630. *Electrophilic Rearrangements: Stereochemistry and Allylic Transformations.*

By B. J. Millard and T. S. Stevens.

Several cases are reported of the migration of a 1-phenylethyl radical with retention of configuration about the asymmetric carbon atom. A substituted allyl group may migrate either with or without " inversion."

In the easy rearrangement of the optically active dimethylphenacyl-1-phenylethylammonium ion, $Ph\cdot CO\cdot CH_2\cdot {}^+NMe_2\cdot CHMePh$, the phenylethyl group migrates from nitrogen to carbon with retention of configuration at the asymmetric carbon atom.[1,2] We have confirmed this result and shown that the same applies to a range of migrations of the

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[1] Campbell, Houston, and Kenyon, *J.*, 1947, 93.

[2] Brewster and Kline, *J. Amer. Chem. Soc.*, 1952, **74**, 5179.

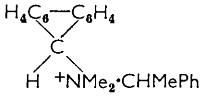
1-phenylethyl group. The conclusions depend on established stereochemical relations: (—)-PhMeCH·OH with[3] (—)-PhMeCH·NH_2 and with[1] (—)-PhMeCH·NMe_2; (—)-PhMeCH·NH_2 with[4] (+)-PhMeCH·CO_2H and with[5] (—)-PhMeCH·CH_2·CO_2H.

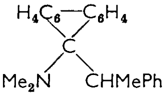
By quaternisation with bromoacetone and bromoacetophenone, respectively, (—)-dimethyl-1-phenylethylamine gave CH_3·CO·CH_2·$^+NMe_2$·CHMePh and Ph·CO·CH_2·$^+NMe_2$·CHMePh, which rearranged to CH_3·CO·CH(NMe_2)·CHMePh and Ph·CO·CH(NMe_2)·CHMePh, separated in each case into a pair of diastereoisomers. The former product was oxidised by hydrogen peroxide to (+)-α-phenylpropionic acid; the latter was synthesised from β-phenylbutyric acid:

$$(-)\text{-}HO_2C{\cdot}CH_2{\cdot}CHMePh \longrightarrow Ph{\cdot}CO{\cdot}CH_2{\cdot}CHMePh \longrightarrow Ph{\cdot}CO{\cdot}CHBr{\cdot}CHMePh \longrightarrow Ph{\cdot}CO{\cdot}CH(NMe_2){\cdot}CHMePh$$

Attempted synthesis of the active fluorenylammonium salt (I) afforded the active rearranged product (II) whose configuration is not established.

(I)





(II)

With diphenylmethyl bromide in the presence of silver sulphate, (—)-1-phenylethanol gave the ether, Ph_2CH·O·CHMePh. This was rearranged by phenyl-lithium to (—)-$Ph_2C(OH)$·CHMePh, which was synthesised from (+)-α-phenylpropionic acid by treating the ester EtO_2C·CHMePh with phenylmagnesium bromide.

Phenacyl 1-phenylethyl ether, prepared from diazoacetophenone and (—)-1-phenylethanol, underwent a double rearrangement (electrophilic rearrangement followed by benzilic change) analogous to that of benzyl phenacyl ether:[6]

$$(-)\text{-}Ph{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}CHMePh \longrightarrow [Ph{\cdot}CO{\cdot}CH(OH){\cdot}CHMePh] \longrightarrow [Ph{\cdot}CO{\cdot}CO{\cdot}CHMePh] \longrightarrow (+)\text{-}PhMeCH{\cdot}CPh(OH){\cdot}CO_2H$$

The final product was synthesised by converting (—)-β-phenylbutyric acid as above into Ph·CO·CHBr·CHMePh, and treating the bromo-ketone with alkali and silver oxide:

$$Ph{\cdot}CO{\cdot}CHBr{\cdot}CHMePh \longrightarrow [Ph{\cdot}CO{\cdot}CH(OH){\cdot}CHMePh] \longrightarrow [Ph{\cdot}CO{\cdot}CO{\cdot}CHMePh] \longrightarrow \longrightarrow PhMeCH{\cdot}CPh(OH){\cdot}CO_2H$$

The work of Collins and Neville[7] shows that it is probably the phenylethyl group which would migrate in such a benzilic change; if our formulation of the reactions is correct, it follows that this group retains its configuration in both migrations.

In these experiments the rotations of the products indicated 93—99% optical purity, showing that the rearrangements proceed with at least greatly predominating retention of configuration, and providing further evidence of the strictly intramolecular character of these transformations.

In some classes of rearrangement a migrating allyl group invariably undergoes the " inversion " exemplified by the conversion of the but-2-enyl ether, CH_3·CH:CH·CH_2·OPh, into *o*-1-methylallylphenol, CH_2:CH·CHMe·C_6H_4·OH. In the case of 1 : 2 electrophilic rearrangements the situation is less simple. Thus but-2-enylmethyl aniline oxide,[8] CH_3·CH:CH·CH_2·^+NMePh·O^-, gives *N*-methyl-*O*-1-methylallylhydroxylamine, CH_2:CH·CHMe·O·NMePh, and the fluorenyl ether, CH_2:CH·CHMe·O·CH$(C_6H_4)_2$, gives 9-but-2′-enylfluoren-9-ol; on the other hand, but-2-enyl fluorenyl ether gives but-2-enylfluorenol, and cinnamyl fluorenyl ether gives cinnamylfluorenol.[6]

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[3] Hughes, Ingold, and Scott, *J.*, 1937, 1203.

[4] Bernstein and Whitmore, *J. Amer. Chem. Soc.*, 1939, **61**, 1324.

[5] Levene and Marker, *J. Biol. Chem.*, 1931, **93**, 749.

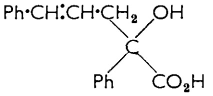
[6] Cast, Stevens, and Holmes, *J.*, 1960, 3521.

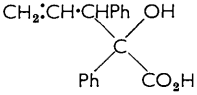
[7] Collins and Neville, *J. Amer. Chem. Soc.*, 1951, **73**, 2471; Wheeler *et al.*, *Chem. and Ind.*, 1962, 1864.

[8] Cope and Kleinschmidt, *J. Amer. Chem. Soc.*, 1944, **66**, 1929.

We examined the behaviour of cinnamyl phenacyl ether and of some phenacylammonium ions. With butanolic sodium butoxide, the ether gave an acid, $C_{17}H_{16}O_3$, which should be, by analogy with the rearrangement of benzyl or 1-phenylethyl phenacyl ether,

(III)





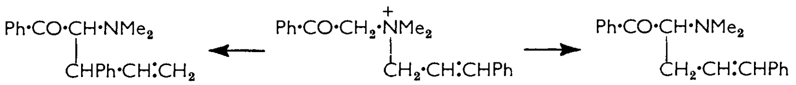
(IV)

either (III) or (IV). The acid gave benzaldehyde on ozonolysis and no formaldehyde, and is therefore regarded as (III), the cinnamyl group migrating as such.

But-2-enyldimethylphenacylammonium bromide, when warmed with alkali, gave the two diastereoisomeric bases (V), each of which afforded formaldehyde on ozonolysis; the migrating group was thus totally inverted. In the same way, the corresponding cinnamyl ion gave products of both types, (VI) and (VII). The isomeric tertiary bases were separated and their constitutions established by ozonolysis. In contrast with the previous case, only one diastereoisomer of (VI) was isolated. The behaviour of more 3-arylallyldimethylphenacylammonium salts was examined, and the velocity of rearrangement measured approximately (see Table). The entries in column 2 of the Table refer to material isolated; the figure 100 does not exclude the formation of minor amounts of non-inverted base. It is not easy to account satisfactorily for these results. The velocity constants were estimated at 0° in methanolic sodium methoxide; here the allyl group migrates some 500 times faster than benzyl. The still faster migration of the cinnamyl radical is not unexpected, and the accelerating effect of the nitro-substituent accords with observations in the benzyl series.

$$Ph{\cdot}CO{\cdot}CH_2{\cdot}{}^{+}NMe_2{\cdot}CH_2{\cdot}CH{:}CHMe \longrightarrow Ph{\cdot}CO{\cdot}CH(NMe_2){\cdot}CHMe{\cdot}CH{:}CH_2 \quad (V)$$

(VI)



$$\begin{array}{c} Ph{\cdot}CO{\cdot}CH{\cdot}NMe_2 \\ | \\ CHPh{\cdot}CH{:}CH_2 \end{array} \longleftarrow \begin{array}{c} Ph{\cdot}CO{\cdot}CH_2{\cdot}\overset{+}{N}Me_2 \\ | \\ CH_2{\cdot}CH{:}CHPh \end{array} \longrightarrow \begin{array}{c} Ph{\cdot}CO{\cdot}CH{\cdot}NMe_2 \\ | \\ CH_2{\cdot}CH{:}CHPh \end{array}$$

(VII)

Migrating radical	Inversion (%)	10^3k (min.$^{-1}$)
$CH_2{:}CH{\cdot}CH_2{\cdot}$	—	6·7
$Me{\cdot}CH{:}CH{\cdot}CH_2{\cdot}$	100	9·0
$Ph{\cdot}CH{:}CH{\cdot}CH_2{\cdot}$	55	1200
o-$Me{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH_2{\cdot}$	50	1200
p-$MeO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH_2{\cdot}$	100	—
o-$NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH_2{\cdot}$	100	>6000
1-$C_{10}H_7{\cdot}CH{:}CH{\cdot}CH_2{\cdot}$	100	—

EXPERIMENTAL

Optically active starting materials had the rotations recorded in the references cited. Statements of identity of solids imply the use of mixed melting points.

Active (−)-dimethyl-1-phenylethylamine was prepared by Campbell, Houston, and Kenyon's route,[1] but by using Clarke's methylation procedure [9] which gave yields of 60—70%.

Acetonyldimethyl-1-*phenylethylammonium Bromide*.—Bromoacetone and (−)-dimethyl-1-phenylethylamine in cold benzene gave (2 days) the bromide as a gum which could not be crystallised, $[\alpha]_D^{25}$ −26·1° (c 1·13 in EtOH). The gum (4 g.) was warmed on a steam-bath with 2N-sodium hydroxide for 30 min.; ether then extracted (α- + β-)3-*dimethylamino*-4-*phenylpentan*-2-*one* (2 g.), a yellow oil, b. p. 124°/14 mm., $[\alpha]_D^{25}$ −30·42° (c 10·32 in acetone) (Found: C, 76·3; H, 9·0; N, 6·4. $C_{13}H_{19}NO$ requires C, 76·1; H, 9·3; N, 6·8%). The diastereoisomers were separated by fractional crystallisation of the picrates: [10] α-*picrate*, pale yellow plates, m. p. 149°, $[\alpha]_D^{22}$ +29·8° (c 0·27 in EtOH) (Found: C, 52·8; H, 5·1; N, 13·0.

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[9] Clarke, *J. Amer. Chem. Soc.*, 1933, **55**, 4576.

[10] Stevens, *J.*, 1930, 2107.

$C_{19}H_{22}N_4O_8$ requires C, 52·5; H, 5·1; N, 12·9%); β-*picrate*, orange-yellow needles, m. p. 143°, $[\alpha]_D^{22}$ +209·7° (*c* 0·19 in EtOH) (Found: C, 52·5; H, 5·2; N, 12·6%). The derived α-base had $[\alpha]_D^{22}$ +27·1° (*c* 0·66 in EtOH) and the β-base $[\alpha]_D^{22}$ −105·2° (*c* 0·14 in EtOH). The base (2 g.; mixed stereoisomers) was warmed for 30 min. with hydrogen peroxide (15%; 100 ml.) and 2N-sodium hydroxide (50 ml.). The acidic product (0·5 g.), b. p. 162°/25 mm., $[\alpha]_D^{25}$ +81·0°, had the odour of α-phenylpropionic acid; the derived amide, $[\alpha]_D^{22}$ +58·0° (*c* 1·2 in $CHCl_3$), was identical with (+)-α-phenylpropionamide [11,12] (Found: C, 72·8; H, 7·1; N, 9·0. Calc. for $C_9H_{11}NO$: C, 72·5; H, 7·4; N, 9·4%).

Dimethylphenacyl-1-*phenylethylammonium Bromide*.—The salt from phenacyl bromide and (−)-dimethyl-1-phenylethylamine was rearranged and the β-base identified with material synthesised as follows. The redistilled acid chloride from (−)-β-phenylbutyric acid [5,13] (20 g.) in dry toluene (20 g.) was dropped into a solution of diphenylzinc prepared by adding zinc chloride (freshly fused) to the Grignard reagent from bromobenzene (19·6 g.) and magnesium (3·2 g.); the ether was removed in a vacuum and replaced by toluene. After 2 hours' refluxing the mixture was treated with aqueous ammonium chloride, and the toluene layer then afforded (+)-*phenyl* 2-*phenylpropyl ketone* (13 g.), as colourless needles, m. p. 72° (from ligroin), $[\alpha]_D^{20}$ +28·8° (*c* 1·05 in EtOH) and +9·35° (*c* 5·4 in $CHCl_3$) (Found: C, 86·0; H, 7·1. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%). Bromination in cold chloroform gave (+)-1-*bromo*-2-*phenylpropyl phenyl ketone*, which crystallised from ligroin in needles, m. p. 81°, $[\alpha]_D^{20}$ +20·0° (*c* 2·02 in $CHCl_3$) and +36·8° (*c* 1·65 in EtOH) (Found: C, 63·2; H, 5·0. $C_{16}H_{15}BrO$ requires C, 63·4; H, 4·9%). The bromo-ketone (2 g.) with dimethylamine (1 g.) in ethanol (50 ml.) was kept for 15 hr. and refluxed for 2 hr. The basic product, $[\alpha]_D^{22}$ +10·5° (*c* 1·82 in acetone) and +4·8° (*c* 1·6 in MeOH), was identical with the product of rearrangement.

Fluorene Series.—9-Bromofluorene (10 g.) and (−)-dimethyl-1-phenylethylamine (6 g.) were kept in benzene for 1 week; (−)-*dimethyl*-1-*phenylethylamine hydrobromide* (1 g.), m. p. 178°, was deposited (Found: N, 6·1. $C_{10}H_{16}BrN$ requires N, 6·1%). The filtrate was shaken with 10% hydrochloric acid (100 ml.); after 2 hr. 9-*dimethylamino*-9-1′-*phenylethylfluorene hydrochloride* separated, needes, m. p. 182° (from ethanol–ether) (Found: N, 4·3. $C_{23}H_{24}ClN$ requires N, 4·0%). The *hydrobromide*, m. p. 185°, had $[\alpha]_D^{20}$ +56·4° (*c* 0·48 in EtOH) (Found: N, 3·6. $C_{23}H_{24}BrN$ requires N, 3·6%). Free 9-*dimethylamino*-9-1′-*phenylethylfluorene* crystallised from ligroin in needles, m. p. 99—100° (Found: C, 88·6; H, 7·3; N, 4·7. $C_{23}H_{23}N$ requires C, 88·3; H, 7·4; N, 4·5%); it did not combine with methyl iodide, and no L-malate could be prepared. The *picrate* had m. p. 207° (once from ethanol) and $[\alpha]_D^{20}$ +9·1° (*c* 0·22 in acetone) (Found: N, 9·8. $C_{29}H_{26}N_4O_7$ requires N, 10·3%); further crystallisation raised the m. p. to 209°, and the liberated base had $[\alpha]_D^{22}$ +37·1° (*c* 0·62 in acetone).

Diphenylmethyl 1-*Phenylethyl Ether*.—Diphenylmethyl bromide (2 g.), (−)-1-phenylethanol [14] (3 g.), benzene (20 ml.), and acetonitrile (5 ml.) were heated on a steam-bath for 30 min. with finely powdered silver sulphate (2 g.). The ether-soluble material, freed from phenylethanol as far as possible by washing with water, gave (−)-*diphenylmethyl* 1-*phenylethyl ether*, b. p. 118°/0·02 mm., $[\alpha]_D^{20}$ −36·6° (*c* 5·45 in EtOH) (Found: C, 87·3; H, 7·2. $C_{21}H_{20}O$ requires C, 87·5; H, 6·9%). Ethereal phenyl-lithium (12 ml., 0·5M) was added to the (−)-ether (2 g.) in dry ether, and after 2 min., the mixture was poured on crushed ice. The *product* (1 g.) had m. p. 95° (from ethanol), $[\alpha]_D^{20}$ −32·6° (*c* 1·26 in EtOH) (Found: C, 87·4; H, 6·6. $C_{21}H_{20}O$ requires C, 87·5; H, 6·9%), and was identical with the alcohol prepared from the ethyl ester, b. p. 230°, α_D^{20} +12·2° (*l* 0·25), of (+)-hydratropic acid [11] and phenylmagnesium bromide. Pure 1,1,2-*triphenylpropan*-1-*ol* had m. p. 97°, $[\alpha]_D^{20}$ −35·0° (*c* 3·42 in EtOH), −27·2° (*c* 2·44 in acetone), and −54·2° (*c* 4·88 in $CHCl_3$) (Found: C, 88·0; H, 6·5%).

Phenacyl 1-*Phenylethyl Ether*.—A few drops of boron trifluoride etherate were added to (−)-1-phenylethanol (12 g.) and diazoacetophenone [15] (7·5 g.) in benzene (100 ml.) with stirring. Nitrogen (>90%) was evolved, and after 2 hr. the dark red solution was refluxed for 1 hr. Benzene was removed in a vacuum and the residue, in ether, was washed free from acid. It gave (−)-*phenacyl* 1-*phenylethyl ether*, b. p. 110°/1 mm., not quite pure after three distillations (Found: C, 80·9; H, 6·7. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%); $[\alpha]_D^{20}$ −79·9° (*c* 15·07 in

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[11] Raper, *J.*, 1923, **123**, 2557.

[12] Bonner and Zderic, *J. Amer. Chem. Soc.*, 1956, **78**, 3218.

[13] Golmov and Chai Kun, *J. Gen. Chem.* (*U.S.S.R.*), 1959, **29**, 3661.

[14] Downer and Kenyon, *J.*, 1939, 1156.

[15] Bradley and Robinson, *J.*, 1928, 1310.

acetone), −78·2° (*c* 5·78 in EtOH), and −84·8° (*c* 7·82 in $CHCl_3$). The bright red 2,4-*dinitrophenylhydrazone* had m. p. 148° (Found: N, 13·4. $C_{22}H_{20}N_4O_5$ requires N, 13·3%). The (−)-ether (2 g.) in ligroin (b. p. 80—100°; 25 ml.) was refluxed for 2 hr. with a solution of sodium (0·8 g.) in butanol (10 ml.). The dark red mixture was treated with water and ether; the aqueous layer afforded an oily acid (1 g.) which solidified after 1 month over concentrated sulphuric acid and then crystallised from ligroin in needles, m. p. 172°, $[\alpha]_D^{20}$ +66·6° (*c* 1·44 in acetone) (Found: C, 74·8; H, 6·2. $C_{16}H_{16}O_3$ requires C, 74·9; H, 6·3%). It was identical with (+)-α-*hydroxy*-αβ-*diphenylbutyric acid*, synthesised thus: to (+)-1-bromo-2-phenylpropyl phenyl ketone (above; 2 g.) in 20% ethanolic potassium hydroxide (50 ml.) was added silver nitrate (10 g.) in water (20 ml.) and the mixture heated on a steam-bath for 1 hr. The acidic product, isolated from the filtered solution as above, had $[\alpha]_D^{20}$ +69·1° (*c* 2·04 in acetone) (Found: C, 75·2; H, 6·3%).

Ozonisation.—The compound (~0·8 g.) and acetic acid (50 ml.) in a Drechsel bottle were cooled while ozone (4%) was passed through and into a second bottle charged with water. The contents of the bottles were steam-distilled from zinc dust (2 g.); formaldehyde was recognised in the distillate and determined by dimedone, and other aldehydes as 2,4-dinitrophenylhydrazones.

Cinnamyl Phenacyl Ether.—Diazoacetophenone reacted with cinnamyl alcohol, as with phenylethanol (above), to give the *ether*, b. p. 181—182°/2 mm. (Found: C, 80·7; H, 6·6. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%). The ether (10 g.) in ligroin (b. p. 80—100°; 200 ml.) was refluxed for 3 hr. with a solution of sodium (8 g.) in butanol (100 ml.), while air was bubbled through the mixture. The acidic reaction products were isolated as an orange oil, from which boiling ligroin (b. p. 60—80°) extracted a white solid (1 g.). Recrystallised from ether–ligroin, this 2-*hydroxy*-2,5-*diphenylpent*-4-*enoic acid* had m. p. 184° (Found: C, 75·6; H, 6·6. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%); on ozonolysis it gave benzaldehyde (40%) and no formaldehyde.

Allyldimethylphenacylammonium Bromide.—By refluxing, allyldimethylamine and phenacyl bromide gave the *salt*, which crystallised from ethanol–ether in needles, m. p. 128—129° (Found: C, 54·3; H, 6·2; N, 4·7. $C_{13}H_{18}BrNO$ requires C, 54·7; H, 6·3; N, 4·9%). When warmed with alkali, it (12 g.) yielded 1-*dimethylaminobut*-3-*enyl phenyl ketone* (6 g.), b. p. 80—81°/0·05 mm. (Found: N, 6·9. $C_{13}H_{17}NO$ requires N, 6·6%), which gave 90% of formaldehyde on ozonolysis. The picrate [16] formed orange needles, m. p. 100° (from ethanol).

But-2-*enyldimethylphenacylammonium Bromide.*—Dimethylphenacylamine was refluxed with technical but-2-enyl bromide in dry ether for 3 hr.; the quaternary *bromide*, crystallised repeatedly from ethanol, had m. p. 121—122° (Found: C, 56·0; H, 6·9. $C_{14}H_{20}BrNO$ requires C, 56·4; H, 6·7%). Rearranged by warming with alkali, it (5·5 g.) gave (α + β)-1-*dimethylamino*-2-*methylbut*-3-*enyl phenyl ketone* as a yellow oil (2·5 g.), b. p. 145—150°/18 mm. (Found: C, 77·3; H, 9·0; N, 6·7. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·8; N, 6·4%). The derived picrate was separated by fractional crystallisation into 1-*dimethylamino*-2-*methylbut*-3-*enyl phenyl ketone picrate* (α-form), yellow needles, m. p. 145—146° (from acetone–ligroin) (Found: C, 53·4; H, 4·8. $C_{20}H_{22}N_4O_8$ requires C, 53·8; H, 4·9%), and the β-*form*, yellow needles, m. p. 122—123° (from methanol) (Found: C, 54·3; H, 5·1%). The diastereoisomers, produced in the approximate ratio 3 : 2, gave, respectively, 45% and 40% of formaldehyde on ozonisation, and no acetaldehyde.

Cinnamyldimethylphenacylammonium Bromide.—Prepared from cinnamyl bromide and dimethylphenacylamine, the *salt* had m. p. 159° (from ethanol–ether) (Found: N, 3·9. $C_{19}H_{22}BrNO$ requires N, 3·9%). Ozonolysis gave benzaldehyde but no formaldehyde. The related iodide formed leaflets, m. p. 163—164°. The bromide (36 g.) was rearranged by warm aqueous alkali and the solid product fractionally crystallised from ligroin, giving (a) 1-*dimethylamino*-2-*phenylbut*-3-*enyl phenyl ketone* (VI) as yellow needles (12 g.), m. p. 100—101° (Found: N, 5·3. $C_{19}H_{21}NO$ requires N, 5·1%); *picrate*, deep yellow needles from ethanol, m. p. 173° (Found: C, 59·4; H, 4·9; N, 10·8. $C_{25}H_{24}N_4O_8$ requires C, 59·1; H, 4·9; N, 11·0%); and (b) 1-*dimethylamino*-4-*phenylbut*-3-*enyl phenyl ketone* (VII), deep yellow warts (9·5 g.), m. p. 101—102° (Found: N, 5·2%); *picrate*, yellow prisms, m. p. 165° (Found: C, 59·2; H, 4·9; N, 10·7%).

The *methiodide* of (VI) had m. p. 152° (from ethanol–ether) (Found: C, 56·6; H, 5·7. $C_{20}H_{24}INO$ requires C, 57·0; H, 5·7%). Heated on a steam-bath for 1 hr. with zinc wire and

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[16] Dunn and Stevens, *J.*, 1934, 279.

10% sulphuric acid, it gave an oily ketone which was oxidised with potassium permanganate in cold acetone. The acidic product, crystallised from ether–ligroin was identical with $\alpha\gamma$-diphenyl-γ-oxobutyric acid.[17] When hydrogenated over palladium in 50% ethanol (1·2 atm.; 12 hr.), (VI) gave 1-*dimethylamino*-2-*phenylbutyl phenyl ketone* as pale yellow needles, m. p. 108° (Found: C, 81·0; H, 8·2; N, 5·3. $C_{19}H_{23}NO$ requires C, 81·1; H, 8·2; N, 5·0%); *picrate*, yellow needles, m. p. 171—172° (from ethanol) (Found: C, 58·8; H, 5·2; N, 10·8. $C_{25}H_{26}N_4O_8$ requires C, 58·8; H, 5·1; N, 11·0%); *methiodide*, m. p. 168° (from water) (Found: N, 3·0. $C_{20}H_{26}INO$ requires N, 3·3%). On reduction with zinc and sulphuric acid, the methiodide gave phenyl 2-phenylbutyl ketone, m. p. 61° (lit.,[18] 61°) (Found: C, 85·7; H, 7·5. Calc. for $C_{17}H_{18}O$: C, 85·7; H, 7·6%). Ozonisation of (VI) gave formaldehyde (64%) and no benzaldehyde, while that of (VII) yielded benzaldehyde (25%) and no formaldehyde. The *methiodide* of (VII), m. p. 184° (Found: C, 57·6; H, 5·4%), gave, on reduction and oxidation as above, only benzoic acid.

Dimethyl-o-*methylcinnamylphenacylammonium Bromide*.—The *salt*, prepared from dimethylphenacylamine and *o*-methylcinnamyl bromide[19] in boiling ether, crystallised from ethanol–ether in needles, m. p. 150—151° (Found: C, 63·8; H, 6·3; N, 3·6. $C_{20}H_{24}BrNO$ requires C, 64·2; H, 6·4; N, 3·7%). The product of alkaline rearrangement of the bromide (5·5 g.), dissolved in ligroin, gave deep yellow crystals (1 g.) of 1-*dimethylamino*-2-o-*tolybut*-3-*enyl phenyl ketone*, m. p. 107—108° (Found: C, 81·4; H, 7·9; N, 5·0. $C_{20}H_{23}NO$ requires C, 81·8; H, 7·8; N, 4·8%), which gave 45% of formaldehyde on ozonolysis and no tolualdehyde. The *picrate* crystallised from ethanol–acetone in yellow rhombs, m. p. 180° (Found: C, 59·6; H, 5·2; N, 10·8. $C_{26}H_{26}N_4O_8$ requires C, 59·8; H, 5·0; N, 10·7%). The ligroin mother-liquors afforded an oily base (1 g.); the derived 1-*dimethylamino*-4-o-*tolylbut*-3-*enyl phenyl ketone picrate* formed yellow needles from ethanol–acetone, m. p. 184—185° (Found: C, 59·4; H, 5·1%). Ozonolysis of the free base gave *o*-tolualdehyde (25%) and no formaldehyde.

Dimethyl-p-*methoxycinnamylphenacylammonium Bromide*.—Prepared as above from phenacyl bromide and dimethyl-*p*-methoxycinnamylamine,[20] the *salt* had m. p. 165° (Found: N, 3·9. $C_{20}H_{24}BrNO_2$ requires N, 3·6%). Rearrangement gave a non-crystalline undistillable gum which yielded 1-*dimethylamino*-2-p-*methoxyphenylbut*-3-*enyl phenyl ketone picrate*, yellow leaflets from ethanol, m. p. 160° (Found: C, 58·4; H, 5·2. $C_{26}H_{26}N_4O_9$ requires C, 58·0; H, 4·9%). Ozonolysis of the free base gave formaldehyde (38%) but no anisaldehyde.

Dimethyl-o-*nitrocinnamylphenacylammonium Bromide*.—A solution of *o*-nitrocinnamaldehyde[21] (30 g.) and aluminium isopropoxide (8 g.) in isopropyl alcohol (100 ml.) was distilled slowly with replacement of solvent. After 5 hr. no more ketone was produced, and yellow *o*-nitrocinnamyl alcohol[22] (26 g.), isolated by ether, had m. p. 61° (from benzene–ligroin) (Found: N, 8·0. Calc. for $C_9H_9NO_3$: N, 7·8%). When heated with 45% hydrobromic acid at 100° for 1 hr. it gave *o*-nitrocinnamyl bromide as a black, unpurifiable oil. The crude bromide, refluxed in ether for 3 hr. with dimethylphenacylamine, yielded *dimethyl*-o-*nitrocinnamylphenacylammonium bromide*, m. p. 178° (from ethanol) (Found: N, 6·9. $C_{19}H_{21}BrN_2O_3$ requires N, 6·9%). On rearrangement, the bromide (3·5 g.) gave a yellow oil which was extracted with boiling ligroin, leaving some tar. The ligroin deposited yellow needles (2 g.) of 1-*dimethylamino*-2-o-*nitrophenylbut*-3-*enyl phenyl ketone*, m. p. after recrystallisation 107° (Found: C, 69·8; H, 6·4. $C_{19}H_{20}N_2O_3$ requires C, 70·3; H, 6·2%). Ozonisation gave 30% of formaldehyde and no *o*-nitrobenzaldehyde. The *picrate*, fine yellow needles from ethanol–acetone, had m. p. 160—161° (Found: C, 54·3; H, 4·7. $C_{25}H_{23}N_5O_{10}$ requires C, 54·3; H, 4·2%).

Dimethyl-3-1′-*naphthylallylphenacylammonium Bromide*.—Acraldehyde (14 g.) in ether (200 ml.) was added at 0° to the Grignard reagent from 1-bromonaphthalene (52 g.) and magnesium (6 g.), and the mixture refluxed for 2 hr., giving 1-1′-*naphthylallyl alcohol* (30 g.), b. p. 128°/0·5 mm. (Found: C, 82·6; H, 6·2. $C_{13}H_{12}O$ requires C, 83·0; H, 6·5%). Treated as in the previous case, it gave a non-crystalline quaternary bromide, regarded as the title compound since it gave no formaldehyde on ozonisation. Rearrangement gave a gummy base; the

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derived 1-*dimethylamino*-2-1′-*naphthylbut*-3-*enyl phenyl ketone picrate* crystallised from ethanol in needles, m. p. 160° (Found: C, 62·7; H, 5·1. $C_{29}H_{26}N_4O_8$ requires C, 62·4; H, 4·7%). The free base recovered from the picrate could not be crystallised; when ozonised it gave 27% of formaldehyde and no 1-naphthaldehyde.

Rate constants for the rearrangement of quaternary bromides were determined in methanol at 0° (solutions 0·1N in sodium methoxide and 0·05M in bromide) by the approximation method used by Stevens.[10] At 25° the allyl and crotyl salts gave the k values $2{\cdot}0 \times 10^{-1}$ and $2{\cdot}6 \times 10^{-1}$, respectively, the high temperature coefficient indicating a high energy of activation.

The authors thank the Department of Scientific and Industrial Research for a maintenance grant to B. J. M.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY,
SHEFFIELD, 10.

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