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TRANSITION METAL CARBENE COMPLEXES

LIII*. PROOF OF THE ABSENCE OF A FREE CARBENE IN THE PREPARATION OF A CYCLOPROPANE FROM A METAL–CARBENE COMPLEX

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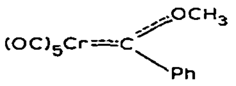
SUMMARY

By using an optically active metal–carbene complex we were able to isolate an optically active cyclopropane from the reaction of diethyl fumarate with [(−) (*R*)-methylphenylpropylphosphine] (phenylmethoxycarbene) tetracarbonylchromium. In addition to being synthetically useful for the preparation of cyclopropanes of optical activity, this reaction demonstrates that no free carbene is involved in the mechanism for the reaction.

Carbenes, like other highly reactive organic molecules, may be coordinated to a transition metal to yield a stable complex[2]. Recently, a synthetically useful stereospecific reaction has been reported[3,4]: heating a carbene complex (I) in certain olefins yields a cyclopropane by transfer of the carbene entity.



(I)

To demonstrate whether or not this reaction involves a "free carbene" is more difficult than to show the intermediacy of relatively long-lived species such as cyclobutadiene, which Pettit and his coworkers were able to separate from its tricarbonyliron derivative and subsequently trap with acetylenes[5]. For a short-lived species such as a carbene we have had to use another approach. Where more than one product is formed, modification of the metal complex might result in a changed product ratio if reaction occurs within the metal complex. Fischer and Dötz[4] have reported the effect of change of metal atom—the product ratio did indeed vary, which proved that at least part of the reaction involved the metal complex. A more powerful technique is to observe the presence of a product which could only be formed by reaction within a metal complex. Provided that the properties of this compound are sufficiently different from those of the normal product, detection of this new

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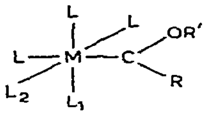
* For Part LII see ref. 1.

compound becomes limited only by instrument sensitivity. For such a property we have chosen chirality.

Reaction of a suitable olefin with a carbene CRR′ within its metal complex will result in partial or complete enantioselective synthesis[6]. (A Z-olefin like diethyl maleate yields only achiral cyclopropanes; a free carbene of the type CRR′ reacts with an E-olefin like diethyl fumarate to give a racemic mixture). The resulting excess of one enantiomer over the other is readily detected by polarimetry, if not at the sodium D-line, then certainly in the neighbourhood of an absorption maximum (*cf.* the Cotton effect).

Rather than synthesise and resolve a metal–carbene complex such as (II),



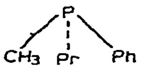
(II)

which is asymmetric at the metal atom, we chose to use a chiral ligand. Of the two routes[7,8], to the carbenephosphinetetracarbonylchromium complex, that given in eqn. (2) gives a higher yield based on optically active phosphine. The relatively

$$\mathrm{Cr(CO)_6} \rightarrow \mathrm{Cr(CO)_5PR_3} \xrightarrow{\text{Ref. 7}} \mathrm{Cr(CO)_4PR_3{-}C(OR')R''} \qquad (1)$$

$$\mathrm{Cr(CO)_6} \rightarrow \mathrm{Cr(CO)_5{-}C(OR')R''} \xrightarrow{\text{Ref. 8}} \mathrm{Cr(CO)_4PR_3{-}C(OR')R''} \qquad (2)$$

long half-life of the (−)(*R*)-methylphenylpropylphosphine (III)[9], for which a convenient synthesis has recently been reported[10,11], allowed us to use (III) without danger of racemization of the phosphine.



(III)

The product obtained from reaction of equimolar amounts of (III) and (I) was isolated as a deep red oil, whose ^{1}H NMR and IR spectra are consistent with it being a *cis*/*trans* mixture of the required complex (IV).

$$\mathrm{Cr(CO)_4[P(CH_3)(Ph)(Pr)]{-}C(OCH_3)Ph}$$

(IV)

Although the *cis* and *trans* isomers of the corresponding tri-n-butylphosphine complex have been separated and shown to interconvert readily at room temperature[12] we were not able to separate completely the *cis* and *trans* isomers of (IV), but obtained only fractions enriched in either the *cis* or *trans* isomer. This enabled us, however, to assign each of the ^{1}H NMR and IR (CO region) bands to one or the other of the isomers. The chemical shifts and ν(CO) bands are given in Table 1.

The data show that the component of higher R_f whose methoxyl protons absorb at lower field shows clearly one carbonyl absorption in its IR spectrum at 1940 cm^{-1}. The other appears as a shoulder at about 1896 cm^{-1}. Both these ob-

TABLE 1

^{1}H NMR SPECTRUM OF (IV)

(10% Solution in acetone-d_6)

Chemical shift *τ(ppm)*	*Integration*	*Multiplicity*	*Assignment*
2.2–2.9	10	Multiplet	P–Ph+C–Ph
5.33	3	Singlet	*trans*-OCH_3
5.88		Singlet	*cis*-OCH_3
8.18	10	Doublet (*J* 7 Hz)	P–CH_3
7.83–9.15		Multiplet	P–C_3H_7

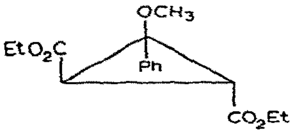
IR ABSORPTION FREQUENCIES OF THE CO GROUPS OF (IV)

(n-Hexane solution)

Frequency (cm^{-1})	*Cis/trans*
1888 vs	*cis*
~1896 m(sh)	*trans*
1912 s	*cis*
1920 m	*cis*
1940 vw	*trans*
2005 m	*cis*

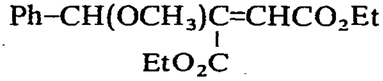
servations are consistent with the assignment of the *trans* configuration of the phosphine and carbene ligands to this component. The other component which had a slightly lower R_f value shows four carbonyl absorptions in the region 2100–1850 cm^{-1} which is consistent with the absorptions in a molecule which has the symmetry C_{2v} when the carbene and phosphine ligands are not taken into account. That the *trans*-component is eluted slightly faster with hexane/benzene from silica gel is consistent with the behaviour of other phosphinecarbenetetracarbonylchromium complexes[12].

Fortunately our inability to separate the isomers was immaterial, since it was necessary to heat (IV) to 40° for 6 h to cause reaction with diethyl fumarate. The major of the two products, which were separated only with difficulty using the technique of dry column chromatography[13], was identified as (VII) (or its mirror image) on the basis of chemical analysis, and comparison of its GLC retention time, ^{1}H NMR, IR, and mass spectra with those previously reported[4,14]. Our sample of (VII) was, however, optically active (rotations given in Experimental) and repeated recrystallisation did not change its melting point or observed rotation.



(VII)

The minor product was characterised as diethyl 3-methoxy-3-phenyl-1-propene-1,2-dicarboxylate (VIII) on the basis of its elemental analysis, ^{1}H NMR, IR and mass spectra. Elemental analysis, and the molecular ion at *m/e* 292 confirm the empirical formula $C_{16}H_{20}O_5$. The ^{1}H NMR spectrum given in Table 2 is consistent only with the structure (VIII). The coupling constant between the two doublets is 1.5 Hz which is typical for either *cis* or *trans* systems of this type. The stereochemistry of the double bond cannot be assigned unequivocally.



$$\mathrm{Ph{-}CH(OCH_3)}\underset{\mathrm{EtO_2C}}{\underset{|}{\mathrm{C}}}\mathrm{{=}CHCO_2Et}$$

(VIII)

TABLE 2

^{1}H-NMR SPECTRUM OF (VIII)

(10% Solution in CCl_4)

Chemical shift *τ(ppm)*	*Integration*	*Multiplicity*[a]	*Assignment*
2.77	5	s	Ph
4.02	1	d, *J* 1.5 Hz	C=CH
5.17	1	d, *J* 1.5 Hz	CHOMe
5.91	2	q, *J* 7.0 Hz	CH_2
6.03	2	q, *J* 7.0 Hz	
6.75	3	s	OCH_3
8.80	3	t, *J* 7.0 Hz	C–CH_3
8.98	3	t, *J* 7.0 Hz	

[a] s=Singlet, d=doublet, t=triplet, and q=quartet.

IR SPECTRUM OF (VIII)

(Liquid film)

3080w, 3040w, 3025w, 2980s, 2935m, 2900w, 2870w, 2822w, 1728vs, 1652s, 1601w, 1493w, 1465w, 1453m, 1392w, 1373s, 1350w, 1337w, 1312w, 1298w, 1258s, 1169s, 1084s, 1032s, 985w, 962m, 918w, 892m, 863m, 825m, 752s, 698s cm^{-1}.

Also the IR spectrum (given in Table 2) is consistent with (VIII). The carbonyl stretch of the α, β-unsaturated ester groups occurs at 1728 cm^{-1}; the trisubstituted olefin gives rise[15] to the absorptions at 1652 and 825 cm^{-1}.

CONCLUSION

The isolation of optically active (VII) demonstrates that the cyclopropane (VII) is formed by transfer of carbene within the metal complex. That we have obtained stereospecificity is particularly noteworthy because the olefin we have used was the ester of a carboxylic acid and not the acid itself. The latter type of olefin has been shown to be more effective in asymmetric hydrogenations using a Rh catalyst[16].

Although we have measured the CD spectrum of (VII) we have not been able to assign the strong positive dichroism observed at 265 and 263 nm to one absolute structure. Because of the low m.p. of (VII) we have not undertaken an X-ray study. Further conclusions about the stereochemical requirements, and hence details of the mechanism of the reaction, must await the assignment of the absolute configuration of (VII).

EXPERIMENTAL

All solvents were dry and oxygen-free. The silica gel used for chromatography (Merck 0.05–0.2 mm) was deoxygenated by heat under vacuum. For deactivation 2% w/w water was added. The alumina used in dry column chromatography[13] (Laporte Type 'H') was deactivated with 6% w/w water.

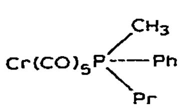
^{1}H NMR spectra were recorded using TMS as internal standard on a Varian A 60 spectrometer. Infrared spectra were recorded on a Perkin–Elmer PE 21 (with lithium fluoride prism) for metal carbonyl absorptions, and a Beckman IR 10 for organic compounds. Rotations were measured on a Perkin–Elmer 421 polarimeter equipped with thermostatted cells. Mass spectra were recorded using an Atlas CH4 with direct insertion. CD spectra were provided by Dr. I. O. Walker, Oxford University.

Melting points were taken on a Kofler Block and are uncorrected. Diethyl fumarate (Fluka) and methylphenyl-n-propylphosphine (prepared as in ref. 11) were redistilled under nitrogen immediately before use.

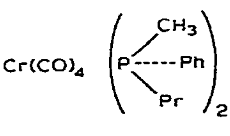
(Phenylmethoxycarbene)(methylphenyl-n-propylphosphine)tetracarbonylchromium (IV)

Optically pure methylphenyl-n-propylphosphine (4.9 g, 30 mmol) (III) and (phenylmethoxycarbene)pentacarbonylchromium (I) (10.0 g, 45 mmol)[17] in benzene (100 ml) were warmed to 40±1°. After 6 h, when ca. 400 ml CO had been evolved, and the IR spectrum showed no further change, the benzene was evaporated under reduced pressure, and the residue (ca. 20 ml) was chromatographed over silica-gel. Hexacarbonylchromium and unreacted (I) were eluted with pentane, and impure (IV) with ether. Rechromatographing the impure (IV) over fresh silica gel yielded *cis/trans* (IV) (8.50 g). Attempts to separate these isomers using a variety of absorbents and solvents were unsuccessful. With $2\frac{1}{2}$% benzene/$97\frac{1}{2}$% pentane and silica gel as absorbent 10 mg of a fraction was obtained which was 95% *cis* (IV) (% determined from integrals of NMR peaks). IR and NMR spectra are given in Table 1.

Due to the very low volatility of (IV), extensive decomposition occurred in the mass spectrometer and fragments of (V) and (VI) were observed in the mass spectrum.



(V)



(VI)

Reaction of (IV) with diethyl fumarate

A solution of (IV) (7.4 g, 16.4 mmol) in diethyl fumarate (30 ml, 154 mmol) was heated at 60° for 24 h, after which no further change was observed in its IR spectrum. The green solution was distilled, and the excess diethyl fumarate recovered (b.p. 65–70°/1 mmHg). The residue was chromatographed over alumina (1.5×60 cm column), and unreacted diethyl fumarate eluted with benzene/pentane (25/75) (500 ml). The colourless oil eluted with pure benzene (300 ml) was separated by dry-column chromatography with ether as solvent to yield two products. That with R_f 0.1–0.3 was characterised as (VII). (Found C, 66.05; H, 7.16; O, 27.30. $C_{16}H_{20}O_5$ calcd.: C, 65.74; H, 6.90; O, 27.36%.) M.p. 31–32°. Yield 85 mg. α_λ^{20} (2½% soln. in cyclohexane) 3.57(589), 3.68(578), 4.35(546), 8.51(4.36), 16.1(365 nm).

The minor component (R_f 0.35–0.50) was characterised as diethyl 3-methoxy-3-phenyl-1-propene-1,2-dicarboxylate (VIII). (Found C, 65.45; H, 6.90. $C_{16}H_{20}O_5$ calcd.: C, 65.74; H, 6.90%.) n_D^{21} 1.5025; $\alpha_D^{20} = 0°$. Yield 12 mg.

The reaction was repeated at 40° for 3 days and then worked up as above. The isolated (VII) and (VIII) were as above, and no change was observed in the rotation of (VII) or of (VIII).

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