alumina, giving fractions: (*a*) m. p. 45° after crystallisation from ethanol (Found: C, 90·2; H, 10·0%; *M*, 265, 278. $C_{20}H_{26}$ requires C, 90·2; H, 9·8%; *M*, 266), probably $Ph\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CMe_2Ph$ or $Ph\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CMe_2Ph$; (*b*) oil; (*c*) needles (from ethanol), m. p. 128° (Found: C, 90·3; H, 10·1%; *M*, 248, 263), no doubt $Ph\cdot CH_2\cdot CMe_2\cdot CMe_2\cdot CH_2Ph$;[35] subsequent fractions were unidentified oils.

(*E*) Decomposition (6 hours' refluxing) of the peroxide (20·6 g.) in chlorobenzene (230 ml.), followed by the usual working up, gave much brown acid from which only a little methylnitrophenylbutyric acid could be isolated. The volatile portion of the neutral material, b. p. 125—135°/10—0·5 mm., showed no absorption at 1035 cm.$^{-1}$ (absence of cyclopropane ring) and absorbed strongly at 2885 cm.$^{-1}$, indicating the presence of an olefinic linkage and hence a skeletal rearrangement of the radical $NO_2\cdot C_6H_4\cdot CMe_2\cdot CH_2\cdot$. Neither this material nor pure specimens of *p*-isobutylnitrobenzene and *p*-nitro-t-butylbenzene showed peaks on attempted vapour-phase chromatography; presumably the nitro-compounds adhered to the column.

(*F*) The peroxide (17 g.) was refluxed for 5 hr. in benzene (200 ml.) and worked up as usual. The only acidic product was β-phenylbutyric acid (mixed m. p.). The alkali-insoluble material included 0·1 g. of an organic solid, insoluble in solvents. Fractionation of the remainder gave materials: (*a*), b. p. 135—180°/760 mm.; (*b*) b. p. 90—110°/11 mm., absorption peak at 3300 cm.$^{-1}$, probably alcoholic; (*c*) b. p. 120—180°/11 mm., regarded as mainly C_{18} hydrocarbons; and (*d*) a brown, gummy residue. Vapour-phase chromatography of (*a*) on an Apiezon L

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[28] Schlenk, Appenrodt, Michael, and Thal, *Ber.*, 1914, **47**, 478.

[29] Cope, Smith, and Cotter, *Org. Synth.*, 1954, **34**, 42; Smith and Hoehn, *J. Amer. Chem. Soc.*, 1941, **63**, 1184.

[30] Bergmann, *J.*, 1936, 505.

[31] Ipatieff and Schmerling, *J. Amer. Chem. Soc.*, 1943, **65**, 2470.

[32] After A. I. Vogel, " Practical Organic Chemistry," Longmans, Green and Co., London, 1945, p. 869.

[33] Bains and Mills, *J.*, 1925, **127**, 2504.

[34] Backer and Winter, *Rev. Trav. chim.*, 1937, **56**, 691.

[35] Conant and Blatt, *J. Amer. Chem. Soc.*, 1928, **50**, 557.

column at 75° gave peaks whose attribution to n-propylbenzene, 1-phenylpropene, and isopropylbenzene was based on experiments with authentic hydrocarbons.

We thank the Department of Scientific and Industrial Research for a maintenance grant to W. R.

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[*Received, January 7th*, 1963.]