SHORT PAPER

J. Chem. Research (S),
2002, 224–225

A new synthesis of alkenes *via* a boron trifluoride mediated reaction of aliphatic ketones with aromatic ketones[†]

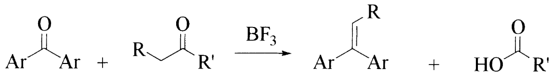
Rama R. Malladi and George W. Kabalka*

Departments of Chemistry and Radiology; The University of Tennessee Knoxville, TN 37996-1600, USA

Aromatic ketones react with aliphatic ketones to produce alkenes in the presence of boron trifluoride.

Keywords: aramatic ketones, aliphatic ketones

During the course of an investigation focused on the synthesis of (*E*)-1-aryl-1-alkenes from aldehydes *via* a boron trifluoride catalysed Aldol–Grob reaction sequence,[1–4] we found that the new reaction sequence could be successfully carried out utilising ketones (Eqn 1).

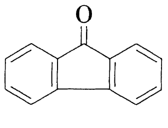
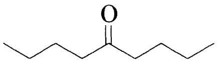
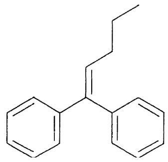
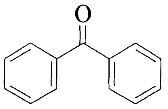
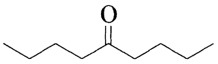
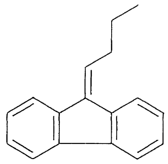
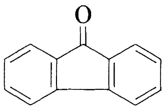
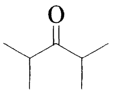
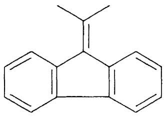
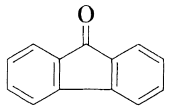
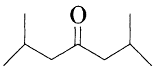
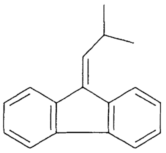


(1)

We first examined the efficiency of various boron trifluoride complexes in the new reaction. When an equimolar mixture of nonan-5-one fluorenone and boron trifluoride (as its diethyl ether complex) was refluxed for 24h in mixed hexanes, the desired alkene was obtained in 59% yield. The reaction also occurred in the presence of other boron trifluoride complexes but yields were substantially lower. For example the use of either neat boron trifluoride or its acetic acid complex produced alkene in 17% yields whereas the use of the phosphoric acid complex of boron trifluoride resulted in only traces of alkene.

We then examined the reaction of nonan-5-one with fluorenone in the presence of BF_3 •OEt_2 in various solvents. A donor solvent such as diethyl ether completely inhibited the formation of alkene but traces of alkene product were obtained in CH_2Cl_2 and CCl_4. The yields of aikene were sigmficantly lower in toluene (12%) than in hexane (59%). Thus subsequent reactions were carried out using BF_3 •OEt_2 in hexane solvent. Our results are summarised in Table 1.

Table 1 Reaction of aromatic ketones with aliphatic ketones in the presence of boron trifluoride diethyl ether complex[a]

Aromatic ketone	Aliphatic ketone	Product[b]	Yield/%[c]
			59
			43
			28
			31

[a]Reactions carried out in hexane at reflux for 24h. [b]Physical and spectral characteristics are in agreement with proposed structures. [c]Isolated yields.

---

[*] To receive any correspondence. E-mail: kabalka@utk.edu

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Dehydration and reduction reactions can also occur and generally lead to loss of the desired product. Mixtures of alphatic ketones failed to produce alkene products suggesting that a benzylic carbocation intermediate is involved. A reasonable mechanism would involve the formation of the mixed Aldol product followed by the formation and subsequent non-synchronous ring opening of a lactol which is reminiscent of the two step Grob[5] fragmentation that has been reported for *N*-halo-α-amino acids[6] and cyclobutane hemiacetals[7] as well as the acid catalysed fragmentation of β-hydroxy acetals.[8,9]

In conclusion, we have developed a new reaction in which aromatic ketones are converted into alkenes *via* reaction with aliphatic ketones.

Experimental

All reactions were carried out in dry hexane in oven dried glassware under a nitrogen atmosphere. Air and moisture sensitive compounds were introduced by means of a syringe through a rubber septum. All reagents were used as received (Aldrich Chemical Co.). The products were purified by chromatography using 230–240 mesh ASTM 60 Å silica gel. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC250 NMR spectrometer and resonances are given in ppm (δ) relative to TMS. Elemental analyses were performed by Atlantic Micro Labs, Norcross, Georgia.

9-Butylidene-9H-fluorene: Representative procedure: to a dry 25ml round-bottomed flask were added nonan-5-one (1 mmol), fluorenone (1 mmol), hexane (5 ml) and $BF_3 \bullet OEt_2$ (1 mmol). The reaction mixture was stirred at reflux for 24 h and then quenched with water (5 ml). The alkene product was extracted into diethyl ether (3 × 10 ml) and purified by silica gel chromatography (hexane as eluent) to yield 0.59 mmol (59%) of 9-butylidene-9H-fluorene as viscous yellow oil. ^{1}H NMR.

($CDCl_3$/TMS) δ 1.03–1.09 (t, 3H), 1.62–1.76 (m, 2H), 2.74–2.83 (q, 2H), 6.68–6.74 (t, 1H), 7.22–7.34 (m, 4H), 7.62–7.85 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 140.77, 139.39, 138.53, 137.56, 135.47, 130.98, 127.57, 127.28, 126.81, 124.91, 119.73, 119.61, 119.42, 31.36, 22.86, 14.08. Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.43; H, 7.53.

1,1-Diphenyl-but-1-ene: colourless viscous oil. ^{1}H NMR ($CDCl_3$/TMS) δ 0.87–0.93 (t,3H), 1.39–1.53 (m, 2H), 2.05–2.13 (q,2H), 6.05–6.11 (t, 1H), 7.16–7.39 (m, 10H); ^{13}C NMR($CDCl_3$) δ 142.92, 141.58, 140.35, 130.10, 129.97, 128.09, 128.05, 127.20, 126.79, 126.74, 31.84, 23.18, 13.87. Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.64; H, 8.34.

9-Isopropylidene-9H-fluorene: pale yellow gummy oil. ^{1}H NMR ($CDCl_3$/TMS) δ 2.56 (s, 6H), 7.25–7.33 (m, 4H), 7,77–7.87 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 141.02, 139.58, 139.18, 126.74, 126.34, 124.97, 119.35, 26.36. Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 92.97; H, 6.99.

9-Isobutylidene-9H-fluorene: yellow semi-solid. ^{1}H NMR ($CDCI_3$ /TMS) δ 1.25–1.27 (d, 6H), 3.48–3.57 (m, 1H), 6.56–6.59 (d, IH), 7.25–7.32 (m, 4H), 7.64–7.86 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 140.79, 139.53, 138.53, 137.14, 133.40, 127.61, 127.33, 126.88, 124.97, 119.79, 119.67, 119.34, 43.23,23.02, 22.77. Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.47; H, 7.50.

We wish to thank the US Department of Energy and the Robert H. Cole Foundation for their support of this research.

Received 3 March 2001; accepted 1 July 2001
Paper 01/784

References

1 G.W. Kabalka, D. Tejedor, N.-S Li, R.R. Malladi and S. Trotman, *Tetrahedron Lett.* 1998, **39**, 8071.
2 G.W. Kabalka, D. Tejedor, N.-S. Li, R.R. Malladi and S. Trotman, *J. Org. Chem.,* 1998, **63**, 6439.
3 G.W. Kabalka, D. Tejedor, N.-S. Li, R.R. Malladi and S. Trotman, *Tetrahedron,* 1998, **56**, 15525.
4 G.W. Kabalka, N.-S. Li, D. Tejedor, R.R. Malladi and S. Trotman, *J. Org. Chem.,* 1999, **64**, 3157.
5 C.A. Grob, *Angew. Chem. Int. Ed. Eng.,* 1969, **8**, 535.
6 X.L. Armesto, M. Canle, M. Losada, J.A. Santaballa, *J. Org. Chem.,* 1994, **59**, 4659.
7 M. De Giacomo, R.M. Bettolo, R. Scarpelli, *Tetrahedron Lett.,* 1997, **38**, 3469.
8 H. Yamamoto, H. Suemune, K. Sakai, *Tetrahedron,* 1991, **47**, 8523.
9 S. Nagumo, A. Matsukuma, F. Inoue, T. Yamamoto, H. Suemune and K. Sakal, *J. Chem. Soc., Chem. Commun.,* 1990, 1538.