Kinetics and Mechanism of Addition and Cyclialkylation Reactions of ω-Arylalkenes with Trifluoroacetic Acid

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The rate constants for the reactions with trifluoroacetic acid of oct-1-ene, 4-phenylbut-1-ene, 5-phenylpent-1-ene and four ring-substituted derivatives, and 6-phenylhex-1-ene have been measured at 25°. The products are trifluoroacetate esters, the formation of some of which involves rearrangement, and in some cases tetralins. There is evidence for anchimeric assistance in the reaction of 5-phenylpent-1-ene, and its nature is discussed in the light of the results for its derivatives.

THE generation and cyclialkylation of carbonium ions by the treatment of phenyl-substituted olefins and alcohols with strong mineral acids or Lewis acids is well established as a synthetic route to bicyclic and polycyclic hydrocarbons.[1-3] Mechanistic investigations have demonstrated a propensity for migration of the positive charge in the carbonium ion by hydride shifts along the alkyl side-chain, resulting in species disposed to close to indanes, tetralins, or benzocycloheptenes. In cases where cyclisations are stereochemically unfavourable, polymerisation is a common alternative pathway in strong mineral acid.

We have studied the generation of carbonium ions from phenyl-substituted olefins in trifluoroacetic acid, with the prime objective of finding whether the phenyl group can provide anchimeric asistance to the reaction. We have found evidence that it does so in 5-phenylpent-1-ene, and have probed the nature of the rate enhancement by the introduction of substituents into the aromatic ring. The work has also indicated the potential utility of the reaction for the synthesis of specific disubstituted tetralins and naphthalenes.

RESULTS

The rates of the reactions of eight ω-arylalk-1-enes in trifluoroacetic acid at 25° were measured by withdrawing aliquot portions of the reaction mixture periodically, quenching with sodium hydrogen carbonate, and estimating the residual olefin by g.l.c. against an added standard. In each case, the loss of the alkene followed first-order kinetics; the rate constants in Table 1 are mean values from two experiments and were reproducible to within ±2%.

TABLE 1

First-order rate constants for the reactions of olefins in trifluoroacetic acid at 25°

Olefin No.	Structure	$10^5k/s^{-1}$
(1)	$CH_3[CH_2]_5CH=CH_2$	1·20
(2)	$Ph[CH_2]_2CH=CH_2$	0·16
(3)	$Ph[CH_2]_3CH=CH_2$	1·86
(4)	$Ph[CH_2]_4CH=CH_2$	0·57
(5)	p-$MeC_6H_4[CH_2]_3CH=CH_2$	3·80
(6)	m-$MeC_6H_4[CH_2]_3CH=CH_2$	3·58
(7)	p-$MeOC_6H_4[CH_2]_3CH=CH_2$	0·86
(8)	m-$MeOC_6H_4[CH_2]_3CH=CH_2$	0·53

For the identification of products, reaction mixtures were quenched after at least ten half-lives and analysed by g.l.c. combined with mass spectrometry both before and after hydrolytic treatment. The products were of two types: tetralins, the structures of which were in most cases confirmed by isolation by preparative g.l.c. followed by aromatisation to identifiable naphthalenes; and trifluoroacetate esters which were converted into alcohols by hydrolysis, isolated by preparative g.l.c., and identified by mass spectrometry, n.m.r. spectroscopy, and microanalysis.

In each case the total amount of product corresponded to the amount of olefin which had been lost. With 5-phenylpent-1-ene and its ring-substituted derivatives, the relative amounts of the products were constant throughout the reaction, but with the olefins (1), (2), and (4) they changed with time as described later, eventually reaching constant values. The final yields are in Table 2. In addition, partial isomerisation of 4-phenylbut-1-ene was detected during the course of the reaction.

Oct-1-ene gave three trifluoroacetate esters. The relative amounts of the esters (9) and (10) fell from *ca.* 5 : 1 early in the reaction to 3 : 1 at completion; in a control experiment, the former was found to be stable under the reaction conditions. 4-Phenylbut-1-ene gave the esters (12) and (13). G.l.c. analysis during the course of the reaction showed that the proportion of (13) increased slightly relative to that of (12), and also that two other products were formed whose combined yields grew to *ca.* 10% by the time the reaction was 70% over and then fell to zero by the time it was complete. These were isolated by preparative g.l.c. and identified as *cis*- and *trans*-4-phenylbut-2-ene. 6-Phenylhex-1-ene gave tetralin (18) and esters (16) and (17); the amounts of the esters increased during the reaction time relative to that of the tetralin.

DISCUSSION

The g.l.c. technique used for measuring the rate constants had the advantage over other methods that the products could be monitored throughout the course of the reaction. This has enabled a number of features of the process to be recognised, as shown by considering the results for oct-1-ene and 4-phenylbut-1-ene. The 7·5-fold lower rate constant for the latter compound is attributable to the $-I$ effect of the phenyl group in rate-determining protonation; Peterson *et al.*[4] reported a factor of 5·8 for the same reaction at 60°. However,

[1] R. O. Roblin, jun., D. Davidson, and M. T. Bogert, *J. Amer. Chem. Soc.*, 1935, **57**, 151.

[2] J. C. Bardhan and D. N. Mukherji, *J. Chem. Soc.*, 1956, 4629; A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, 1972, **37**, 4227.

[3] L. R. C. Barclay, ' Cyclialkylation of Aromatics,' in ' Friedel–Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, vol. 2, p. 944.

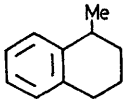
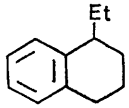
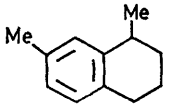
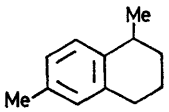
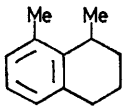
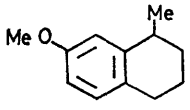
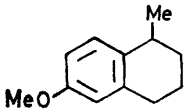
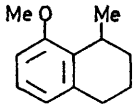
[4] P. E. Peterson, D. M. Chevli, and K. A. Sipp, *J. Org. Chem.*, 1968, **33**, 972.

whereas under those conditions they found only the esters (9) and (12), under our conditions isomeric esters were also formed. The carbonium ion isomerism which is implied could occur in either of two ways, following formation of the initial carbonium ion [*e.g.* (29) from the olefin (2)]: by a hydride shift; or by deprotonation to give a new olefin followed by protonation at a different site, as illustrated for the esters from the olefin (2). Two observations provide evidence for the latter path. First, the *cis*- and *trans*-isomers of the olefin (30) were generated and then removed during the reaction of 4-phenylbut-1-ene. Secondly, the fact that the amounts of the esters (10) and (13) were found to increase relative to their isomers (9) and (12), respectively, during the course of reaction cannot be accounted for by the hydride-shift mechanism but is consistent with the alternative explanation, since the olefins from which (10) and (13) are formed were not present at the start of the reaction. However, the possibility that hydride shifts occur in addition to olefin isomerism cannot be discounted.

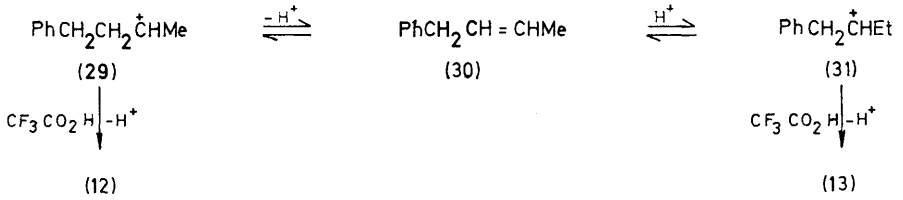
Despite evidence for the involvement of the cation (29) in the reaction of 4-phenylbut-1-ene, no 1-methylindane was detected amongst the products. It is notable that

TABLE 2

Products from the reactions of olefins with trifluoroacetic acid at 25° (R = $COCF_3$)

Olefin	Products (yields in mol %)		
(1)	$CH_3[CH_2]_5CHCH_3$ (OR) (9) (73%)	$CH_3[CH_2]_4CHCH_2CH_3$ (OR) (10) (22%)	$CH_3[CH_2]_3CH[CH_2]_2CH_3$ (OR) (11) (5%)
(2)	$Ph[CH_2]_2CHCH_3$ (OR) (12) (90%)	$PhCH_2CHCH_2CH_3$ (OR) (13) (10%)	
(3)	 (14) (74%)	$Ph[CH_2]_3CHCH_3$ (OR) (15) (26%)	
(4)	$Ph[CH_2]_4CHCH_3$ (OR) (16) (73%)	$Ph[CH_2]_3CHCH_2CH_3$ (OR) (17) (9%)	 (18) (18%)
(5)	 (19) (86%)	*p*-$MeC_6H_4[CH_2]_3CHCH_3$ (OR) (20) (14%)	
(6)	 (21) (46%)	 (22) (41%)	*m*-$MeC_6H_4[CH_2]_3CHCH_3$ (OR) (23) (13%)
(7)	 (24) (70%)	*p*-$MeO{\cdot}C_6H_4[CH_2]_3CHCH_3$ (OR) (25) (30%)	
(8)	 (26) (43%)	 (27) (26%)	*m*-$MeOC_6H_4[CH_2]_3CHCH_3$ (OR) (28) (29%)

neither this olefin nor 4-phenylbutan-2-ol give 1-methylindane with sulphuric acid, whereas 2-methyl-4-phenylbut-2-ene and -butan-2-ol yield 1,1-dimethylindane under these conditions.[1] Since the reaction of 4-phenylbutan-1-ol with sulphuric acid [1] and the formolysis of



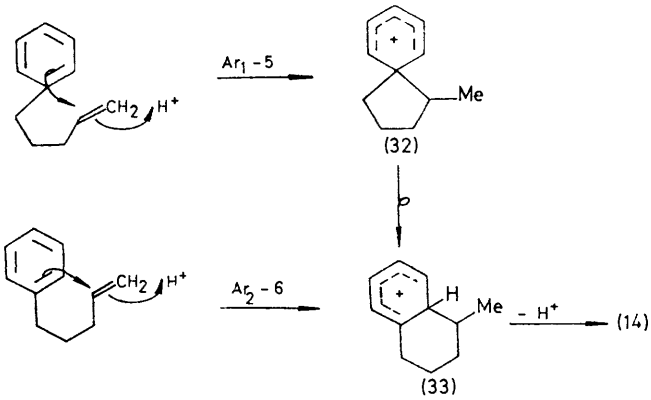
4-phenylbutyl *p*-bromobenzenesulphonate [5] give tetralin, the absence of tetralin from 4-phenylbut-1-ene with trifluoroacetic acid indicates that there is essentially no anti-Markovnikov protonation.

If the phenyl group were to act only through its $-I$ effect in the reactions of the olefins $Ph[CH_2]_nCH{:}CH_2$ with trifluoroacetic acid, the rate constants should increase in the order $n = 2 < 3 < 4$. However, the rate constant when $n = 3$ is not only greater than can be accounted for on this basis but is also greater than that for oct-1-ene. Evidently the $-I$ effect is in this case outweighed by anchimeric assistance by the phenyl ring in the protonation step.

Although such phenyl participation has not previously been observed in proton addition, a parallel exists in certain solvolytic displacements. For example, the rate constant for the formolysis (though not for the acetolysis) of 4-phenylbutyl *p*-bromobenzenesulphonate is fractionally larger (*ca.* 1%) than that for the corresponding 5-phenylpentyl compound and is out of step with the expected rate based on the $-I$ influence of the benzene ring; the tetralin (17%) formed in this reaction is considered to arise from the anchimerically assisted path and the alcoholic product (72%) from solvent-assisted reaction.[5] However, the effect on the rate in this instance is very small compared with the factor of *ca.* 3 between the rate constants for proton addition to 5-phenylpent-1-ene and 6-phenylhex-1-ene. Moreover, the effect on a solvolysis which involves a secondary carbonium ion, with which our own system should more appropriately be compared, is expected to be still smaller [5] (for instance, the introduction of methoxy-groups at the 2- and 4-positions of the phenyl ring in creases the formolysis rate for the 4-phenylbutyl compound ten-fold but that for the 1-methyl-4-phenylbutyl analogue only 2·5-fold [5]). We infer that proton addition, at least in trifluoroacetic acid, is a more sensitive probe for anchimeric assistance than the solvolyses referred to.

Two possible modes of participation have been suggested for the phenyl substituent, namely,[5,6] Ar_1-5 and Ar_2-6; they are illustrated in the Scheme for the formation of the tetralin (14) from 5-phenylpent-1-ene under our conditions. There is evidence that both occur, their relative importance depending on substituents in the aromatic ring. Thus, in the formolysis of 4-phenylbutyl *p*-bromobenzenesulphonate, the Ar_2-6 mode dominates when a *m*-OMe group is introduced [6] but the Ar_1-5 mode dominates for the *p*-OMe compound [$k(Ar_1\text{-}5) : k(Ar_2\text{-}6) = 5{\cdot}6 : 1$].[7] However, with a less strongly electron-releasing group (methyl) in the *para*-position, $k(Ar_1\text{-}5) : k(Ar_2\text{-}6)$ falls to 0·4 : 1,[7] from which it can be inferred that the Ar_2-6 path is favoured except when the alternative route is specifically and strongly activated.

We examined the methyl- and methoxy-substituted 5-phenylpent-1-enes (5)—(8) in order to probe the nature



SCHEME

of the anchimeric assistance provided by the aryl group under our conditions. The rate constants in Table 1 have been dissected in Table 3, on the basis of product ratios, into values for tetralin formation and ester formation.

TABLE 3

Rate constants for formation of tetralins and esters from 5-arylpent-1-enes

Olefin	(3)	(5)	(6)	(7)	(8)
10^5k(tetralin)/s^{-1}	1·38	3·27	3·11	0·60	0·38
10^5k(ester)/s^{-1}	0·48	0·53	0·47	0·26	0·15

For the methyl-substituted compounds, both the higher (total) rate constants and larger ratios of the yields of tetralins to esters, compared with the unsubstituted olefin (3), are consistent with increased anchimeric assistance, whether the methyl group is *meta*- or *para*-substituted. We note first that the rate of formation of the esters is approximately the same in all three

[5] R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 3105.

[6] R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, 1957, **79**, 3114.

[7] V. R. Haddon and L. M. Jackman, *J. Amer. Chem. Soc.*, 1971, **93**, 3832.

cases. Now, if there were two independent protonations, one being anchimerically assisted and leading to a cyclic ion such as (33) and thence a tetralin and the other being solvent assisted, leading to an essentially 'open' carbonium ion, $Ar[CH_2]_3CHMe$, and thence only esters, we should expect k(ester) to be slightly but significantly larger for both the methyl-substituted olefins compared with the unsubstituted one; for example, the ratio of rate constants for the corresponding 4-phenylbut-1-enes at 60°, where there is no phenyl participation, is [4] *p*-Me : *m*-Me : H = 1·6 : 1·4 : 1 (a somewhat smaller spread might be expected in our case because the $+I$ effect of methyl is attenuated by an extra methylene group), and the methoxy-substituents (which behave under our conditions as electron-attracting groups; see later) have a significant retarding influence on the rate of ester formation from 5-phenylpent-1-ene. It is therefore likely that either, if 'open' carbonium ions are formed with assistance only from solvent, a proportion of them subsequently cyclise in preference to yielding esters, or almost the entire reaction is anchimerically assisted, the esters arising from the cyclic ions such as (33) by reaction with solvent as an alternative to deprotonation. There is indeed some evidence for the latter, for if the esters came mainly from 'open' carbonium ions, we should have expected to find at least a few per cent of isomeric esters such as $Ph[CH_2]_2CH(OCOCF_3)Et$ amonst the products [*cf.* the behaviour of the olefins (1), (2), and (4)].

There are four possible combinations of the two types of aryl participation which could apply to the methyl-substituted olefins (5) and (6). (i) Both react by the Ar_2-6 mechanism. This can be ruled out since the *m*-methyl compound should then react the faster of the two. (ii) Both react by the Ar_1-5 mechanism. This would be in accord with the greater activating influence of the *p*-methyl substituent, but is unlikely in view of the very small rate ratio for the *m*- and *p*-methyl compounds compared with that for the *m*-methyl and parent compounds. Thus, treating the reaction as an electrophilic substitution gives $\rho^+ = -4{\cdot}3$ from k_H and $K_{m\text{-Me}}$ (from Table 1) and $\sigma^+_{m\text{-Me}} = -0{\cdot}066$,[8] corresponding to a predicted rate constant for the *p*-methyl compound ($\sigma^+ = -0{\cdot}311$) [8] 20 times larger than for the parent compound. [The nature of this argument is unaffected if only the k(tetralin) values are used.] (iii) The olefins (5) and (6) react, respectively, by the Ar_2-6 and Ar_1-5 routes. This can be discounted since, if the former olefin were to react by the Ar_2-6 path, the latter would be more prone to do so, and *vice versa*. (iv) The converse of (iii) could obtain. This would be in accord with directing influences of *m*- and *p*-Me and is the only reasonable explanation amongst these four extreme possibilities. However, the results do not necessarily indicate that the *m*- and *p*-methyl-substituted compounds react exclusively by the Ar_2-6 and Ar_1-5 paths respectively but only that $k(Ar_2\text{-}6)$: $k(Ar_1\text{-}5)$ is larger for the former isomer than for the latter; when the data are compared with those for the solvolysis of 4-*p*-tolylbutyl *p*-bromobenzenesulphonate referred to above, the likeliest explanation is that the *m*-methyl compound reacts essentially exclusively by the Ar_2-6 route and the *p*-methyl isomer by a combination of the two.

Comparison of the rate constants for the reaction of the methoxy-substituted olefins (7) and (8) with those for (2) and (4) shows that the reaction of the former is certainly anchimerically assisted and that of the latter almost certainly so, while comparison with the rate constant for the olefin (3) shows that the methoxy-substituent in each compound acts in an electron-withdrawing capacity. The latter result has precedent in the reactions of 4-*m*- and -*p*-methoxyphenylbut-1-enes with trifluoroacetic acid and has been attributed to hydrogen bonding of the substituent to the strongly acidic hydrogen atom of the solvent.[4] Comparison of the rate constants for the olefins (7) and (8) and an analysis corresponding to that above for the methyl-substituted olefins suggests that anchimeric assistance in both cases is mainly or solely of the Ar_2-6 type.

There is no evidence for anchimeric assistance in the initial protonation of 6-phenylhex-1-ene; the rate constant is very much lower than that for both oct-1-ene and 5-phenylpent-1-ene, and no 1-methylbenzocycloheptene could be detected. The amounts of both the ester (17) and the tetralin (18) increased relative to that of the ester (16) during the course of the reaction, suggesting that the first two are formed at least in part by way of the deprotonation–reprotonation sequence described earlier; the formation of the tetralin (18) and analogy with the behaviour of 5-phenylpent-1-ene leaves little doubt that the reprotonation step is, at least in the main, anchimerically assisted.

EXPERIMENTAL

^{1}H N.m.r. spectra were measured with a Varian A-60 or Perkin-Elmer R10 spectrometer; chemical shifts (δ) are reported relative to tetramethylsilane as internal standard in carbon tetrachloride. Analytical and preparative g.l.c. were on a Pye series 104 chromatograph with glass columns, nitrogen as carrier gas, and a flame-ionisation detector. The analytical columns (5 ft × ¼ in), used with a carrier-gas flow of 60 ml min^{-1}, were: (a) 10% Apiezon L on Celite (60—100), (b) 10% Carbowax 20M on Chromosorb W (60—80). The preparative columns (6 ft × ⅜ in), used in conjunction with a 100 : 1 splitter at the outlet port and with a carrier-gas flow of120 ml min^{-1}, were: (c) 10 % Apiezon L on Celite (60—100), (d) 10% silicone oil SE30 on Celite (60—72). The chromatograph was coupled to an A.E.I. MS12 spectrometer for the determination of mass spectra.

Olefins.—Oct-1-ene and 4-phenylbut-1-ene were available commercially. 5-Phenylpent-1-ene [9] and 6-phenylhex-1-ene [10] were obtained from the appropriate arylalkyl bromides with magnesium followed by allyl bromide. The substituted 5-phenylpent-1-enes were prepared by the

[8] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

[9] N. C. Sih and H. Pines, *J. Org. Chem.*, 1965, **30**, 1462.

[10] N. C. Sih, H. Pines, and E. Lewicki, *J. Org. Chem.*, 1965, **30**, 1457.

sequence ArBr ⟶ $ArCH_2CH_2OH$ [11] ⟶ $ArCH_2CH_2OSO_2Ph$ ⟶ $ArCH_2CH_2Br$ ⟶ $Ar[CH_2]_3CH{:}CH_2$ with, successively, magnesium followed by ethylene oxide, benzenesulphonyl chloride, lithium bromide in acetone, and [10] magnesium followed by allyl bromide, and were as follows: 5-(p-*tolyl*)*pent*-1-*ene*, b.p. 87—92° at 8 mmHg, δ 7·00 (4H, s), 5·90—5·40 (1H, m), 5·05 (1H, m), 4·85 (1H, m), 2·90—1·60 (6H, c), and 2·30 (3H, s) (Found: C, 89·9; H, 9·9. $C_{12}H_{16}$ requires C, 89·9; H, 10·1%); 5-(m-*tolyl*)*pent*-1-*ene*, b.p. 77—79° at 6·5 mmHg, δ 7·15—6·80 (4H, c), 5·90—5·40 (1H, m), 5·05 (1H, m), 4·85 (1H, m), 2·90—1·60 (6H, c), and 2·30 (3H, s) (Found: C, 90·1; H, 10·0%); 5-(p-*methoxyphenyl*)*pent*-1-*ene*, b.p. 89—92° at 0·2 mmHg, δ 7·00 and 6·65 (4H, ABq, J_{AB} 8 Hz), 6·10—5·40 (1H, m), 5·05 (1H, m), 4·80 (1H, m), 3·72 (3H, s), 2·50 (2H, t, *J* 7 Hz), and 2·80—1·40 (4H, c) (Found: C, 81·5; H, 9·1. $C_{12}H_{16}O$ requires C, 81·8; H, 9·15%); and 5-(m-*methoxyphenyl*)*pent*-1-*ene*, b.p. 94—98° at 3 mmHg, δ 7·30—6·20 (4H, c), 6·10—5·40 (1H, m), 5·05 (1H, m), 4·80 (1H, m), 3·72 (3H, s), 2·57 (2H, t, *J* *J* 7 Hz), and 2·30—1·20 (4H, c) (Found: C, 81·8; H, 9·3%).

Kinetic Measurements.—In a typical run, 4-phenylbut-1-ene (100 mg) was dissolved in trifluoroacetic acid (Fisons S.L.R; 7 ml) and equilibrated at 25 ± 0·1° in a constant temperature bath for 5—10 min. Thereafter aliquot portions (0·7 ml) were removed periodically and quenched in saturated sodium hydrogen carbonate solution (20 ml). The ether extracts (3 × 20 ml) were washed with saturated sodium chloride solution (2 × 10 ml) and dried ($MgSO_4$), 1 ml of a solution of mesitylene (100 mg) in ether (10 ml) was added, and the filtered solution was concentrated (rotary evaporator at room temperature) and analysed by g.l.c. on column (a) at 120°. The quantity of alkene remaining was determined by triangulation relative to the mesitylene. Nine such determinations were made and the first-order rate constant was computed with a least-squares programme.

Column (a) was used throughout for kinetic studies. The standards, chosen so that their g.l.c. peaks were fully resolved from those of both reactants and products, were anisole for oct-1-ene, mesitylene for 5-phenylpent-1-ene as well as for 4-phenylbut-1-ene, and durene for the remaining compounds.

Product Studies.—The alkene (200 mg) in trifluoroacetic acid (15 ml) was allowed to react for at least ten half-lives and then quenched with saturated sodium hydrogen carbonate solution until it was no longer acidic. The ether extract (3 × 50 ml) was washed with saturated sodium chloride solution (2 × 25 ml), dried ($MgSO_4$), filtered, and evaporated under reduced pressure at room temperature. A sample of the residue was retained and the remainder was stirred overnight at room temperature with 5% potassium hydroxide solution in 90% methanol (10 ml). This solution was diluted with saturated sodium chloride solution (20 ml) and the ether extract (3 × 50 ml) was treated as above. It was shown that cyclised products were unaffected by this treatment whereas trifluoroacetates were hydrolysed to alcohols.

Analytical g.l.c. combined with mass spectrometry was on column (a) or (b). Preparative g.l.c. on column (c) gave pure samples of the constituents for microanalysis, n.m.r. spectroscopy, and calibration of the g.l.c.

Isolated tetralins were heated overnight in boiling mesitylene in the presence of 5% palladium–charcoal. After filtration, the naphthalene was purified by preparative g.l.c. on column (d). Control experiments showed that the tetralins were unaffected by trifluoroacetic acid under the conditions of the reactions.

We thank the S.R.C. for a fellowship to T. J. M.

[3/849 *Received*, 25*th April*, 1973]

[11] E. Bergmann and A. Weizmann, *J. Org. Chem.*, 1939, **4**, 266.