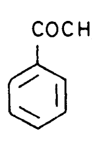
Reductive Coupling of Aromatic Ketones by Low-valent Titanium Salts

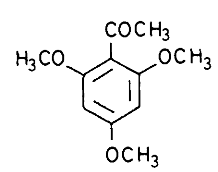
By **Francesco A. Bottino, Paolo Finocchiaro,*** **Emanuela Libertini, Antonino Reale,** and **Antonino Recca,** Faculty of Engineering of the University, Viale A. Doria 6, 95125 Catania, Italy

Reaction of sterically congested aromatic ketones with the McMurry reagent ($4TiCl_3,LiAlH_4$) in tetrahydrofuran yields is not only the olefins (*E*- and *Z*-isomers), but also the corresponding ethanes and some other products. We have studied the minor or non-normal products of this reaction.

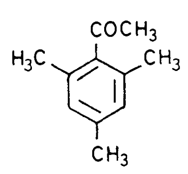
McMurry reductive coupling [1] of aldehydes and ketones by low-valent titanium salts has so far been used for the syntheses of new [2-6] or highly sterically congested [7] olefins. However, little attention has been devoted to the coupling reactions of sterically congested aromatic ketones and to the minor or non-normal products of this reaction. Therefore, we have studied the behaviour of the aromatic ketones (1a—g) with the above reagents in order to ascertain the role played by steric and electronic effects in this coupling reaction and to elucidate its stereoselectivity with the assumption that the olefins (2a—g) generated exist in two diastereoisomeric forms (*E* and *Z*).



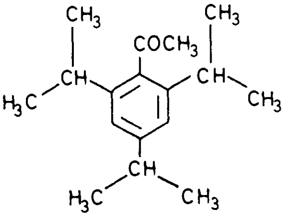
(1a)



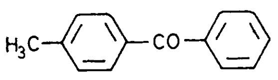
(1b)



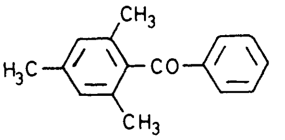
(1c)



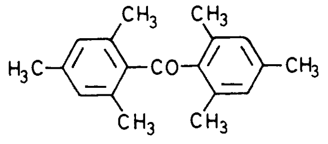
(1d)



(1e)



(1f)



(1g)

EXPERIMENTAL

Instrumentation.—^1H N.m.r. spectra were recorded on a Bruker WP-80FT spectrometer equipped with variable temperature accessories. Temperatures are considered to be accurate to ±1 °C. Saturation of the n.m.r. signals was avoided. N.m.r. samples were *ca.* 2% w/v solution containing tetramethylsilane as internal standard.

Mass spectra were obtained on an LKB-9000S high resolution mass spectrometer with an ionizing voltage of 70 eV.

G.l.c. analyses were performed on a Dani 3600 Instrument using a 2 m column filled with 3% SP 2100 on Supelcoport 800—100 mesh.

Ketones (1b—g) were obtained by Friedel–Crafts reactions according to procedures already reported [8] and their physical characteristics were found to be identical with those given. Acetophenone was a high purity commercial sample (C. Erba) purified by distillation.

2′,4′,6′-*Trimethoxyacetophenone* (1b). This had δ ($CDCl_3$; 25 °C) 2.40 (3 H, s, CH_3), 3.70 (6 H, s, OCH_3), 3.80 (3 H, s, OCH_3), and 6.10 (2 H, s, ArH).

2′,4′,6′-*Trimethylacetophenone* (1c). This had δ ($CDCl_3$; 25 °C) 2.19 (6 H, s, CH_3), 2.24 (3 H, s, CH_3), 2.42 (3 H, s, CH_3), and 6.77 (2 H, s, ArH).

2′,4′,6′-*Tri-isopropylacetophenone* (1d). This had δ ($CDCl_3$; 25 °C) 1.26 (18 H, d, $^3J_{H,H}$ 6.5 Hz, $CHCH_3$), 2.50 (3 H, s, CH_3), 2.80 (3 H, m, $CHCH_3$), and 7.00 (2 H, s, ArH).

p-*Methylbenzophenone* (1e). This had δ ($CDCl_3$; 25 °C) 2.40 (3 H, s, CH_3), 7.28 (2 H, d of AA′BB′ system, $^3J_{AB}$ 8 Hz, ArH), 7.54 (3 H, m, ArH), 7.73 (2 H, d, of AA′BB′ system, $^3J_{AB}$ 8 Hz, ArH), and 7.75 (2 H, m, ArH).

2,4,6-*Trimethylbenzophenone* (1f). This had δ ($CDCl_3$; 25 °C) 2.08 (6 H, s, CH_3), 2.33 (3 H, s, CH_3), 6.88 (2 H, s, ArH), 7.48 (3 H, m, ArH), and 7.76 (2 H, m, ArH).

Dimesitylketone (1g). This had δ ($CDCl_3$; 25 °C) 2.15 (6 H, s, CH_3), 2.32 (3 H, s, CH_3), and 6.88 (2 H, s, ArH).

Typical Procedure for the Reductive Coupling of Ketones (1a—g).—The McMurry reagent ($4TiCl_3$–$LiAlH_4$) (Ventron Alfa Division) (13.0 g, 0.02 mol) was added to dry tetrahydrofuran (THF) under nitrogen and the resulting slurry was maintained at the reflux temperature for 30 min. After cooling, a solution of an equimolar amount of ketone in THF was then added and the mixture was refluxed for 8 h. After cooling, light petroleum was added, the mixture filtered off, and the solvent removed under reduced pressure. The mixture of products was analysed by g.l.c. and ^1H n.m.r. spectroscopy in order to estimate the yields of products. Separation by column chromatography (SiO_2; n-heptane or light petroleum–ethyl ether) or by fractional recrystallizations afforded the compounds listed here and in Table 1.

Variation in the reaction times does not produce substantial changes in the nature or percentage of the products obtained, as demonstrated by different reaction batches.

Reductive coupling of acetophenone (1a). The crude product (70%) was separated by column chromatography (SiO_2; n-hexane) yielding (*Z*)- and (*E*)-2,3-diphenylbut-2-ene. (E)-2,3-*Diphenylbut-2-ene* (2a) was a solid, m.p. 98—100 °C, δ ($CDCl_3$; 25 °C) 1.88 (3 H, s, CH_3) and 7.30 (5 H, s, ArH). (Z)-2,3-*Diphenylbut-2-ene* (2a) had δ ($CDCl_3$; 25 °C) 2.23 (3 H, s, CH_3) and 7.02 (5 H, s, ArH). The assignment of the signals to the two diastereoisomers was made according to Light and Zeiss.[9] McMurry,[1] for the coupling reaction of ketone (1a) with $TiCl_3$ and lithium, obtained a 1 : 9 *E* : *Z* ratio for the corresponding olefins.

TABLE 1

Products isolated from condensation reaction of aromatic ketones (1a—g) with $4TiCl_3$–$LiAlH_4$ in THF solution

Ketone	Olefin (yield %)	*E* : *Z*	Ethane (yield %)	*meso* : racemic	Methane (yield %)	Others (yield %)
(1a)	(2a) (70)	1 : 4.5				
(1b)	(2b) (42)	1 : 1.8				Polymeric tars (55)
(1c)	(2c) (22.5)	1 : 1.2	(3c) (41.5)	1 : 1.1	(4c) (3)	2,4,6-Trimethylstyrene (3), polymeric tars (30)
(1d)			(3d) (17.5)	1 : 1	(4d) (8.2)	2,4,6-Tri-isopropylstyrene (9.3), polymeric tars (65)
(1e)	(2e) (70)	1 : 1				Polymeric tars (30)
(1f)	(2f) (18)	1 : 0.45	(3f) (42)	1 : 0.8 [a]		Polymeric tars (40)
(1g)					(4g) (57)	Unreacted ketone (43)

[a] Assignment can be reversed.

Reductive coupling of 2′,4′,6′-trimethoxyacetophenone (1b). The crude product (45%) was separated by column chromatography (SiO_2; light petroleum–Et_2O 70 : 30) yielding (*Z*)- and (*E*)-2,3-bis-(2,4,6-trimethoxyphenyl)but-2-ene and *meso*- and racemic 2,3-bis-(2,4,6-trimethoxyphenyl)butane. (E)-2,3-bis-(2,4,6-*trimethoxyphenyl)but-2-ene* (2b) was a solid, m.p. 205—206 °C (Found: C, 67.7; H, 7.4. $C_{22}H_{28}O_6$ requires C, 68.0; H, 7.25%), δ ($CDCl_3$; 25 °C) 1.64 (3 H, s, ethylenic CH_3), 3.82 (9 H, s, OCH_3), and 6.20 (2 H, s, ArH); δ (C_6D_6; 25 °C) 2.13 (3 H, s, ethylenic CH_3), 3.45 (3 H, s, OCH_3), 3.52 (6 H, s, OCH_3), and 6.28 (2 H, s, ArH). Thus, the aromatic solvent resolves the accidental isochrony of the diastereoisotopic *o*- and *p*-methoxy-groups. Furthermore the ethylenic methyl group shows a dramatic downfield shift in C_6D_6 indicating the formation of an oriented molecular complex with the aromatic solvent.

(Z)-2,3-*Bis*-(2,4,6-*trimethoxyphenyl)but*-2-*ene* (2b) was a solid, m.p. 230 °C (Found: C, 67.85; H, 7.2%), δ ($CDCl_3$; 25 °C) 2.08 (3 H, s, ethylenic CH_3), 3.60 (6 H, s, OCH_3), 3.72 (3 H, s, OCH_3), and 5.90 (2 H, s, ArH); δ (C_6D_6; 25 °C) 2.32 (3 H, s, ethylenic CH_3), 3.30 (3 H, s, OCH_3), 3.36 (6 H, s, OCH_3), and 5.99 (2 H, s, ArH). Assignments of these resonances to the *Z*- and *E*-isomers were made on the basis of inspection of molecular models which reveals that the methyl group attached to the double bond lies in the shielding region of the phenyl ring in the *E*-isomer, and in analogy with the chemical shifts of the known [9] *cis*- and *trans*-isomers of 2,3-diphenylbut-2-ene (δ 2.23 and 1.88, respectively).

Reductive coupling of 2′,4′,6′-trimethylacetophenone (1c). The crude product (70%) was separated by column chromatography (SiO_2; light petroleum–diethyl ether 85 : 15) yielding the olefins (2c) (*E* and *Z*), the ethanes (3c) (*meso* and racemic), ethylmesitylene (4c), and 2,4,6-trimethylstyrene (5c) (Table 1). (E)-2,3-*Dimesitylbut*-2-*ene* (2c) was a solid, m.p. 165 °C (Found: C, 90.45; H, 9.55. $C_{22}H_{28}$ requires C, 90.35; H, 9.65%), δ ($CDCl_3$; 25 °C) 1.55 (3 H, s, ethylenic CH_3), 2.29 (9 H, s, CH_3), and 6.89 (2 H, s, ArH); δ (C_6D_6; 25 °C) 1.61 (3 H, s, ethylenic CH_3), 2.21 (3 H, s, CH_3), 2.30 (6 H, s, CH_3), and 6.87 (2 H, s, ArH), *m/e* 292 ($M^{+\bullet}$). (Z)-2,3-*Dimesitylbut*-2-*ene* (2c) was an oil (Found: C, 90.7; H, 9.35%), δ ($CDCl_3$; 25 °C) 2.21 (6 H, s, CH_3), 2.27 (3 H, s, CH_3), 2.44 (3 H, s, ethylenic CH_3), and 6.83 (2 H, s, ArH), *m/e* 292 ($M^{+\bullet}$). Assignment of the *Z*- and *E*-isomers was made on the basis of inspection of molecular models which reveals that the methyl group attached to the ethylenic bond lies below the shielding region of the mesityl ring in the *E*-isomer, and by analogy with the chemical shifts of the known [9] *cis*- and *trans*-isomers of 2,3-diphenylbut-2-ene (δ 2.23 and 1.88, respectively). *meso*-2,3-Dimesitylbutane (3c) formed crystals, m.p. 142 °C (lit.,[10] 140 °C), δ ($CDCl_3$; 25 °C) 1.03 (3 H, d, $^3J_{H,H}$ 6.8 Hz, CH_3CH), 2.25 (3 H, s, CH_3), 2.40 (3 H, s, CH_3), 2.54 (3 H, s, CH_3), 3.87 (1 H, q, $^3J_{H,H}$ 6.8 Hz, CH), and 6.85 (2 H, s, ArH), *m/e* 294 ($M^{+\bullet}$). Racemic 2,3-dimesitylbutane (3c) was an oil (Found: C, 89.5; H, 10.45. Calc. for $C_{22}H_{30}$: C, 89.75; H, 10.25%), δ ($CDCl_3$; 25 °C) 1.42 (3 H, d, $^3J_{H,H}$ 7.00 Hz, CH_3CH), 1.70 (3 H, s, CH_3), 2.14 (3 H, s, CH_3), 2.45 (3 H, s, CH_3), 3.60 (1 H, m, CH), and 6.72 (2 H, s, ArH), *m/e* 294 ($M^{+\bullet}$). Assignment of resonances to the racemic and *meso*-ethanes was by analogy with the chemical shifts reported for the nor-methyl analogues.[11]

2-*Ethylmesitylene* (4c) was obtained by column chromatography together with 2,4,6-trimethylstyrene in a 1 : 1 mixture. It was characterized by g.l.c. analysis [10] and ^1H n.m.r. spectroscopy, δ ($CDCl_3$; 25 °C) 1.08 (3 H, t, $^3J_{H,H}$ 7.25 Hz, CH_3), 2.22 (3 H, s, CH_3), 2.27 (6 H, s, CH_3), 2.56 (2 H, q, $^3J_{H,H}$ 7.25 Hz, CH_2), and 6.84 (2 H, s, ArH).

2,4,6-*Trimethylstyrene* (5c) was an oil, δ ($CDCl_3$; 25 °C) 2.22 (3 H, s, CH_3), 2.27 (6 H, s, CH_3), 5.21 (1 H, q of an ABC system, $^2J_{H,H}$ 2.2, $^3J_{H,H}$ 17.8 Hz, CH_2), 5.47 (1 H, q of an ABC system, $^2J_{H,H}$ 2.2, $^3J_{H,H}$ 11.6 Hz, CH_2) 6.66 (1 H, q of an ABC system, $^3J_{H,H}$ 17.8, $^3J_{H,H}$ 11.6 Hz, CH), and 6.82 (2 H, s, ArH). These values are in agreement with those reported.[12]

Recently Lenoir and Lemmen [7b] studied the coupling reaction of ketone (1c) with Ti^{II} and Ti^0 but, at variance with our results, they reported the isolation of only ethylmesitylene in 51 and 85% yield, respectively.

Reductive coupling of 2′,4′,6′-tri-isopropylacetophenone (1d). The crude product (35%) was obtained as a 1 : 1 mixture of an oil and a solid. The oil was decanted off and distilled yielding 8.2% 1-ethyl-2,4,6-tri-isopropylbenzene (4d) and 9.3% 2,4,6-tri-isopropylstyrene (5d); the solid (17.5%) was crystallized from benzene yielding *meso*- and racemic 2,3-bis-(2,4,6-tri-isopropylphenyl)butane (3d). 1-*Ethyl*-2,4,6-*tri-isopropylbenzene* (4d) was a pale yellow oil (Found: C, 88.0; H, 12.05. $C_{17}H_{28}$ requires C, 87.85; H, 12.15%), δ ($CDCl_3$; 25 °C) 1.18 (6 H, d, $^3J_{H,H}$ 6.5 Hz, $CHCH_3$), 1.24 (15 H, d, $^3J_{H,H}$ 6.5 Hz, $CHCH_3 + CH_2CH_3$), 2.5—3.2 (5 H, m, $CH_2 + CHCH_3$), and 6.98 (2 H, s, ArH), *m/e* 232 ($M^{+\bullet}$). 2,4,6-*Tri-isopropylstyrene* (5d) was a pale yellow oil (Found: C, 88.75; H, 11.2. $C_{17}H_{26}$ requires C, 88.6; H, 11.35%), δ ($CDCl_3$; 25 °C) 1.18 (6 H, d, $^3J_{H,H}$ 6.5 Hz, $CHCH_3$), 1.24 (12 H, d, $^3J_{H,H}$ 6.5 Hz, $CHCH_3$), 2.5—3.2 (3 H, m, $CHCH_3$), 5.16 (1 H, q of an ABC system, $^2J_{H,H}$ 2.5 and $^3J_{H,H}$ 17.8 Hz, CH_2), 5.49 (1 H, q of an ABC system, $^2J_{H,H}$ 2.5, $^3J_{H,H}$ 11.2 Hz, CH_2), 6.79 (1 H, q of an ABC system, $^3J_{H,H}$ 17.8, 11.2 Hz, CH), and 7.00 (2 H, s, ArH), *m/e* 230 ($M^{+\bullet}$).

meso- *and racemic* 2,3-*bis*-(2,4,6-*tri-isopropylphenyl*)-*butanes* (3d). Separation of the two diastereoisomers was not accomplished. The mixture showed m.p. 215 °C;

δ ($CDCl_3$) 1.05—1.55 (21 H, $CHCH_3$), 2.80 (1 H, m, $CHCH_3$), 3.50 (2 H, m, $CHCH_3$), 3.94br (1 H, m, CH), and 7.02 (2 H, s, ArH), *m/e* 462 ($M^{+\bullet}$), 461 ($M - 1^+$), 432 (m^*), 446 ($M - 1 - 15^+$), 417 ($M - 45^+$), and 231 ($M/2^+$).

Reductive coupling of p-*methylbenzophenone* (1e). The product (70%), m.p. 120 °C, was found to be a 1 : 1 mixture of *E*- and *Z*-olefins. All attempts to separate the isomers failed. The ^1H n.m.r. spectrum of a 1 : 1 unseparated mixture of the *Z*- and *E*-olefins featured separated signals for the tolyl methyl groups at δ ($CDCl_3$; 25 °C) 2.23 and 2.24. In the aromatic region there were resonances at δ 6.89 (4 H, s, ArH), 6.91 (4 H, s, ArH), 7.03 (5 H, s, Ph), and 7.06 (5 H, s, Ph), *m/e* 360 ($M^{+\bullet}$).

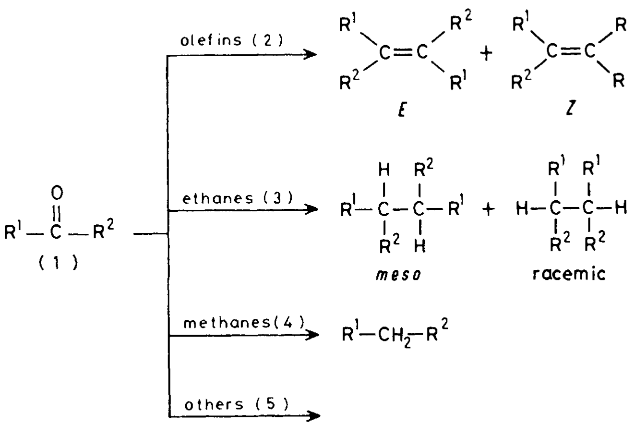
Reductive coupling of 2,4,6-*trimethylbenzophenone* (1f). The crude product (60%) was extracted with n-hexane and the soluble fraction was separated by column chromatography (SiO_2; n-hexane) yielding a mixture of (*Z*)- and (*E*)-1,2-diphenyl-1,2-dimesitylethylene, m.p. 148—150 °C, and one of two diastereoisomers of 1,2-diphenyl-1,2-dimesitylethane, m.p. 198—200 °C. Another part of the product was fractionally recrystallized from benzene yielding the other diastereoisomeric ethane, m.p. 186 °C. The yields of the products are reported in Table 1. (*Z*)- and (*E*)-1,2-*Diphenyl*-1,2-*dimesitylethylene* (2f) had δ ($CDCl_3$; 25 °C) 2.12 (6 H, s, CH_3), 2.25 (3 H, s, CH_3), 6.77 (2 H, s, ArH), and 7.00 (5 H, m, ArH) for one isomer, δ ($CDCl_3$; 25 °C) 2.06 (6 H, s, CH_3), 2.16 (3 H, s, CH_3), 6.64 (2 H, s, ArH), and 7.00 (5 H, m, ArH) for the other, *m/e* 416 ($M^{+\bullet}$), 279 [$M - (60 + 77)^+$], and, 178 [$M - (119 + 119)^{+\bullet}$]. 1,2-*Diphenyl*-1,2-*dimesitylethane* (3f) (one diastereoisomer), m.p. 184 °C, had δ ($CDCl_3$; 25 °C) 2.07 (3 H, s, CH_3), 2.12 (3 H, s, CH_3), 2.23 (3 H, s, CH_3), 5.48 (1 H, s, CH), 6.58 (2 H, s, ArH), and 7.05 (5 H, m, ArH), *m/e* 418 ($M^{+\bullet}$), 403 ($M - 15^+$), 388 ($M - 30^{+\bullet}$), 373 ($M - 45^+$), and 209 ($M/2^+$). 1,2-*Diphenyl*-1,2-*dimesitylethane* (3f) (other diastereoisomer), m.p. 198—200 °C, had δ ($CDCl_3$; 25 °C) 2.10 (3 H, s, CH_3), 2.21 (3 H, s, CH_3), 2.31 (3 H, s, CH_3), 5.48 (1 H, s, CH), 6.73 (2 H, s, ArH), and 6.95 (5 H, m, ArH), δ (C_6D_6; 25 °C) 1.94 (3 H, s, CH_3), 2.13 (3 H, s, CH_3), 2.29 (3 H, s, CH_3), 5.67 (1 H, s, CH), 6.55 (2 H, s, ArH), and 7.17 (5 H, m, ArH), *m/e* 418 ($M^{+\bullet}$), 403 ($M - 15^+$), 388 ($M - 30^{+\bullet}$), 373 ($M - 45^+$), and 209 ($M/2^+$).

Reductive coupling of dimesityl ketone (1g). The product was purified by column chromatography (SiO_2; n-heptane) yielding 43% unchanged ketone and 57% dimesitylmethane (4g), whose physical and spectral characteristics were found to be coincident with those already reported.[13] This result is in harmony with that recently found by Lenoir and Lemmen for the coupling of ketone (1g) with $TiCl_3$ and potassium in THF solution.[7b]

RESULTS AND DISCUSSION

The compounds isolated from the coupling reaction of aromatic ketones (1a—g) with the McMurry reagent in THF at reflux temperature (independent of reaction time) are listed in Table 1. The products obtained clearly indicate that the McMurry reaction occurs with these ketones, but, in contrast to less hindered carbonyl compounds, the yield of olefins decreases upon increasing the steric congestion around the carbonyl group.

In the olefins formed from the diaryl ketones the *E* : *Z* ratio is 1 : 1 for ketone (1e) as expected from the remote position of the *p*-methyl group, whereas it is 1 : 0.45 for (1f) in agreement with the fact that the two bulky mesityl groups prefer to reside in the *trans*-position. Acetophenone (1a) yields preferentially the *Z*-olefin, but on increasing the size of the aromatic ring, the relative amount of *Z*-isomer dramatically decreases, indicating that the *E*-isomer has a much lower degree of steric congestion.



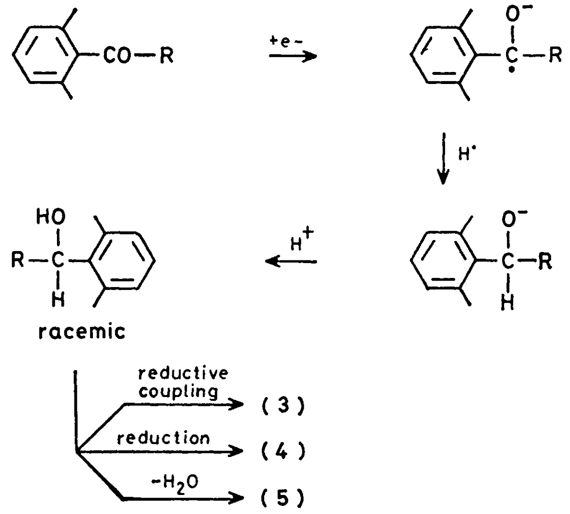
SCHEME 1

For the *ortho*-substituted arylmethyl and diaryl ketones, 2,3-diarylbutanes or 1,1,2,2-tetra-arylethanes are formed in sizable amounts with respect to the olefin derivatives, and the yield of such alkanes increases upon increasing the steric congestion around the carbonyl group. This can be ascribed to a tendency by the molecule to release the steric compression by elongation of its central C–C bond, through hydrogenation or *via* reduction of the congested ketone to the corresponding carbinol and subsequent coupling to give the corresponding alkane. In fact the isolation of methanes (4) and vinylic derivatives (5) (Scheme 1), whose amount increases upon increasing the congestion around the carbonyl group, suggests that the mechanism of the reaction is more complex than previously proposed.[1]

The ratio of *meso* to racemic isomers for the isolated ethanes (3) is *ca.* 1 : 1 in all the compounds investigated, suggesting that the reaction is not stereoselective at all.

Thus, these data favour the ' non-concerted A_2 pathway ' postulated by McMurry *et al.*,[1] whereas the formation of the ethane derivatives (3) and of compounds (4) and (5) indicates that the reductive reaction (without coupling) probably yields racemic 1-mesitylethanol, which in turn undergoes a reductive coupling reaction to yield the ethanes (3) by analogy with the reaction of $CrCl_2$ with carbinols.[14,15] Subsequent reactions of 1-mesitylethanol could yield 1-ethyl-2,4,6-trimethylbenzene by reduction and 2,4,6-trimethylstyrene by dehydration (Scheme 2).

A variable-temperature ^1H n.m.r. stereochemical study was also carried out on (2c), (3c), and (3f). Both *E*- and *Z*-olefins (2c) show a single peak for the mesityl *o*-methyl groups indicating that these compounds assume a time-averaged conformation in which the mesityl ring



SCHEME 2

is perpendicular to the $CH_3-C=C-CH_3$ plane (point group symmetry C_{2h}, *E*-isomer; C_{2v}, *Z*-isomer).

On the other hand *meso*- and racemic (3c), by virtue of the ethane torsion angle and of the orientational ability of the mesityl ring can assume, in principle, a variety of different conformations. However, Mislow and his co-workers [16] pointed out, on the basis of empirical force field calculations and n.m.r. spectroscopy, that both racemic and *meso*-2,3-dixylylbutane [the demethyl analogues of (3c)] exist in the *anti*-conformation with C_i (*meso*) and C_2 (racemic) point group symmetry.

TABLE 2

Products isolated from the condensation reaction of ketones (1c and f) with Li–$TiCl_3$ in THF solution

Ketone	Olefin (yield %)	*E* : *Z*	Ethane (yield %)	*meso* : racemic	Methane (yield %)	Others (yield %)
(1c)	(2c) (22.2)	1 : 1.02	(3c) (47.8)	1 : 1.02	(4c) (3)	2,4,6-Trimethylstyrene (3), polymeric tars (24)
(1f)	(2f) (24.4)	*a*	(3f) (8.0)	*a*	(4f) (29.3)	Polymeric tars (38.3)

[a] Not separated.

These results are in agreement with the ^1H n.m.r. spectra of compounds (3c) at room temperature, which show two equally intense singlets for the *ortho*-methyl groups in both derivatives (see Experimental section). Coalescence of the signals at δ 2.36 and 2.50 (in *o*-dichlorobenzene solution) occurs at 171 °C for *meso*-(3c), with an associated energy ΔG^* of 23.5 kcal mol^{-1},† whereas for racemic (3c) coalescence of the signals at δ 1.71 and 2.40 (in *o*-dichlorobenzene) is observed at 104 °C with an associated [17] ΔG^* of 18.6 kcal mol^{-1}.*

The two diastereoisomers (*i.e.* the *meso*- and racemic forms) of (3f) although separated were not assigned. An assignment could have been made on the basis of the n.m.r. spectra in conditions in which conformational interconversions are frozen on the n.m.r. time-scale.[15] In fact, on the basis of the analysis previously published [15] for 1,2-dimesityl-1,2-bis-(2,4,6-trimethoxyphenyl)ethane, which corresponds to (3f), racemic (3f) should exist as four conformational isomers (two racemic pairs) which should display two unequally intense sets of signals, each consisting of three singlets of equal intensity, two for the *ortho*- and one for the *para*-methyl groups. On the other hand *meso*-(3f) can exist as only one conformational pair which should feature six signals of equal intensity in the methyl region, when interconversion between the two enantiomers is slow on the n.m.r. time-scale. Unfortunately, low-temperature ^1H n.m.r. spectra ($CDCl_3$–CS_2 at −90; chlorobenzene at −40 °C) of the two diastereoisomers of (3f) failed to show additional splitting of the methyl signals and thus the assignment was not made.

However, at ambient temperature both diastereoisomers of (3f) display in the methyl region of the ^1H n.m.r. spectrum three equally intense signals, due to residual diastereotopism.[15]

Coalescence of the two signals at δ 2.12 and 2.22 (chlorobenzene) occurs at 58 °C for the isomer with m.p. 184 °C from which ΔG^*_{58} 17.2 kcal mol^{-1} was calculated.[17] For the other isomer with m.p. 198—200 °C the two signals at δ 2.10 and 2.31 (chlorobenzene) coalesce at 75 °C with an associated [17] ΔG^*_{75} of 18.0 kcal mol^{-1}.

Ketones (1c and f) were also coupled with lithium–$TiCl_3$ according to the procedure described in ref. 1. The results of such experiments are listed in Table 2. No dramatic differences are found for ketone (1c), whereas for ketone (1f) Li–$TiCl_3$ coupling greatly increases the amount of the methane derivative.

Financial support of this research by the Italian C.N.R. is gratefully acknowledged.

[1/679 *Received, 28th April*, 1981]

---

* The coalescence temperatures found for *meso*- and racemic (3c) are the same, but reversed, as those reported in ref. 11. Probably this is due to a printing mistake. On the other hand, the values of the free energies of activation calculated here using the Gutowsky–Holm [17] approximation are different from those reported in ref. 11; this is due to the different approximation used.

† 1 cal = 4.184 J.

REFERENCES

[1] J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *J. Org. Chem.*, 1978, **43**, 3255 and references therein.

[2] B. Feringa and H. Wynberg, *J. Am. Chem. Soc.*, 1977, **99**, 602.

[3] R. F. Langler and T. T. Tidwell, *Tetrahedron Lett.*, 1975, 777.

[4] A. L. Baumstark, E. J. H. Bechera, and M. J. Semigra, *Tetrahedron Lett.*, 1976, 3265.

[5] P. D. Mollere, K. N. Houk, D. L. Bomse, and T. H. Morton, *J. Am. Chem. Soc.*, 1976, **98**, 4732.

[6] S. Nishida and F. Kataoka, *J. Org. Chem.*, 1978, **43**, 1612.

[7] (*a*) D. Lenoir, *Chem. Ber.*, 1978, **111**, 411; (*b*) D. Lenoir and P. Lemmen, *Chem. Ber.*, 1980, **113**, 3112.

[8] G. A. Olah in ' Friedel–Crafts and Related Reactions,' Interscience, New York, 1964, vol. III, Part 1.

[9] J. R. C. Light and H. H. Zeiss, *J. Organomet. Chem.*, 1970, **21**, 517.

[10] P. E. Verkade, K. S. De Vries, and B. M. Wepster, *Recl. Trav. Chim. Pay-Bas*, 1963, **82**, 637.

[11] A. J. M. Reuvers, A. Sinnema, F. Van Rautwijk, J. D. Remijuse, and H. Van Bekkum, *Tetrahedron*, 1969, **25**, 4455.

[12] Gurutada, J. B. Stothers, and J. D. Talman, *Can. J. Chem.*, 1967, **45**, 731.

[13] J. H. Cornell, jun., and M. H. Gollis, *Org. Synth.*, 1962, **42**, 57.

[14] C. F. Castro and W. C. Kray, jun., *J. Am. Chem. Soc.*, 1963, **85**, 2768.

[15] P. Finocchiaro, D. Gust, W. D. Hounshell, J. P. Hummel, P. Maravigna, and K. Mislow, *J. Am. Chem. Soc.*, 1976, **98**, 4945.

[16] H. D. Beckhaus, K. J. McCullough, H. Fritz, C. Ruchardt, B. Kitschke, H. J. Lindner, D. A. Dougherty, and K. Mislow, *Chem. Ber.*, 1980, **113**, 1867.

[17] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.