# The Preparation and Rates of Deprotonation of Some Cyclopropylcarbinyl Ketones

By **M. John Perkins,* N. Bekir Peynircioğlu,** and **Brian V. Smith,*** Department of Chemistry, Chelsea College, Manresa Road, London SW3 6LX

A group of cyclopropylcarbinyl phenyl ketones has been prepared, and the rates of base-catalysed isotope exchange of the α-hydrogen atoms have been compared with those of suitable model compounds. The results support an earlier finding which suggests that a cyclopropyl group exerts little stabilisation on an adjacent carbanionic centre, whereas the effect of a vinyl group is considerable. Only small rate variations are found when the cyclopropane ring contains a phenyl or *p*-nitrophenyl substituent. Some novel reactions occurring during the synthesis of related polycyclic ketones are noted.

THERE is an abundant literature on the role of olefinic and cyclopropyl groups in accelerating the formation and enhancing the stability of carbonium ions.[1] In contrast, there is relatively little quantitative experimental evidence which illustrates the effect of these groups, especially cyclopropyl, adjacent to a carbanionic centre.

It has been shown that the kinetic effect of a cyclopropyl group on base-catalysed exchange of hydrogen on an adjacent carbon atom is small, although some evidence of interaction and even of homoaromatic stabilisation was noted in the formation of the homoindenyl anion.[2] Since the compounds studied earlier were hydrocarbons, it seemed of interest to synthesise and study a group of ketones in which carbanion formation could be measured under less drastic conditions. Further, in view of the apparent conflict between the stabilising and transmitting effects of cyclopropyl groups,[1] it was of interest to examine the extent of transmission of substituent effects through the three-membered ring to a negative centre.

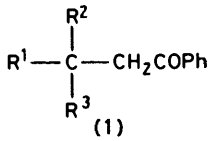
Accordingly, rates of base-catalysed hydrogen isotope exchange in compounds (1a)—(5b) were compared. In addition, exchange in the allylic ketones (6)—(8) was examined, in order to compare the effects of cyclopropyl groups and olefinic unsaturation on the rate of the exchange reaction.

With the exception of (6), the ketones examined were prepared by standard procedures. Thus cyclopropylmethyl phenyl ketone was obtained by Simmons–Smith cyclopropanation of allylphenylmethanol and oxidation of the product with chromic acid; the ketone (2c) was obtained by homologation of 1-phenylcyclopropanecarboxylic acid, and reaction of the chloride of the

[1] C. F. Wilcox, L. M. Loew, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1973, **95**, 8192, and references therein.

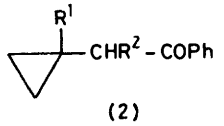
[2] M. J. Perkins and P. Ward, *Chem. Comm.*, 1971, 1134; *J.C.S. Perkin I*, 1974, 667.

homologated acid with diphenylcadmium. The diphenylcadmium procedure was also used in the synthesis of (3a), 2-phenylcyclopropylacetic acid having been prepared by cyclopropanation of the methyl ester of styrylacetic acid and hydrolysis of the product. The cyclic cyclopropylcarbinyl ketones (4c) and (5b) were obtained by carefully controlled aluminium chloride-catalysed cyclisation of the appropriate acid chlorides.



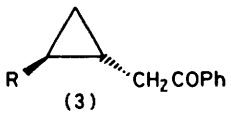
(1)

a ; $R^1 = R^2 = H$, $R^3 = CH_3$
b ; $R^1 = H$, $R^2 = R^3 = CH_3$
c ; $R^1 = R^2 = H$, $R^3 = Ph$
d ; $R^1 = R^2 = H$, $R^3 = 4\text{-}NO_2C_6H_4$
e ; $R^1 = R^2 = H$, $R^3 = PhCH_2$
f ; $R^1 = R^2 = H$, $R^3 = 4\text{-}NO_2C_6H_4CH_2$
g ; $R^1 = R^2 = CH_3$, $R^3 = Ph$



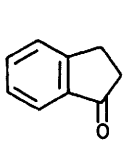
(2)

a ; $R^1 = R^2 = H$
b ; $R^1 = H$, $R^2 = CH_3$
c ; $R^1 = Ph$, $R^2 = H$
d ; $R^1 = 4\text{-}NO_2C_6H_4$, $R^2 = H$

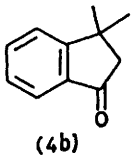


(3)

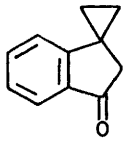
(a); R = Ph
(b); $R = 4\text{-}NO_2C_6H_4$



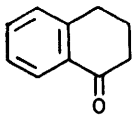
(4a)



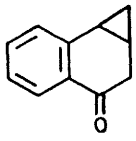
(4b)



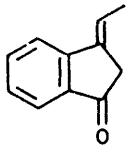
(4c)



(5a)



(5b)



(6)

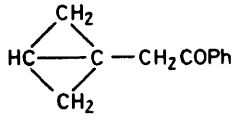
$CH_2{=}CH{-}CHR{-}COPh$

(7)

a ; R = H
b ; R = $CH_3$

$trans\text{-}PhCH{=}CH{-}CH_2COPh$

(8)



(9)

Rearrangements accompanying the formation of (4c) have already been noted,[3] and details are given in the Experimental section; the initial product of over-exposure to aluminium chloride was (6), which could be isolated in high yield. All of the nitro-compounds listed were obtained by controlled nitration of the corresponding aralkyl phenyl ketones and chromatographic separation of the products.

In order to compare the behaviour of cyclopropyl and bicyclobutyl groups in the ketone series, an attempt was made to synthesise (9) by double Simmons–Smith addition to 1-phenylbut-3-yn-1-ol. All attempts to separate the products were unsuccessful, although it was shown that the triple bond was no longer present. This experiment was based on reports of facilitation of Simmons–Smith cyclopropanation by neighbouring hydroxy, although the evidence for this is not compelling.[4] In the event, no evidence could be found for the formation of bicyclobutanes, although the triple bond was no longer present in the products. The result parallels other attempts to prepare bicyclobutanes by this procedure.[5]

[3] M. J. Perkins, N. B. Peynircioglu, and B. V. Smith, *Tetrahedron Letters*, 1975, 4165.
[4] H. E. Simmons, T. L. Cairns, S. A. Vladuchik, and C. M. Haines, *Org. Reactions*, 1973, **20**, 1.
[5] See *e.g.* M. Vidal, C. Dumond, and P. Arnaud, *Tetrahedron Letters*, 1966, 5081; M. Jautelat and V. Schwarz, *ibid.*, p. 5101; S. D. Andrews and J. C. Smith, *Chem. and Ind.*, 1966, 1636.

RESULTS

(i) *Kinetic Measurements.*—The base-catalysed deuterium exchange of the ketones was followed by n.m.r. spectroscopy according to the general method,[6] and at the probe temperature (35.5 °C). Initial experiments in dioxan–water mixtures were suitable for only some members of the series, and comparisons were therefore based on pyridine–$D_2O$–NaOD mixtures adjusted to give satisfactory solubilities and convenient rates of exchange. The pyridine alone was insufficiently basic to effect exchange at a detectable rate under the conditions employed. In order to overcome variation between kinetic runs arising from external causes, relative rates were determined by a competition method using pairs of ketones. These were chosen so that differences in the chemical shifts of the exchanging protons allowed direct observations of the exchange of both individual ketones. It also proved desirable to select pairs whose exchange rates were similar. All the results were then related to a standard (isovalerophenone) which was assigned an arbitrary rate of unity. It was established that there was close agreement between the relative rates of exchange of a given ketone measured with respect to two different intermediate ketones and related through these to the standard.

TABLE 1

Rate of exchange of isovalerophenone (1b) (*ca.* 0.5M) in pyridine–($D_2O$–NaOH) (2 : 1 v/v)

| Run | Concentration of NaOH in $D_2O$ (M) | $10^5$ Slope (log I *versus* t) |
|---|---|---|
| 1 | 0.0259 | −26.3 |
| 2 | 0.0173 | −18.0 |
| 3 | 0.0130 | −12.2 |
| 4 | 0.0086 | −8.0 |
| 5 | 0.0043 | −3.4 |

Exchange was assumed to be effectively irreversible during the initial stages, and to follow a first-order kinetic form. In each case the reaction was followed for at least 50% (and in some cases 80—90%) of its course, and was found to obey first-order kinetics. No significant exchange occurred at any other sites than those adjacent to the carbonyl group with any of the substrates, except in the allylic series where the faster isomerisation and exchange at the terminal position made any kinetic comparison impossible. The five-fold variation in base concentration (Table 1) was linearly reflected in the rate of exchange.

TABLE 2

Rates for base-catalysed exchange of the ketones at 35.5 °C relative to isovalerophenone

| Compound | Rel. rate | Compound | Rel. rate |
|---|---|---|---|
| (1a) | 2.9 | (4a) | 15.8 |
| (1b) | 1.0 | (4b) | 10.7 |
| (1c) | 8.6 | (4c) | 33.1 |
| (1d) | 39.1 | (5a) | 6.2 |
| (1e) | 4.2 | (5b) | 6.9 |
| (1f) | 20.3 | (6) | Fast |
| (1g) | 1.0 | (7a) | Fast * |
| (2a) | 4.8 | (7b) | Fast * |
| (2b) | 0.76 | (8) | Fast * |
| (2c) | 7.9 | | |
| (2d) | 36.1 | | |
| (3a) | 11.1 | | |
| (3b) | 50.6 | | |

* Rearrangement observed in each case.

In some cases the solubility of the ketone was such that the proportion of pyridine in the medium was increased to keep the reaction mixture homogeneous; the relative reactivities were assumed to be unaffected, and this was supported by control experiments with pairs of more soluble ketones which could be studied in solvent mixtures of various compositions. Table 2 lists the relative rates for the compounds (1)—(8), at a constant concentration of base. Isovalerophenone (1b) is taken as an arbitrary standard (relative rate 1.0).

(ii) *Stereoselectivity of Exchange in* (5b).—Three separate experiments with different base concentrations (see Experimental section) showed that *ca.* 20, 33, and 43% exchange had occurred in 45 min. From the n.m.r. it was shown that (a) no side reaction occurred and (b) that no significant stereoselectivity in the exchange could be detected. The recovery of the samples was good (*ca.* 80%).

DISCUSSION

It has been pointed out recently that kinetic acidities may give only a rough guide to carbanion stabilities.[7] For a series of closely related molecules studied under the same conditions this criticism is probably not serious; certainly, to draw any conclusions from the present results, it is necessary to assume that the variations in reaction rates do reflect variations in enolate stability, and are not unduly perturbed by *e.g.* differential internal return. It is gratifying to note that, where comparisons can be made, the present results usually parallel those found for deprotonation of aralkanes (see Table 3).

In general, the present work supports the idea that cyclopropyl group stabilisation of carbanions is small, and that the transmission of substituent effects is poor. The olefinic ketones showed much greater reactivity, in line with the previously observed rate difference of *ca.* $10^4$ between olefinic and cyclopropyl substituent effects on benzylic carbanion formation.[2]

Theoretical considerations suggest that the three-membered ring might be expected to stabilise an adjacent negative charge by virtue of (i) its relatively low-lying LUMO and (ii) the inductive stabilisation arising from the electronegativity of the cyclopropyl group. Calculations have shown that the cyclopropylcarbinyl anion has classical character,[8] although in other calculations there seems to be disagreement on whether interaction between the three-membered ring and the carbanion centre is stabilising or destabilising.[9,10] Earlier work of a non-kinetic nature suggested that any stabilising effect is small, even when electron-withdrawing groups are attached to the cyclopropane.[11]

Against this background it was of interest to examine the kinetic behaviour of a series of compounds in which

[6] J. Warkentin and C. Barnett, *J. Amer. Chem. Soc.*, 1968, **90**, 4629.
[7] F. G. Bordwell, W. S. Matthews, and N. R. Vanier, *J. Amer. Chem. Soc.*, 1975, **97**, 443.
[8] M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, 1963, **2**, 403.
[9] I. J. Miller, *Austral. J. Chem.*, 1970, **23**, 29.
[10] W. C. Danen, *J. Amer. Chem. Soc.*, 1972, **94**, 4335.
[11] See *e.g.* G. W. Cannon, A. A. Santilli, and P. Shenian, *J. Amer. Chem. Soc.*, 1959, **81**, 4264; A. I. Shatenshtein, *Adv. Phys. Org. Chem.*, 1963, **1**, 176; A. F. Maerker and J. D. Roberts, *J. Amer. Chem. Soc.*, 1966, **88**, 1742.

the orientation of the cyclopropane ring was fixed with respect to the carbanionic centre. It is convenient to divide the following discussion into two parts, relating to (a) open chain and (b) cyclic ketones.

(a) *Open-chain Ketones.*—Comparison of the rates for (1a), (1b), and (2a) shows some enhancement by the cyclopropyl group (*ca.* 5). The faster rate for (1a) over that for (1b) is consistent with an inductive destabilisation of the incipient anions, with possibly a steric effect contributing; this is also seen with the α-methyl substituted (2b) *versus* (2a). Two methyl groups have almost twice the effect on the rate [(1g) *versus* (1c)]. Ketone (1b) rather than (1a) is chosen as a reference compound for (2a), since (1a) lacks any steric or inductive retardation due to a β-methyl substituent. Similarly, (1g) is a better reference than (1c) for (2c); (2c) reacts eight times faster than (1g) whereas the relative rates of (1c) and (2c) are *ca.* 1.

Comparison of (3a) and (1e) shows an enhancement of *ca.* 3, although (1e) lacks any β- or γ-substituents; a larger rate ratio would be expected with a more appropriate model, although steric factors in this comparison should be less significant than in the preceding case. Nitro-substitution in the remote phenyl ring in (3a), (1c), and (1e) led to the expected rate increase; however, the 'nitro-effect' [(3b) *versus* (3a) = 4.56; (1f) *versus* (1e) = 4.83] is not enhanced by transmission across the three-membered ring, which is a poor transmitter of resonance effects. Furthermore, the comparison of (2d) *versus* (2c) (4.57 : 1) shows that the nitro-group exerts its effect inductively as this value is identical to that for (3b) *versus* (3a). It is also of interest to note that for (1d and c) and (1f and e) the enhancement due to the nitro-group is 4.49 and 4.83, respectively, despite the more remote situation of the nitro-group in (1f). Similar behaviour in other systems has been ascribed by Bordwell to through-space effects.[12] The near identity of the enhancements due to a nitro-group suggests that the electron demand of the nitrophenyl group cannot compete significantly with stabilisation of the negative charge by the carbonyl oxygen.

By comparison with earlier work, the effect of a three-membered ring is less in the series $RCH_2COPh$ than for $RCH_2Ph$ (Table 3). This is to be expected, since the

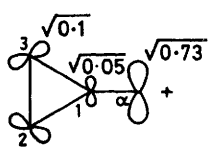
TABLE 3

Comparisons of the relative rates of base-catalysed H–D exchange of $RCH_2COPh$ and $RCH_2Ph$

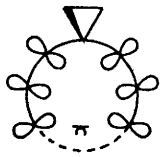
| R | $k_{RCH_2COPh}$ | $k_{RCH_2Ph}$ |
|---|---|---|
| $(CH_3)_2CH$ | 1 | 1 |
| $CH_3CH_2CH_2$ | | 3.84 |
| $CH_3CH_2$ | 2.9 | |
| cyclo-$C_3H_5$ | 4.9 | 42 |
| $CH_2$=CH | v. fast | $2 \times 10^5$ |

enolate anions are inherently more stable than benzylic ones.

Taken together, these observations support the conclusion that the ability of the cyclopropyl group to stabilise an adjacent negative charge or to transmit resonance effects is very small. There is a very considerable difference in the stabilisation of cyclopropylcarbinyl cations and anions; in the carbanion series the effect of olefinic groups is far greater than that of cyclopropyl. In respect of the transmission of electron effects, the present work reveals no appreciable conjugative transfer across the cyclopropyl ring. Indeed, it now seems quite clear that the only circumstances in which conjugation between electron-rich and -poor centres may be transmitted through a cyclopropane ring to a significant extent actually involve fission of a cyclopropane bond ('frangomeric participation').[13] The failure to transmit conjugative effects has been rationalised in terms of a simple MO picture.[1] The Walsh-like *p* orbital coefficients in the LUMO of a cyclopropylcarbinyl cation at C-2 and -3 are $\sqrt{0.1}$ (9). Any resonance interaction with *p* electrons on an atom attached to C-2 or -3 must then be small compared with that to be expected were they on an atom attached to C-α.




(9)




(10)


(11)

We were interested in reports[14,15] of aromatic delocalisation where the normal π-electron system is interrupted by a spiro-fused cyclopropane which contributes electrons to the delocalised system [*cf.* (10)], and it was this which prompted us to extend our experimental investigations to probe the possibility of conjugative stabilisation in the generalised structure (11).

The similarity between the effect of introducing a *p*-nitro-substituent into (2c) ($k_{(2d)}/k_{(2c)}$ 4.6) and that of introducing a similar substituent into (3a) ($k_{(3b)}/k_{(3a)}$ 4.5) suggests that this type of conjugative effect is also negligible. Reference to the orbital diagram (9) shows that the *p* orbital coefficient at C-1 is even smaller than that at C-2 or -3, so that any conjugative transmission in structures typified by (11) should indeed be tiny.

(b) *Cyclic Ketones.*—The observed rates for the cyclic ketones do not differ significantly from each other and, because of the complex interaction of electronic, steric, and conformational effects, a detailed discussion is not justified.

(i) For (*E*)-3-ethylideneindanone (6) the rate of exchange was too fast to be compared with the reference or cyclopropylcarbinyl ketones. The possibility that (6) undergoes prototropic rearrangement to 3-ethylindenone (6a) in base was excluded by the non-occurrence of exchange of the vinyl proton in deuteriated solvents.[3]

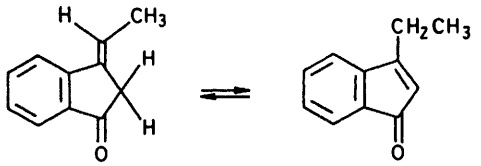
[12] F. G. Bordwell and J. E. Bartmess, *J. Org. Chem.*, in the press.

[13] R. S. Brown and T. G. Traylor, *J. Amer. Chem. Soc.*, 1973, **95**, 8025.

[14] R. A. Clark and R. A. Fiato, *J. Amer. Chem. Soc.*, 1970, **92**, 4736; S. W. Staley and W. G. Kingsley, *ibid.*, 1973, **95**, 5804.

[15] P. Rys, P. Skrabal, and H. Zollinger, *Tetrahedron Letters*, 1971, 1797.

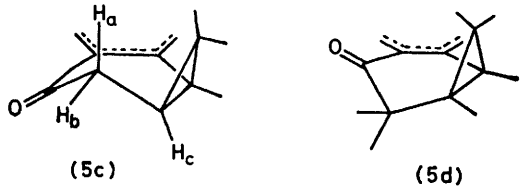
Protonation of the dienolate intermediate to form an antiaromatic indenone [16] is considered unfavourable.



(6) (6a)

(ii) Tetralone (5a) and its 3,4-methylene derivative (5b) were shown to exchange at C-2, and at comparable rates. Using the same argument as was applied in the acyclic series, it is probable that the absence of substituents at C-3 and -4 in (5a) may mean that (5b) is not showing the true kinetic effect of its three-membered ring. It may even be that exchange at C-2 is hindered by the presence of the three-membered ring.

A consideration of the structure of (5b) using Dreiding models suggests that the cyclohexenone ring in (5b) exists in two non-equivalent interconverting conformations (5c) and (5d); of these two forms, (5d) might have



(5c) (5d)

greater stability because the eclipsing of 2-$H_a$ and 2-$H_b$ bonds with 3-$CH_2$ and 3-$H_c$ bonds, respectively, in (5c) is absent in (5d). $H_a$–$H_d$ interaction is also more pronounced in (5d). The 220 MHz n.m.r. spectrum did not suggest a large preference for (5c) however, although some uncertainty exists about the extent to which a Karplus correlation between coupling constant and dihedral angle is modified by a cyclopropane ring. As has been mentioned, no preferential exchange of $H_a$ or $H_b$ was detected in an interrupted exchange experiment.

(iii) In the remaining indanone derivatives, the comparison of (4a) with (4b) shows a small effect (*ca.* 1.5) due to β-methyl substitution. This is much less than that observed in the acyclic series; *e.g.* with (1c and g) the rate difference is a factor of 8.7 due to two β-methyl groups. Possibly this can be associated with relief of eclipsing strain on deprotonation of (4b).

One of the more noteworthy results seems to be that indanone exchanges faster than tetralone by a factor of 2.5. In related work with benzylic carbanions,[2] it had been shown that indane is less reactive than tetralin by a factor of *ca.* 10, and an explanation was offered in terms of the increased ring strain in forming the planar anion. The result with the cyclic ketones is not consistent with this, and although a number of factors can be considered, no compelling explanation emerges for the discrepancy between the two series of compounds.

Comparison of the rate of exchange of indane-3-spirocyclopropan-1-one (4c) with rates for (4a and b) showed modest rate increases, with (4b) as a better reference compound.

There is in (4c) a spatially fixed relationship between the three-membered ring and the developing *p* orbital of the anion, and the plane of the three-membered ring is bisected with respect to the carbanion. Calculations suggest that this geometry is disfavoured by *ca.* 1.5 kcal $mol^{-1}$, with respect to a perpendicular arrangement.[10] Unfortunately the construction of a suitable model compound with the ' perpendicular ' geometry has not been accomplished.

Despite this apparently unfavourable geometry, the actual rate enhancement found for (4c) seems far too small to justify consideration of any ' spiroaromatic ' character [14,15,17] in the enolate anion derived from it.

It may be of interest to investigate further systems in which the geometry of the three-membered ring is defined with respect to the developing carbanion centre, and this is under consideration. In general our work has not so far permitted the separation of inductive and conjugative effects, but the latter, if they exist, must be very small.

## EXPERIMENTAL

$^1H$ N.m.r. spectra were recorded on 60 or 90 MHz Perkin-Elmer spectrometers. 220 MHz Spectra were recorded by P.C.M.U. Harwell, as were high resolution mass spectra. Other mass spectral data were recorded on a Micromass 12F spectrometer. G.l.c. analyses used 15% Carbowax 20M (on acid-washed Celite) or OV 101 columns on a Perkin-Elmer F30 instrument; preparative g.l.c. was by the use of a Pye series 105 chromatograph with a 15 ft column packed with silicone E-30 on acid-washed Celite unless otherwise stated. T.l.c. was on silica gel.

For the kinetic studies pyridine was allowed to stand over sodium hydroxide and then distilled from and stored over molecular sieves; the n.m.r. spectrum of each batch was examined for a water signal. Liquid ketones were washed with dilute alkali, the ethereal extract dried, and the residue distilled. Each sample was examined by g.l.c. and, if necessary, purified by preparative g.l.c., before measurement. Solid ketones were crystallised to constant m.p. Elemental analyses were performed by B.M.A.C., Teddington.

*Preparation of Materials.*—(a) *Compounds* (1a—g). Butyrophenone (1a) and isovalerophenone (1b) were commercial samples which were twice distilled and checked (g.l.c.) for purity. 1,3-Diphenylpropan-1-one (1c) was prepared by reduction ($H_2$–Pd–C) of chalcone and had m.p. 69—70° (lit.,[18] 71—72°). Nitration ($HNO_3$–$Ac_2O$ at −20°) gave (1d) in low yield (15%) and, after purification by t.l.c. on silica gel, this had m.p. 99—100° (lit.,[19] 99.5—100.5°). 1,4-Diphenylbutan-1-one (1e) was prepared from 4-phenylbutanoyl chloride and diphenylcadmium in low yield (19%), m.p. 53—55° (lit.,[20] 53—55°) after recrystallisation

[16] P. H. Lacy and D. C. C. Smith, *J. Chem. Soc.* (*C*), 1971, 41.
[17] C. F. Chiang and J. F. Wilcox, *J. Amer. Chem. Soc.*, 1973, **95**, 2885; M. F. Semmelhack, R. J. de Franco, Z. Margolin, and J. Stock, *ibid.*, p. 426; H. J. Reich and J. M. Renga, *Tetrahedron Letters*, 1974, 2747.
[18] F. Strauss and H. Grindel, *Annalen*, 1924, **439**, 276.
[19] W. Davey and J. A. Hearne, *J. Chem. Soc.*, 1964, 4978.
[20] K. Auwers and K. Möller, *J. prakt. Chem.*, 1925, **109**, 124.

from light petroleum (b.p. 60—80°). This was nitrated to give (1f) following the procedure used with (1c); the *p*-nitro-derivative (1f) was purified [t.l.c., 5—15% EtOAc–light petroleum (b.p. 60—80°)] and after recrystallisation from ether had m.p. 107—109° (lit.,[21] 109—110°).

3-Methyl-3-phenylbutyrophenone (1g) was formed as a by-product accompanying 3,3-dimethylindanone (4b) prepared by the $AlCl_3$-catalysed cyclisation of 3,3-dimethylacryloyl chloride in benzene. Attempted cyclisation of the corresponding acid [22a] gave back unchanged starting material; the reported formation of 3,3-dimethylacrylophenone [22b,c] also failed in our hands. Aluminium chloride (27 g) was added during 1 h to a stirred solution of acid halide [prepared from the acid (18 g) and oxalyl chloride] (27 g) in benzene (100 ml). The mixture was stirred for a further 30 min at room temperature, and then at 70° for 30 min; the organic products were then distilled to give 3,3-dimethylindanone (2.3 g, 8%), b.p. 133—137° at 19—21 mmHg (lit.,[22a] 135° at 20 mmHg), and 3-methyl-3-phenylbutyrophenone (8 g, 34%), b.p. 132—136° at 0.3 mmHg (lit.,[22c] 162—164° at 5 mmHg), m.p. 33—36°; semicarbazone, m.p. 178—179° (lit.,[22c] 178.5—179°).

(b) *Compounds* (2a—d). For the synthesis of cyclopropylmethyl phenyl ketone (2a) and its 1-methyl derivative (2b) the appropriate olefinic alcohol was converted to the cyclopropyl derivative by the Simmons–Smith procedure, and the alcohol then oxidised ($CrO_3$–acetone). Thus 1-phenylbut-3-en-1-ol [23] was converted into 1-phenyl-2-cyclopropylethan-1-ol [24] according to the method of Shank and Shechter [25] in 67% yield and had b.p. 96—100° at 1.5 mmHg (lit.,[24] 125—130° at 12 mmHg). The ketone (2a) was obtained in 44% yield from this alcohol, b.p. 64—66° at 0.2 mmHg (lit.,[26] 124—125° at 10 mmHg). Similarly, 2-methyl-1-phenylbut-3-en-1-ol [27] was cyclopropanated with $CH_2I_2$ and Zn–Cu couple [28] to give *1-phenyl-2-cyclopropylpropan-1-ol* as an oil (61%), b.p. 70° at 0.25 mmHg, 80° at 0.4 mmHg; $\nu_{max.}$ (neat) 3 700—3 150 and 1 020 $cm^{-1}$; $\delta(CDCl_3)$ 7.24 (5 H, s, aromatic), 4.6 (1 H, m, HOC*H erythro* and *threo*), 2.6 (1 H, s, OH), 1.75 (1 H, m, *H*CMe *erythro* and *threo*), 0.85 (4 H, m, $CH_3$ and 1-cyclopropyl), and 0—0.76 (4 H, m, cyclopropyl *erythro* and *threo*); *m/e* 176 ($M^+$). Further characterisation was not attempted, and the alcohol was oxidised ($CrO_3$–acetone) to *1-phenyl-2-cyclopropylpropan-1-one* (2b), isolated as an oil (85%), b.p. 69—71° at 0.3 mmHg. This was further purified by preparative g.l.c. at 190°, $\delta(CCl_4)$ 0.2—0.65 (4 H, m, cyclopropyl), 0.65—1.40 (4 H, d and m, $CH_3$ and cyclopropyl), 2.7 (1 H, m, methine), 7.2—7.6br (3 H, m, aromatic), and 7.7—8.0br (2 H, m, aromatic); $\nu_{max.}$ (neat) 1 690 $cm^{-1}$ (C=O) (Found: *m/e*, 174.104 4. $C_{12}H_{14}O$ requires *M*, 174.104 5).

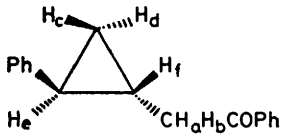
*Phenyl 1-phenylcyclopropylmethyl ketone* (2c). This was prepared by two routes; in our hands the second proved to be more efficient. (i) 3-Phenylbut-3-en-1-yl acetate [29] was cyclopropanated with pre-prepared zinc–copper couple [4] to give *2-(1-phenylcyclopropyl)ethyl acetate* in 76% yield. A small sample was distilled, b.p. 68—72° at 0.2 mmHg, $\nu_{max.}$ (neat) 1 740 and 1 240 $cm^{-1}$; $\delta(CCl_4)$ 7.2 (5 H, m, aromatic), 3.95 (2 H, t, $CH_2O$), 1.7—2.0 (5 H, m, $CH_3$ and $CH_2CH_2O$), and 0.6—0.9 (4 H, m, cyclopropyl), but further characterisation was not attempted. Saponification of the ester gave 2-(1-phenylcyclopropyl)ethanol (98%) with n.m.r. and i.r. spectra in agreement with literature data.[30] The product of attempted cyclopropanation of 3-phenylbut-3-en-1-ol (prepared by saponification of the corresponding acetate [29]) was a mixture from which the desired alcohol was not easily separated; the reaction with the ester gave a cleaner product. Oxidation of the phenylcyclopropylethanol by the procedure of Wilt *et al.*[30] gave the impure acid in poor yield. (ii) (1-Phenylcyclopropyl)acetic acid was synthesised in better yield (*ca.* 50%) from commercial 1-phenylcyclopropanecarboxylic acid *via* the acid chloride [31] and Arndt–Eistert homologation to give a product, m.p. 40—45° (lit.,[30] 52—53°).

(1-Phenylcyclopropyl)acetic acid from (i) or (ii) afforded the acid chloride with oxalyl chloride in benzene, and this was used without further purification, to prepare *phenyl 1-phenylcyclopropylmethyl ketone* (2c) as follows. The acid chloride [from acid (5.79 g)] in dry benzene (30 ml) was added to a stirred suspension of diphenylcadmium [from PhBr (7.98 g)] in dry benzene (70 ml) at room temperature over 15 min. The mixture was refluxed for 6 h, cooled, and treated with excess of dilute hydrochloric acid; the organic layer was washed ($Na_2CO_3$ solution, then $H_2O$), and dried; removal of solvent left a solid which had m.p. 71—73° (from hexane) (3.55 g, 46%), $\nu_{max.}(CHCl_3)$ 1 690 $cm^{-1}$ (C=O), $\delta(CDCl_3)$ 0.95 (4 H, m, cyclopropyl), 3.26 (2 H, s, $CH_2$), 7.0—7.32 (8 H, m, aromatic), and 7.52—8.0 (2 H, m, aromatic) (Found: C, 86.85; H, 7.15. $C_{17}H_{16}O$ requires C, 86.4; H, 6.85%). This ketone (1.10 g) in acetic anhydride (20 ml) was added in portions over 25 min to a stirred mixture of fuming nitric acid (5.0 ml) and acetic anhydride (20 ml) at *ca.* −20°. After a further 5 min the mixture was carefully added to hot water (150 ml) with stirring; the cooled mixture was extracted with ether, washed free of acid, dried, and evaporated to give a yellow residue. Preparative t.l.c. [5% EtOAc in light petroleum (b.p. 60—80°)] permitted isolation of *1-(4-nitrophenylcyclopropyl)methyl phenyl ketone* (2d) (0.05 g, 4.2%), m.p. 81—82°, $\nu_{max.}(CHCl_3)$ 1 695, 1 520, and 1 350 $cm^{-1}$; $\delta(CDCl_3)$ 1.03br (4 H, s, cyclopropyl), 3.32 (2 H, s, $CH_2$), and 7.1—8.15 (9 H, m, aromatic including a distinguishable AA′BB′ pattern for the 4-nitrophenyl group) (Found: *m/e* 281.105 0. $C_{17}H_{15}NO_3$ requires *M*, 281.105 2). *1-(2-Nitrophenylcyclopropyl)methyl phenyl ketone* was also isolated (0.15 g, 12%), $\nu_{max.}(CHCl_3)$ 1 690, 1 525, and 1 355 $cm^{-1}$, $\delta(CHCl_3)$ 0.9 (4 H, m, cyclopropyl), 3.45 (2 H, s, $CH_2$), and 7.17—7.99 (9 H, m, aromatic) (Found: C, 72.95; H, 5.4. $C_{17}H_{15}NO_3$ requires C, 72.6; H, 5.35%).

(c) *Compounds* (3a *and* b). *Phenyl* trans-*(2-phenylcyclopropyl)methyl ketone*. (i) Methyl *trans*-styrylacetate [32]

[21] W. Dale and C. W. Strobel, *J. Amer. Chem. Soc.*, 1954, **76**, 6172.
[22] (*a*) R. Gelin and B. Chantegrel, *Bull. Soc. chim. France*, 1971, 2542; (*b*) G. Darzens, *Compt. rend.*, 1929, **189**, 766; 1940, **211**, 435; (*c*) L. I. Smith and V. A. Engelhardt, *J. Amer. Chem. Soc.*, 1949, **71**, 2671.
[23] G. G. Smith and K. J. Voorhees, *J. Org. Chem.*, 1970, **35**, 2182.
[24] P. T. Lansbury and V. A. Pattison, *J. Amer. Chem. Soc.*, 1962, **84**, 4298.
[25] R. S. Shank and H. Shechter, *J. Org. Chem.*, 1959, **24**, 1825.
[26] M. Hanack and H. M. Ensslin, *Annalen*, 1966, **697**, 100.
[27] O. K.-Hono, *Ann. Chim.*, 1940, **13**, 175.
[28] R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, 1970, **35**, 2057.
[29] E. G. E. Hawkins and R. D. Thompson, *J. Chem. Soc.*, 1961, 370.
[30] J. W. Wilt, L. L. Marawetz, and J. F. Zawadzki, *J. Org. Chem.*, 1966, **31**, 3018.
[31] J. W. Wilt and B. H. Philip, *J. Org. Chem.*, 1959, **24**, 616.
[32] D. Vorlander, *Annalen*, 1906, **345**, 106.

(from styrylacetic acid–$CH_3OH$–$H^+$) was cyclopropanated in the usual way to give methyl *trans*-(2-phenylcyclopropyl)acetate (76%), b.p. 86° at 0.3 mmHg (lit.,[33] 86—88° at 0.1 mmHg), δ($CCl_4$) 0.57—1.8 (4 H, m, cyclopropyl), 2.24 (2 H, d, $CH_2$), 3.55 (3 H, s, $CH_3$), and 7.02 (5 H, m, aromatic); $\nu_{max.}$ (neat) 1 745 $cm^{-1}$ (C=O). (ii) The ester from (i) (14.8 g, 0.078 mol) was saponified by heating under reflux for 5 h with KOH (10 g) in $H_2O$ (32 ml) and MeOH (45 ml). Recovery of the acid gave an oil, solidifying on standing (12.0 g, 90%), b.p. 118—120° at 0.15 mmHg (lit.,[33] 98—100° at 0.1 mmHg); δ($CCl_4$) 0.5—1.95 (4 H, m, cyclopropyl), 2.36 (2 H, d, $CH_2$), and 7.1 (5 H, m, aromatic); $\nu_{max.}$($CCl_4$) 1 710 $cm^{-1}$ (C=O). (iii) The acid, with $SOCl_2$, gave the chloride which showed $\nu_{max.}$ (neat) 1 800 $cm^{-1}$. Attempted condensation with benzene ($AlCl_3$) gave tarry products or, at lower temperature, no reaction. The desired *ketone* (3a) was obtained from $Ph_2Cd$ and the acid chloride by the method described above and, after recrystallisation from hexane–Norit, was obtained as crystals (71%), m.p. 75—76°, δ($CCl_4$; 220 MHz) 0.87 (1 H, m, $H_d$ or $H_c$), 1.05 (1 H, m, $H_d$ or $H_c$), 1.50 (1 H, m, $H_f$), 1.78 (1 H, $H_c$), 2.95 (1 H, 2 × d, $H_a$ or $H_b$), 3.28 (1 H, 2 × d, $H_b$ or $H_a$), 7.0—7.3 (5 H, m, aromatic), 7.35—7.62 (3 H, m, aromatic), and 7.35—7.62 (2 H, d, aromatic); $\nu_{max.}$($CCl_4$) 1 690 $cm^{-1}$ (C=O); *m/e* 236 ($M^+$) (Found: C, 86.75; H, 6.85. $C_{17}H_{16}O$ requires C, 86.4; H, 6.85%).



(3a)

Nitration of ketone (3a) (2.0 g, 0.008 5 mol) by the method described previously gave a yellow solid (2.24 g). By t.l.c., eluting with 5% EtOAc in light petroleum (b.p. 60—80°), there was obtained trans-2-(*4-nitrophenylcyclopropyl*)*methyl phenyl ketone* (3b) (0.15 g, 7%), m.p. 94—96°, $\nu_{max.}$($CHCl_3$) 1 690, 1 520, and 1 350 $cm^{-1}$; δ($CDCl_3$) 0.3—2.25 (4 H, m, cyclopropyl), 3.0—3.1 (2 H, d, $CH_2$), and 7.02—8.2 (9 H, m, aromatic with distinguishable $A_2B_2$ pattern for 4-nitrophenyl group) (Found: C, 72.65; H, 5.65. $C_{17}H_{15}NO_3$ requires C, 72.6; H, 5.35%). A less polar product, isolated as an oil, is believed to be *trans*-2-(2-nitrophenylcyclopropyl)methyl phenyl ketone (0.15 g, 7%), $\nu_{max.}$ (neat) 1 690, 1 525, and 1 350 $cm^{-1}$; δ($CCl_4$) 0.65—1.05 (2 H, m, cyclopropyl), 1.1—1.65 (2 H, m, cyclopropyl), 2.75—3.1 (2 H, 2 × d, $CH_2$), and 7.0—7.9 (9 H, m, aromatic). This was not further purified.

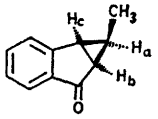
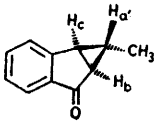
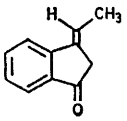
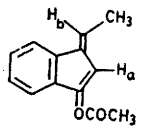
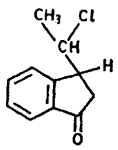
(d) *Compounds* (4a—c), (5a *and* b), *and* (6). Indanone (4a) and tetralone (5a) were commercial samples. The preparation of 3,3-dimethylindanone (4b) has been described earlier [with (1g)].

*Indane-3-spirocyclopropan-1-one* (4c). (1-Phenylcyclopropyl)acetyl chloride [from the acid (2.89 g, 0.016 5 mol)] in dry, freshly distilled methylene chloride (60 ml) was added dropwise, over 30 min, to a magnetically stirred cooled suspension of powdered anhydrous aluminium chloride (3.30 g, 0.024 7 mol) in freshly distilled methylene chloride (100 ml) cooled to −5°. The mixture was then treated with cold dilute HCl, and the organic layer was separated, washed, and dried ($Na_2SO_4$). Removal of solvent left a residue which crystallised on cooling. Recrystallisation from light petroleum (b.p. 60—80°) gave the *ketone*, m.p. 43—45° [2.31 g, 89% (based on the acid used)], b.p. 78—80° at 0.1 mmHg, $\nu_{max.}$ (neat) 1 705 $cm^{-1}$ (C=O); δ($CCl_4$) 0.9br (4 H, s, cyclopropyl), 2.42 (2 H, s, $CH_2$), and 6.19—7.49 (4 H, m, aromatic) (Found: C, 83.55; H, 6.3. $C_{11}H_{10}O$ requires C, 83.5; H, 6.35%).

*Related Experiments illustrating Rearrangement accompanying Cyclisation.* (*For Discussion see ref.* 3).—(i) (1-Phenylcyclopropyl)acetyl chloride (0.18 mol) in dry methylene chloride (30 ml) was added dropwise, over 1 h to a magnetically stirred suspension of powdered anhydrous $AlCl_3$ in methylene chloride (80 ml) at 5°. After 12 h at 3—5° the mixture was hydrolysed (dilute HCl), the organic layer was separated and solvent was removed. The residue was heated under reflux with aqueous $Na_2CO_3$ to remove acid

TABLE 4

Spectroscopic properties of the components isolated from the $AlCl_3$-catalysed cyclisation of (1-phenylcyclopropyl)acetyl chloride

| Compound | Structure | Spectroscopic data |
|---|---|---|
| A |  | δ($CCl_4$) 0.8 (3 H, d, $CH_3$), 1.6—2.9 (m, $H_a$), 2.19—2.492 (d, $H_b$), 2.83—3.04 (2 × d, $H_c$), and 7.05—7.65 (4 H, m), ($J_{ab}$ 5, $J_{ac}$ 5.5 Hz); *m/e* 158 ($M^+$); $\nu_{max.}$($CCl_4$) 1 725 $cm^{-1}$ |
| A |  | δ($CCl_4$) 1.14—1.64 (4 H, d, and m, $CH_3$ and $H_{a'}$), 2.02—2.22 (2 × d, $H_b$), 2.18—2.48 (2 × d, $H_c$), and 6.98—7.60 (4 H, m, aromatic) ($J_{a'b}$ 3, $J_{a'c}$ 3 Hz), *m/e* 158 ($M^+$); $\nu_{max.}$ ($CCl_4$( 1 725 $cm^{-1}$ |
| B[≡6] |  | δ($CCl_4$) 1.80 (3 H, d, $CH_3$), 2.95 (2 H, s, $CH_2$), 5.85—6.45 (1 H, m, vinylic), and 7.0—7.85 (4 H, m, aromatic), no NOE observed in aryl proton resonance on irradiation at δ 1.80; *m/e* 158 ($M^+$); $\nu_{max.}$($CCl_4$) 1 720 $cm^{-1}$ |
| B′ |  | δ($CCl_4$) 2.15 (3 H, d, $CH_3$), 2.30 (3 H, s, $CH_3CO$), 6.65 (1 H, q, $H_b$), 6.75 (1 H, s, $H_a$), 7.0—7.7 (4 H, m, aromatic); on irradiation at δ 6.65, δ 2.15 changes to s; on irradiation at δ 2.15, δ 6.65 changes to s; $\nu_{max.}$($CCl_4$) 1 760and 1 650$cm^{-1}$; $\lambda_{max.}$(EtOH) 265 (log ε 4.97), and 310 nm (4.29); *m/e* 200 ($M^+$) |
| C and C′ |  | |
| (a) C | | δ($CCl_4$) 1.50 (3 H, d, $CH_3$), 2.55 (2 H, d, $CH_2$), 3.42—3.75 (1 H, dt, benzylic), 4.19—4.63 (1 H, dq, β-$CH_3$), and 7.2—7.8 (4 H, m, aromatic); $\nu_{max.}$ ($CHCl_3$) 1 725 $cm^{-1}$; *m/e* 194 ($M^+$) and 159 ($M^+$ − Cl) |
| (b) C′ | | δ($CCl_4$) 1.20 (3 H, d, $CH_3$), 2.10 (2 H, d, $CH_2$), 3.60—4.95 (1 H, dt, benzylic), 4.15—4.48 (1 H, dq, β-$CH_3$), 7.22—7.82 (4 H, m, aromatic); $\nu_{max.}$($CHCl_3$) 1 725 $cm^{-1}$, *m/e* 194 ($M^+$) and 159 ($M^+$ − Cl) |

[33] J. J. Sims, personal communication.

chloride. Extraction (ether), washing, and drying ($Na_2SO_4$) gave 3.0 g of residue after removal of solvent. T.l.c. showed four components were present. Preparative t.l.c. [eluting with 5% EtOAc in light petroleum (b.p. 60—80°)] or preparative g.l.c. gave four fractions, B, A, C, and C′ although complete separation of C and C′ was not possible by the g.l.c. procedure. Preparative g.l.c. on a 15 ft column of Carbowax 20M on acid washed Celite permitted separation of two components A and A′ from A. C and C′ were distinguished on a 2 m analytical g.l.c. column of 2.5% OV 101 on acid-washed Celite. These products were characterised by their spectroscopic properties listed in Table 4.

When the reaction was carried out at lower temperature (−5 °C), (4c) was formed initially, as shown by g.l.c., but after further reaction this disappeared to be replaced by (6) (≡B), together with C and C′ (in the ratio C : C′ = 4 : 1). The formation of A and A′ was thus shown not to occur in the reaction mixture, but only on work-up and exposure to the basic conditions employed to destroy unreacted acid chloride.

(E)-3-*Ethylideneindanone* (6). (1-Phenylcyclopropyl)-acetyl chloride [from the acid (5.56 g, 0.003 2 mol)] in freshly distilled methylene chloride (100 ml) was added dropwise over 40 min to a magnetically stirred suspension of powdered anhydrous $AlCl_3$ (6.13 g, 0.048 7 mol) in freshly distilled methylene chloride (140 ml) at 0°. The mixture was stirred at 0° for 1 h and then hydrolysed with cold dilute HCl. The organic layer was separated, washed in the usual way and dried; removal of solvent left a residue which was distilled to give the *ketone* [4.28 g, 86% (based on the acid)], b.p. 98° at 0.35 mmHg. On cooling it solidified, and was repeatedly crystallised from light petroleum (b.p. 60—80°) to give a pale yellow solid, m.p. 51°, homogeneous on g.l.c. and t.l.c. (Found: C, 83.45; H, 6.35. $C_{11}H_{10}O$ requires C, 83.5; H, 6.35%). No NOE was detected in the aromatic proton signal on irradiation at the methyl resonance; on this basis the compound is assigned the *E* stereochemistry.

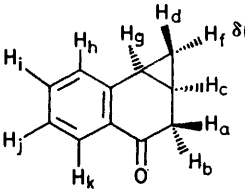
(E)-3-*Ethylideneinden*-1-*yl acetate*. The above ketone (0.095 g) was dissolved in acetic anhydride (10 ml) with sodium acetate (0.2 g) and heated under reflux (2 h). The mixture was concentrated, filtered from sodium acetate, and the product (0.1 g, 85%) obtained as a pale yellow low melting solid, *m/e* 200 ($M^+$) with the spectroscopic properties given in Table 4 (compound B′).

3,4-*Methylenetetralone* (5b). (i) Ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylate, prepared from the addition of ethyl diazoacetate to styrene, was hydrolysed with aqueous alcoholic alkali, and the *cis*-acid separated [34] in 34% yield, m.p. 105—106° (lit.,[35] 106—109°). Homologation of the acid (8.35 g, 0.051 5 mol) *via* the Arndt–Eistert method, gave cis-(2-*phenylcyclopropyl*)*acetic acid* [4.04 g, 44% (based on the starting *cis*-acid)]; $\nu_{max.}(CCl_4)$ 1 705 and 3 600—2 200 $cm^{-1}$; $\delta(CCl_4)$ 0.46—2.26 (6 H, m, $CH_2$ and cyclopropyl) and 7.5br (5 H, s, aromatic), as yellow oil which was not further purified. (ii) *cis*-(2-Phenylcyclopropyl)acetyl chloride [from the acid (4.04 g, 0.023 mol) and oxalyl chloride in benzene] was cyclised under the same conditions as used for the synthesis of (4c) to give 3,4-*methylenetetralone* as a liquid, b.p. 80° at 0.25 mmHg [2.85 g, 85% (based on the acid used)], spectroscopic data in Table 5.

(e) *Olefinic ketones* (7a *and* b) *and* (8). The preparation of (7a) and (7b) was accomplished by oxidation of the allylmethanol precursors to (2a and b) using chromic acid in acetone. Ketone (7a) thus obtained (46%) had b.p. 48—53° at 0.1—0.2 mmHg (lit.,[36] 100—102° at 5 mmHg); the n.m.r. spectrum was substantially in accord with that in the literature,[37] but revealed also *ca.* 5% contamination with 1-phenylbut-2-en-1-one. Ketone (7b) (54%) had b.p. 61—62° at 0.65 mmHg (lit.,[38] 62° at 0.3 mmHg) and was apparently free from the conjugated isomer. The most successful route to *trans*-1,4-diphenylbut-3-en-1-one was that *via* the reaction of diphenylcadmium and *trans*-styrylacetyl chloride.[39] No ketone was produced by the reaction of phenyl-lithium [40] and *trans*-styrylacetic acid, and in our hands the published sequence from 1,4-dinitro-1,4-phenylbut-2-ene [41] gave only poor yields (*ca.* 6%) of the desired ketone, m.p. 91—92° (lit.,[41] 92—93°).

TABLE 5

Spectroscopic data




$\delta(CCl_4$; 220 MHz) 0.25 (1 H, q, $H_d$), 1.48 (1 H, m, $H_f$), 1.85 (1 H, m, $H_c$), 2.24 (1 H, m, $H_g$), 2.83 (1 H, dd, $H_b$), 3.03 (1 H, d, $H_a$), 7.23 (1 H, m, $H_h$), 7.44 (2 H, m, $H_{i,j}$), 7.86 (1 H, d, $H_k$) ($J_{bc}$ 5.5 Hz, $J_{ac}$ not detected); *m/e* 158.0725 ($M^+$; calc.: 158.0732); $\nu_{max.}$(neat) 1 685 $cm^{-1}$

*Attempted Cyclopropanation of* 1-*Phenylbut*-3-*yn*-1-*ol*.—The alcohol [42] (0.25 mol) was treated with zinc (0.77 mol) and methylene iodide (0.54 mol) in ether for 22 h under reflux. The product showed no i.r. absorption due to C≡C, but did show n.m.r. absorption in the cyclopropyl region; by t.l.c. and g.l.c. the presence of several compounds was indicated, but separation was not effected.

*Kinetic Measurements*.—The ketone pair (0.006—0.034 g of each compound) was dissolved in pyridine (150—230 μl) and transferred into a dried stoppered n.m.r. tube; the stock solution of alkali (50—100 μl; preheated in the warming block) was added, and the tube and contents shaken rapidly. The tube was then placed in the spectrometer probe, and readings of the integrated absorptions taken at suitable intervals.

In some cases, overlapping of signals made indirect measurement necessary. Thus with tetralone, for which the signals due to the α- and γ-protons overlapped, the integral amplitude of the β-protons (S) was subtracted from the combined amplitude of α- and γ-protons $I_1$*; thus $I_1$* − S = $I_1$ which may then be compared with $I_2$ for the second ketone of the pair. In this way, reproducible pseudo-first-order behaviour was observed. In other cases where overlap of this kind precluded direct measurement, it was necessary to subtract from the observed integral a

[34] C. Kaiser, J. Weinstock, and M. P. Olmstead, *Org. Synth.*, 1970, **50**, 94.
[35] A. Burger and W. L. Yost, *J. Amer. Chem. Soc.*, 1948, **70**, 2198.
[36] I. A. Favorskaya, E. M. Auvinen, Yu. P. Artsybasheva, and S. M. Kasheeva, *Zhur. Org. Khim.*, 1968, **4**, 368.
[37] G. Combaut and L. Giral, *Bull. Soc. chim. France*, 1970, 3710.
[38] J. Slutsky and H. Kwart, *J. Amer. Chem. Soc.*, 1973, **95**, 8678.
[39] R. P. Linstead and L. T. D. Williams, *J. Chem. Soc.*, 1926, 2735.
[40] M. J. Jorgenson, *Org. Reactions*, 1970, **18**, 1.
[41] G. Wieland and R. Stenzl, *Ber.*, 1907, **40**, 4825; A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *J. Amer. Chem. Soc.*, 1967, **89**, 4435.
[42] H. B. Henbest, E. R. H. Jones, and I. M. S. Walls, *J. Chem. Soc.*, 1949, 2696.

quantity determined by measuring the integrated intensity of a peak due to non-exchanging protons in the second ketone, after correction for the molar proportions of the two ketones. For example, in duplicate experiments rates of 0.54 and 0.53 were obtained for 1,4-diphenylbutan-1-one relative to phenyl 1-phenylcyclopropylmethyl ketone using this procedure.

*Recovery of* 3,4-*Methylenetetralone from Exchange Experiments.*—Two experiments with differing weights of ketone (0.051 3, 0.076 7 g) in pyridine (300, 500 μl) and base (60, 120 μl) were run at 35° for 45 min. The samples were combined and quenched in ether–water, and the ether layer separated; the aqueous layer was repeatedly extracted, and from the combined dried ether layers a residue (0.120 g, *ca.* 80% recovery) was obtained. Examination by n.m.r. (200 MHz) showed that *ca.* 33% exchange had occurred, with no discernible selectivity between $H_a$ and $H_b$. There was no evidence for the formation of any other product during reaction, or for incorporation of deuterium at any position.

We acknowledge the award of a European Scholarship from the British Council, to N. B. P. We are also indebted to P.C.M.U. for helpful and efficient service, and thank Miss P. Y. Siew for some preliminary experiments.

[7/1809 *Received*, 14*th October*, 1977]