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Synthesis of isomeric benchrotrenic alkenes by Ti-induced carbonyl coupling reaction

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Abstract

The benchrotrenic ketones BctCOR (1) (Bct: $Cr(CO)_3C_6H_5$; R = CH_3 (a), C_2H_5 (b), n-C_3H_7 (c), n-C_4H_9 (d)) undergo reductive alkene coupling reaction when treated with $TiCl_3$/Li. The two isomeric forms of Bct(R)C=C(R)Bct (2) were isolated in the ratio Z/E = *ca.* 3:1. Decomplexation of **2** by iodine gave quantitatively the corresponding isomeric alkyl stilbenes $C_6H_5(R)C{=}C(R)C_6H_5$ (3).

Introduction

The reductive coupling of aldehydes and ketones to give alkenes by low valent titanium species has been the subject of extensive synthetic and mechanistic investigations [1]. Many reagent systems have been used (for example, $TiCl_4$/Zn [2a], $TiCl_3/LiAlH_4$ [2b], $TiCl_3$/Li [2c,d] and recently $TiCl_3\ (DME)_{1.5}$/Zn–Cu [2e]) and various experimental conditions tried. A great variety of synthetic uses has been found, especially in the field of natural products [3] and strained olefins [4]. Despite this interest in the titanium induced carbonyl coupling reaction, its use for the preparation of alkenes incorporating the transition metal component has been limited to a series of iron complexes [4a,5]. Indeed, the presence of the organometallic fragment may not be compatible with the strongly reducing Ti(O).

Some of our previous studies [6] dealt with the chemistry and other properties of the π-arene chromium tricarbonyls, the so-called benchrotrenic complexes. We describe here the reductive coupling of benchrotrenic ketones **1** to give benchrotrenic alkenes **2** (Scheme 1). The easy separation by the column chromatography of Z and E isomers of **2** followed by iodine decomplexation leads to the isomeric alkenes **3**.

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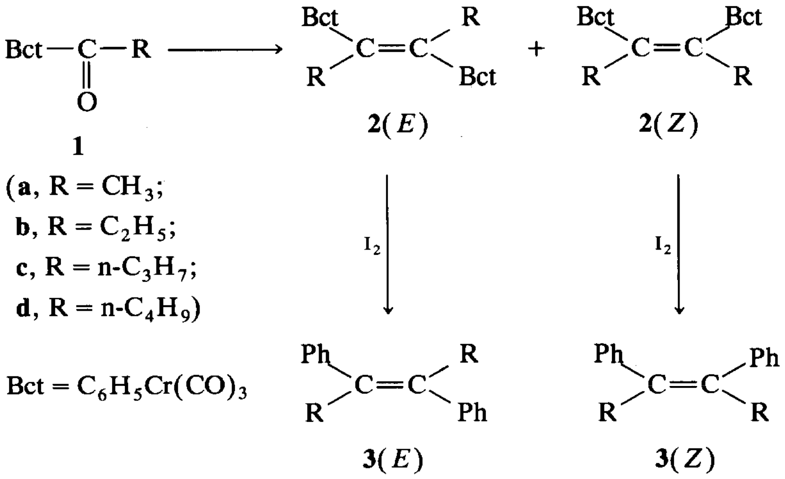
Results and discussion

It has been shown that the alkene-forming coupling reaction proceeds via metallopinacols, and that the subsequent deoxygenation is the rate determining step [7]. In fact, pinacols can be isolated if the reaction is carried out under mild conditions [8].

We reported previously [6a] that the $TiCl_4$/Mg–Hg system can be successfully used in the pinacol coupling of the benchrotrenic ketones. However, the formation of alkenes as byproducts was observed in all cases. In order to promote complete deoxygenation of the intermediate metallopinacols we have now used a more highly reducing agent, namely the $TiCl_3$/Li system. This Ti^0 reagent was introduced by McMurry *et al.* [2c] and used subsequently by several authors [2d,9] to synthesize alkenes from both aromatic and aliphatic substrates.

In the present investigation the ketones **1a–d** (Scheme 1) were used as organometallic substrates for the reductive coupling. In a representative procedure for the benchrotrenyl methyl ketone **1a** the reaction was performed in DME at reflux for 4 h. TLC analysis of the crude product revealed two components which were readily separated by column chromatography and isolated in the ratio of *ca.* 3:1. The ^1H NMR and MS spectra showed them to be isomeric benchrotrenic alkenes. In the NMR spectra the Me resonances of the major products are deshielded by 0.07 ppm with respect to the minor products, whereas the aromatic resonances are shielded by 0.24, 0.17 and 0.14 ppm respectively for the protons at the positions 2, 3 and 4 (Table 1). Similar effects were observed for the isomers of complexes **1b–d**. The differences between the chemical shifts of the *Z*/*E* isomers ($\delta_Z - \delta_E = \Delta\delta$) were noted in all cases. Generally, the $\Delta\delta$ values of the aliphatic protons increase with the distance of these protons from the aromatic ring (for example $\Delta\delta_{CH_3\text{-}\beta}$ for **2b** is larger than $\Delta\delta_{CH_3\text{-}\alpha}$ for **2a**, and $\Delta\delta_{CH_3\text{-}\gamma}$ and $\Delta\delta_{CH_2\text{-}\beta}$ are larger than $\Delta\delta_{CH_2\text{-}\alpha}$ for **2c**). This can be ascribed to the diamagnetic anisotropy effect of $Cr(CO)_3$ fragments, which will be more pronounced for the *Z*- than for the *E*-isomer. Indeed, for the *Z*-isomer the distant aliphatic protons (β, γ...) enter the $Cr(CO)_3$-deshielding region [10] more easily owing to the necessarily



Scheme 1

Table 1

Yield, melting point and ^1H NMR data for the complex series **2**

Complex	Overall yield [a]	m.p. (°C)	^1H NMR ($CDCl_3$) [b]				
			$\delta(CH_3)$	$\delta(CH_2)$	δ(Bct)		
					H_2	H_3	H_4
2a (*E*)	80	254 dec.	2.04s(3)		5.47d(2)	5.26t(2)	5.47t(1)
2a (*Z*)		224	2.11s(3)		5.23d(2)	5.09t(2)	5.33t(2)
2b (*E*)	85	240	1.07t(3)	2.28q(2)	5.46d(2)	5.19t(2)	5.54t(1)
2b (*Z*)		208	1.31t(3)	2.54q(2)	5.26d(2)	4.99t(2)	5.40t(1)
2c (*E*)	75	245 dec.	0.82t(3)	1.46m(2) and 2.23m(2)	5.46d(2)	5.17t(2)	5.54t(1)
2c (*Z*)		208	1.07t(3)	1.67m(2) and 2.35m(2)	5.26d(2)	4.97t(2)	5.39t(1)
2d (*E*)	79	226	0.81t(3)	1.32m(4) and 2.23m(2)	5.47d(2)	5.17t(2)	5.55t(1)
2d (*Z*)		178	1.00t(3)	1.56m(4) and 2.38m(2)	5.28d(2)	4.98t(2)	5.39t(1)

[a] Z/E ratio is *ca.* 3:1 in each case. [b] Chemical shifts are in ppm relative to TMS. s = singlet, t = triplet, q = quadruplet, m = multiplet.

external position of two $Cr(CO)_3$ moieties with respect to the pocket of the molecule. The mass spectra of *Z* and *E* isomers differ in respect of the relative intensities of the more important fragments, *i.e.* M, $M-3CO$, $M-4CO$, $M-5CO$, $M-6CO$ and $M-(6CO+Cr)$ (see Experimental section).

Decomplexation of the isomeric benchrotrenic alkenes **2a–d** was brought about by treatment with iodine [11*]. After recrystallization from pentane the pure alkenes **3a–d** (Scheme 1) were obtained quantitatively. Their melting points and ^1H data are given in Table 2.

The assignment of the Z/E configuration of the alkenes **3a–c** (and consequently of the benchrotrenic alkenes **2a–c**) was carried out by comparison of their melting points and spectral data with the literature values [12]. The assignment of the *Z* and *E* isomers of the 5,6-diphenyl-5-decene **3d** was based upon the ^1H NMR data; as for the alkenes **3a–c**, the CH_3 and the CH_2 resonances of the major isomer **3d** (*Z*) were deshielded with respect to the corresponding resonances of the minor isomer (*E*).

We note that the *Z* isomer is the major one in each case, and that the Z/E ratio of *ca.* 3:1 does not vary with variation in the alkyl chain R. Furthermore, the Z/E ratio is similar to that observed by McMurry *et al.* [7b] for the reductive coupling of acetophenone [13*]. We assume that the $Cr(CO)_3$ unit does not affect significantly the mechanism of the reaction.

In the Ti-induced carbonyl coupling reaction stereoselectivity has been observed in the diol-forming step as well as in the overall alkene forming process [1]. In keeping with that, the second deoxygenation step has been shown to be close to being concerted [7b]. Consequently, the preference for formation of *Z*-products can be attributed to the fact that complexation and stabilization of the two benzenic/benchrotrenic moieties by titanium [11] is possible only in the preceding *meso* form of the intermediate metallopinacolate. In terms of this picture the moderate loss of stereoselectivity in the benchrotrenic series ($Z/E = 75/25$ compared with 90/10 for acetophenone [7b]) can be attributed to the electron-

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* Reference number with asterisk indicates a note in the list of references.

Table 2

Melting point and ^1H NMR data for the alkyl stilbene series **3**

Alkyl stilbenes	m.p. (°C)	^1H NMR $(CDCl_3)$ [a]		
		$\delta(CH_3)$	$\delta(CH_2)$	$\delta(C_6H_5)$
3a (*E*)	106	1.89s(3)		7.30m(5)
3a (*Z*)	68	2.18s(3)		7.02m(5)
3b (*E*)	74	0.78t(3)	2.15q(2)	7.28m(5)
3b (*Z*)	39	0.92t(3)	2.57q(2)	6.99m(5)
3c (*E*)	94	0.70t(3)	1.18m(2) and 2.12m(2)	7.29m(5)
3c (*Z*)	42	0.92t(3)	1.34m(2) and 2.54m(2)	6.98m(5)
3d (*E*)	60	0.69t(3)	1.12m(4) and 2.13m(2)	7.26m(5)
3d (*Z*)	22	0.89t(3)	1.32m(4) and 2.56m(2)	6.99m(5)

[a] Chemical shifts are in ppm relative to TMS. s = singlet, t = triplet, q = quadruplet, m = multiplet.

withdrawing effect of $Cr(CO)_3$, which leads to weaker Ti-complexation. On the other hand the steric effect of the $Cr(CO)_3$ fragment is not sufficiently pronounced to alter markedly the stereochemical course of the reaction.

Experimental

All reactions were performed under argon. Spectra were recorded with the following instruments: ^1H NMR, Jeol FX 100 (δ (ppm) $CDCl_3$/TMS); mass spectra, Finnigan 3002.

The benchrotrenic ketones BctCOR were prepared as described previously [15]: **1a**, R = CH_3; m.p. 85°C; **1b**, R = C_2H_5, m.p. 98°C; **1c**, R = n-C_3H_7, m.p. 65°C; **1d**, R = n-C_4H_9, m.p. 61°C.

Preparation of benchrotrenic alkenes 2

All these complexes were prepared by modification of the general procedure previously described [7b] for intermolecular coupling using $TiCl_3$/Li. A mixture of lithium wire (0.656 g, 94.6 mmol) and $TiCl_3$ (7.810 g, 31.2 mmol) in 80 ml of dry dimethoxyethane (DME) was refluxed for 1 h, then allowed to cool. A solution of benchrotrenic ketone **1** (7 mmol) in 20 ml of DME was added, and the mixture refluxed for a further 4 h, then cooled to room temperature, diluted with diethyl ether, and filtered through Celite to remove the residual Li. The filtrate was treated with water and extracted with diethyl ether, the extract was dried over $CaCl_2$ and filtered, and the filtrate was concentrated on the rotary evaporator to yield yellow crystals. From these the two *Z*/*E* isomers were separated by flash column chromatography or (and) by preparative thin layer chromatography with a 2/1/0.1 petroleum ether/toluene/diethyl ether mixture as eluant (Kieselgel 60 Merck 230–400 mesh). The last two yellow bands were collected and removal of the solvents followed by recrystallization from diethyl ether/hexane gave the *Z* and *E* isomers of the corresponding benchrotrenic alkenes **2** (the *E* isomer was eluted before the *Z* one).

From acetophenone chromium tricarbonyl **1a**: crude 2,3-diphenylchromiumtricarbonyl-2-butene *E/Z* **2**, 1.34 g (80%). Chromatography: fraction **2a** (*E*), 0.121 g, m.p. 254°C dec. M.S.: 480 (2) M^+, 396 (3) $M^+ - 3CO$, 368 (4) $M^+ - 4CO$, 340 (1) $M^+ - 5CO$, 312 (17) $M^+ - 6CO$, 260 (100) $M^+ - Cr - 6CO$; fraction **2a** (*Z*), 0.330 g, m.p. 224°C. M.S.: 480 (18) M^+, 396 (15) $M^+ - 3CO$, 368 (6) $M^+ - 4CO$, 340 (6) $M^+ - 5CO$, 312 (39) $M^+ - 6CO$, 260 (100) $M^+ - Cr - 6CO$.

From propiophenone chromiumtricarbonyl **1b**: crude 3,4-diphenylchromiumtricarbonyl-3-hexene *E/Z*, 1.5 g (85%). Chromatography: fraction **2b** (*E*), 0.120 g, m.p. 240°C. M.S.: 508 (3) M^+, 424 (2) $M^+ - 3CO$, 396 (4) $M^+ - 4CO$, 368 (0.5) $M^+ - 5CO$, 340 (22) $M^+ - 6CO$, 288 (100) $M^+ - Cr - 6CO$; fraction **2b** (*Z*), 0.700 g, m.p. 208°C. M.S.: 508 (26) M^+, 424 (16) $M^+ - 3CO$, 396 (7) $M^+ - 4CO$, 368 (9) $M^+ - 5CO$, 340 (34) $M^+ - 6CO$, 288 (100) $M^+ - Cr - 6CO$.

From butyrophenone chromiumtricarbonyl **1c**: crude 4,5-diphenylchromiumtricarbonyl-4-octene *E/Z* **2**, 1.40 g (75%). Chromatography: fraction **2c** (*E*), 0.040 g, m.p. 245°C dec; M.S.: 536 (3) M^+, 452 (2.6) $M^+ - 3CO$, 424 (5) $M^+ - 4CO$, 396 (0.5) $M^+ - 5CO$, 368 (29) $M^+ - 6CO$, 316 (100) $M^+ - Cr - 6CO$; fraction **2c** (*Z*), 0.610 g, m.p. 208°C. M.S.: 536 (3.7) M^+, 452 (5.3) $M^+ - 3CO$, 424 (5) $M^+ - 4CO$, 396 (4) $M^+ - 5CO$, 368 (22) $M^+ - 6CO$, 316 (100) $M^+ - Cr - 6CO$.

From valerophenone chromiumtricarbonyl **1d**: crude 5,6-diphenylchromiumtricarbonyl-5-decene *E/Z* **2**, 1.55 g (79%). Chromatography: fraction **2d** (*E*), 0.156 g, m.p. 226°C; M.S.: 564 (4) M^+, 480 (3) $M^+ - 3CO$, 452 (5) $M^+ - 4CO$, 424 (0.5) $M^+ - 5CO$, 396 (21) $M^+ - 6CO$, 344 (100) $M^+ - 3Cr - 6CO$; fraction **2d** (*Z*), 0.650 g, m.p. 178°C; M.S.: 564 (13) M^+, 480 (18) $M^+ - 3CO$, 452 (17) $M^+ - 4CO$, 424 (13) $M^+ - 5CO$, 396 (100) $M^+ - 6CO$, 344 (55) $M^+ - Cr - 6CO$.

Decomplexation of benchrotrenic alkenes 2

As described in ref. 11*, in a typical reaction at room temperature a solution of iodine (4 mmol) in 15 ml of THF was added dropwise during 15 min to a solution of benchrotrenic alkenes (1 mmol) in 10 ml of THF. The mixture was stirred for 3 h, then shaken with ether and 5% aqueous sodium bisulphite. The ethereal layer was washed with water, dried over $CaCl_2$ and filtered. The filtrate was concentrated on a rotary evaporator to yield the crude product. Recrystallization from pentane gave the decomplexed alkenes **3** quantitatively as white crystals.

The following relationships, with melting points, were observed (melting points previously reported [12] are given in parentheses):

2a, m.p. 254°C dec.: **3a** (*E*), m.p. 106°C (104°C);
2a, m.p. 224°C: **3a** (*Z*), m.p. 68°C (65°C);
2b, m.p. 240°C: **3b** (*E*), m.p. 74°C (67–69°C);
2b, m.p. 208°C: **3b** (*Z*), m.p. 39°C (oil);
2c, m.p. 245°C dec.: **3c** (*E*), m.p. 94°C (86–87°C);
2c, m.p. 208°C: **3c** (*Z*), m.p. 42°C (42–43°C);
2d, m.p. 226°C: **3d** (*E*), m.p. 60°C;
2d, m.p. 178°C: **3d** (*Z*), m.p. 22°C.

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