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HIGH SPEED LIQUID CHROMATOGRAPHIC ANALYSIS OF ORGANO-IRON COMPOUNDS

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SUMMARY

Mixtures which include tricarbonyliron complexes of dienes and dienones plus *m*-xylene and 2,4-dimethylacetophenone have been separated, and the ketones have been determined quantitatively using reversed phase high speed liquid–liquid partition chromatography.

INTRODUCTION

Gas chromatography (GC) was for some time the single method of general utility for rapid separation and quantitative analysis of mixtures on a micro scale. Unfortunately the requirement that substrates be stable at elevated temperatures has denied the routine use of GC to many organotransition metal chemists. High speed liquid chromatography (LC) has capabilities comparable to GC but can be carried out at or below ambient temperature[1]. Veening *et al.* have reported analysis of tricarbonyl(arene)chromium compounds by LC using a normal phase (Carbowax 400/Porasil C stationary phase, iso-octane mobile phase) system[2]. We report here analysis of tricarbonyl(dienone)iron compounds using a reversed phase (non-polar stationary phase, polar mobile phase) liquid–liquid partition system.

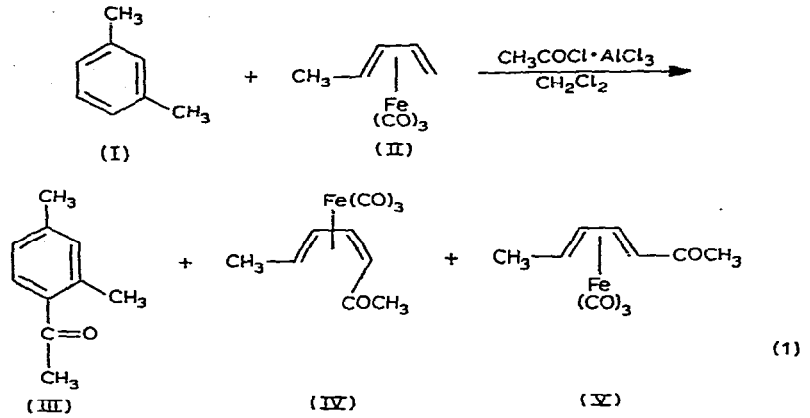
RESULTS AND DISCUSSION

A study of reactivity of tricarbonyl(diene)iron compounds toward electrophiles by a competition technique required rapid quantitative analysis of small amounts of products (III)–(V) from reactions like eqn. (1) in the presence of larger amounts of starting materials (I) and (II)*.

The dienone complexes were not stable at GC temperatures and thin layer chromatography (TLC) did not provide sufficient resolution**. Liquid chromatography seemed uniquely suited to our requirements. A reversed phase system, in which the

* All compounds have been identified by isolation of pure material. Satisfactory IR, NMR, mass spectral and combustion analyses were obtained. For differentiation of *cis–trans* isomers (IV) and (V) see ref. 6.

** IR, NMR, and UV methods were also investigated.



(1)

more polar products (III)–(IV) would elute rapidly to give narrow peaks unobscured by large amounts of (I) and (II) which would elute more slowly, was selected.

Best performance was achieved using a 50 cm × 2.0 mm (i.d.) glass column packed with DuPont ODS Permaphase (< 37 μ) with 20% aqueous methanol as mobile phase. When 1.0 μl samples of ca. 10^{-3} *M* total ketone concentration in methanol containing ca. 10% dichloromethane were injected onto the column using a flow rate of 0.3 ml/min (maximum pressure 200 lbf/in.^{2}), a clean separation of (III)–(V) was achieved in 10 min (see Fig. 1). Peaks were identified by injection of authentic samples dissolved in aqueous methanol in which the diene and dienone complexes are stable for at least a period of several weeks. A UV detector operating at 254 nm was employed*. Integrated peak areas corrected for molar absorptivity at 254 nm were used as a basis for quantitative determinations**.

ODS Permaphase is a controlled surface porosity support with a thin film of silicone polymer permanently bonded to its surface[4,5]. This film constitutes a non-elutable, non-polar stationary phase for liquid–liquid partitioning. Our system exhibited strictly reversed phase behavior, the elution order being exactly the reverse of that observed with TLC on silica gel or alumina. The column was highly selective. A 40% aqueous methanol mobile phase was necessary for elution of benzoylated diene complexes, and non-polar compounds like (I) and (II) had long retention times even under these conditions and did not elute from the column at all. Typical retention times are listed in Table 1.

High speed liquid chromatography will rapidly become an immensely valuable analytical technique for organometallic chemists. In our opinion, normal phase chromatography, with which most chemists are familiar, will prove most generally useful. However, as in the case above, reversed phase chromatography will

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* Our chromatograph was assembled from purchased components: Milton Roy Minipump, Chromatronix columns and fittings, and a Laboratory Data Control UV Monitor, model 1205, as detector. This system, except for the detector, was modelled after that described by Siggia and Dishman[3].

** Calibration curves showed linearity of detector response in the range 0.02 to 0.64 absorbance units. Relative peak areas were reproducible to ±2%. Sensitivity was sufficient for determination of 1.0 nmole of a compound with $\varepsilon_{254} = 10^3$ with ±5% accuracy (single determination). Practical determinations were made on samples with components which differed in concentration by as much as 50-fold. Detailed results will be presented in a separate paper.

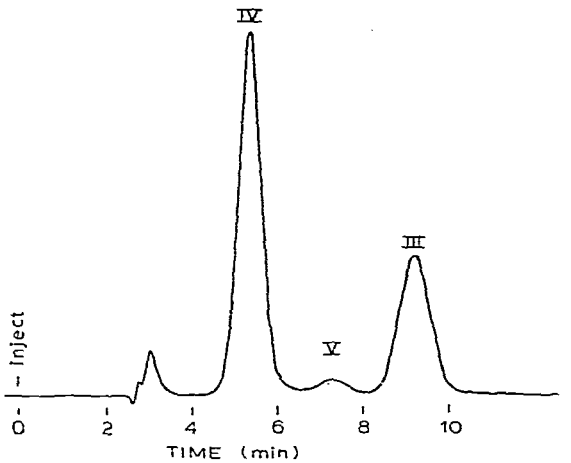

Fig. 1. Recorder trace for liquid chromatographic separation of compounds (III) (IV), and (V); ordinate is linear in relative optical density units. Peaks at 2.3 min are associated with emergence of the solvent front.

TABLE 1

LIQUID CHROMATOGRAPHIC RETENTION TIMES AND CAPACITY FACTORS OF TRICARBONYL(DIENONE)IRON COMPLEXES

Complexed dienone	*Retention time (min)*[a]		*Capacity factor*[c]	
	cis[b]	*trans*[b]	*cis*	*trans*
3,5-Hexadienone	3.6	4.8	0.57	1.08
3,5-Heptadienone (IV) and (V)	5.4	7.4	1.35	2.22
5-Methyl-3,5-hexadienone	4.8	7.0	1.08	2.04
4-Methyl-3,5-hexadienone	4.6	8.8	1.00	2.83
5-Methoxy-3,5-hexadienone	4.9	7.4	1.13	2.22
6-(*p*-Bromophenyl)-3,5-hexadienone	6.5[d]	9.6[d]	1.83[d]	3.17[d]
1-Phenyl-2,4-pentadienone	2.6[d]	4.2[d]	0.13[d]	0.82[d]
1-Phenyl-2,4-hexadienone	4.2[d]	6.7[d]	0.82[d]	1.91[d]

[a] 50 cm × 2.0 mm (i.d.) DuPont ODS Permaphase with 20% aqueous methanol mobile phase at ambient temperature (25–30°), flow rate 0.3 ml/min. Solvent front elutes at 2.3 min. [b] Configuration of the ketone function, *e.g.* (IV) is *cis* and (V) is *trans*. [c] Capacity factor is the ratio of amount of solute in the stationary phase to that in the mobile phase and is calculated as $(t_R - t_0)/t_0$ where t_R is the retention time of the solute and t_0 the retention time of a nonsorbed component, see ref. 1, p. 10. [d] Same conditions except 40% aqueous methanol employed as mobile phase.

sometimes offer a uniquely suitable solution to a specific problem and should complement the normal phase method.

ACKNOWLEDGEMENTS

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