Photochemical Studies on Binuclear Hydrido-molybdenocene Compounds

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Photolysis of $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (3), gives first *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ (4) and then $[\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ (1). Previously it was thought that the formation of (1) did not proceed *via* the intermediacy of *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$. A new mechanism for the photolysis of (3) to (1) is presented.

Previously we have described the synthesis of the compound $[\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ by photolysis of $[Mo(\eta\text{-}C_5H_5)_2H_2]$ (2) in diethyl ether [1] and also by photolysis of the binuclear compound $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (3).[2] A mechanism for the conversion of (3) to (1) was proposed involving initial transfer of a hydrogen atom followed by photoinduced loss of dihydrogen.[2]

Here we report further studies designed to gain insight into the mechanisms of the photochemical reactions of these binuclear molybdenocene compounds.

Results

The photolysis of (3) in toluene was carried out in the presence of a small excess of tri-n-propylphosphine in the hope that an intermediate such as $[H_2(\eta\text{-}C_5H_5)Mo(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)Mo(\eta\text{-}C_5H_5)(PPr^n_3)]$ might be trapped. However, after a 3 h photolysis the major products were found to be the *cis* and *trans* isomers of the yellow dimer $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ (4), in 80% yield, and there was no evidence for formation of the red dimer (1). The dimer (4) has been prepared previously.[2,3]

Prolonged photolysis of a solution of (4) in the presence of PPr^n_3 gave very slow formation of the red dimer (1) and after 72 h a 30% yield of the red dimer (1) could be isolated from the reaction mixture. This observation contrasts with the photolysis of (4) in the absence of the tertiary phosphine but under otherwise similar conditions, when (1) is formed in 80% yield after only 24 h.

Recently we have prepared a black molybdenocene dimer $[H(\eta\text{-}C_5H_5)_2Mo(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)Mo(\eta\text{-}C_5H_5)]$ (5) and have shown that this thermally rearranges to (4) which, in turn, thermally rearranges to (3).[4] We have studied the photolysis of (5) to see if a similar rearrangement pathway could be induced.

Photolysis of (5) in toluene alone forms the red dimer (1). However, when the photolysis is carried out in the presence of PPr^n_3, the first formed product is the yellow dimer (4).

Since it is now possible to synthesise (3) in gram quantities *via* the thermolysis of the black dimer (5) [4] it was decided to attempt to convert (3) to (1) by photolysis on a substantial scale in order to study the reactions of (1). In particular we were interested in preparing the molybdenum compound $[H(\eta\text{-}C_5H_5)Mo(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2Mo(\eta\text{-}C_5H_5)Me]$ (7): we have shown previously that the tungsten analogue of (7) is stable to isolation.[2]

When a large scale photolysis of 0.1 mol dm^{-3} solutions of (3) was carried out, smooth conversion to (1) did not occur, possibly due to side reactions which deposited material on the walls of the reaction vessel. However, it was found possible to convert (3) to (1) efficiently on a 2—3 g scale using *ca.* 0.05 mol dm^{-3} solutions.

Treatment of (1) with iodomethane causes a smooth reaction giving brown-red crystals of low solubility which analysis (see Experimental section) shows to be the desired product $[Me(\eta\text{-}C_5H_5)Mo(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2Mo(\eta\text{-}C_5H_5)I]$ (8).

Several attempts to prepare (7) by substituting the iodo ligand of (8) for the hydrido ligand were made. For example, (8) was treated with $Na[AlH_2(OCH_2CH_2OMe)_2]$ in benzene. Isolation of the reaction mixture gave the green hydrido dimer (3) in 60% yield. Similar reactions were found using sodium tetrahydroborate or $Na[BHEt_3]$.

An alternative route to (7) would be *via* methylation of the Mo–Cl bond in the compound $[H(\eta\text{-}C_5H_5)Mo(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2Mo(\eta\text{-}C_5H_5)Cl]$ which we sought to prepare by treatment of (1) with hydrogen chloride. However, this reaction gave only the mononuclear dichloro compound $[Mo(\eta\text{-}C_5H_5)_2Cl_2]$, in 95% yield.

Discussion

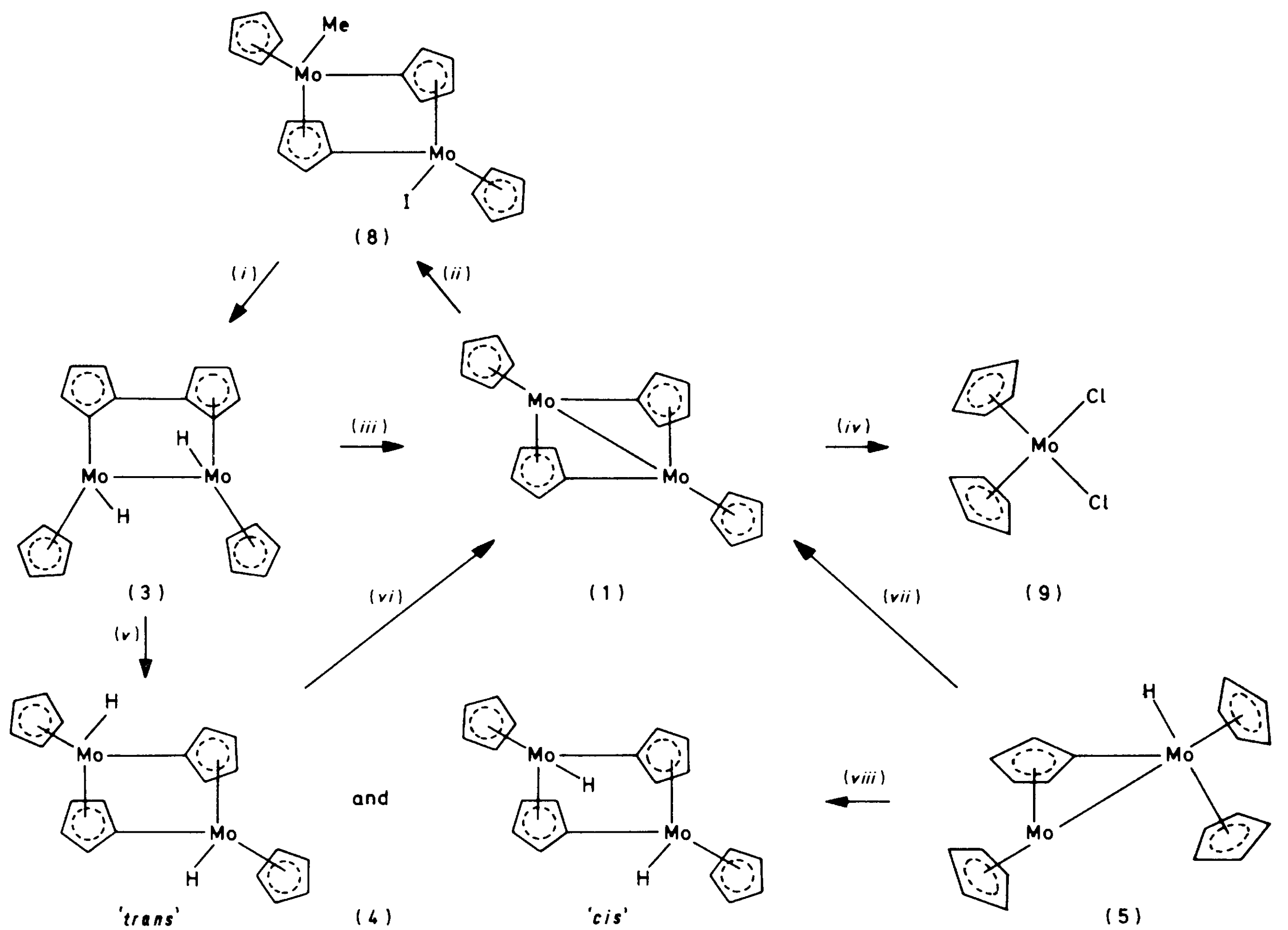
The photochemical conversion in high yield of (3) to (4) in the presence of a tertiary phosphine was unexpected since the previous mechanism proposed for the formation of (1) by photolysis of (3) did not evoke the intermediacy of (4). The above results seem now to question this earlier mechanism.

We have proposed [2] that the thermal conversion of (4) to (3) proceeds *via* a four-centre transition state and it seems reasonable that the reverse reaction, which is photochemically induced, will proceed by the same mechanism. We also proposed that the elimination of dihydrogen from (3), which has a HMo–MoH system, would proceed by an initial transfer of a hydrogen atom giving a H_2Mo–Mo intermediate wherefrom the dihydrogen would then be eliminated, giving (1).[2]

Since we now find that (3) is photolysed from (4), our original mechanism must be incorrect. A new mechanism for the conversion of (4) to (1) which incorporates the principle whereby the dihydrogen is eliminated from a single metal centre is shown in Scheme 2. This mechanism provides a simple explanation for the role of the tertiary phosphine. This inhibits the conversion of (4) to (1) by trapping the intermediate (A) and thus restricts the formation of intermediate (B) from which the reductive elimination of dihydrogen is proposed to occur.

Experimental

All operations were performed under vacuum or in an inert atmosphere. All solvents were rigorously dried before use by standard procedures. Infrared spectra were determined using mulls on a Pye Unicam SP 2000 spectrophotometer, and were calibrated with polystyrene. Preparative photolysis experiments were carried out in a standard borosilicate glass apparatus cooled by tap water. The lamps used were 100 or



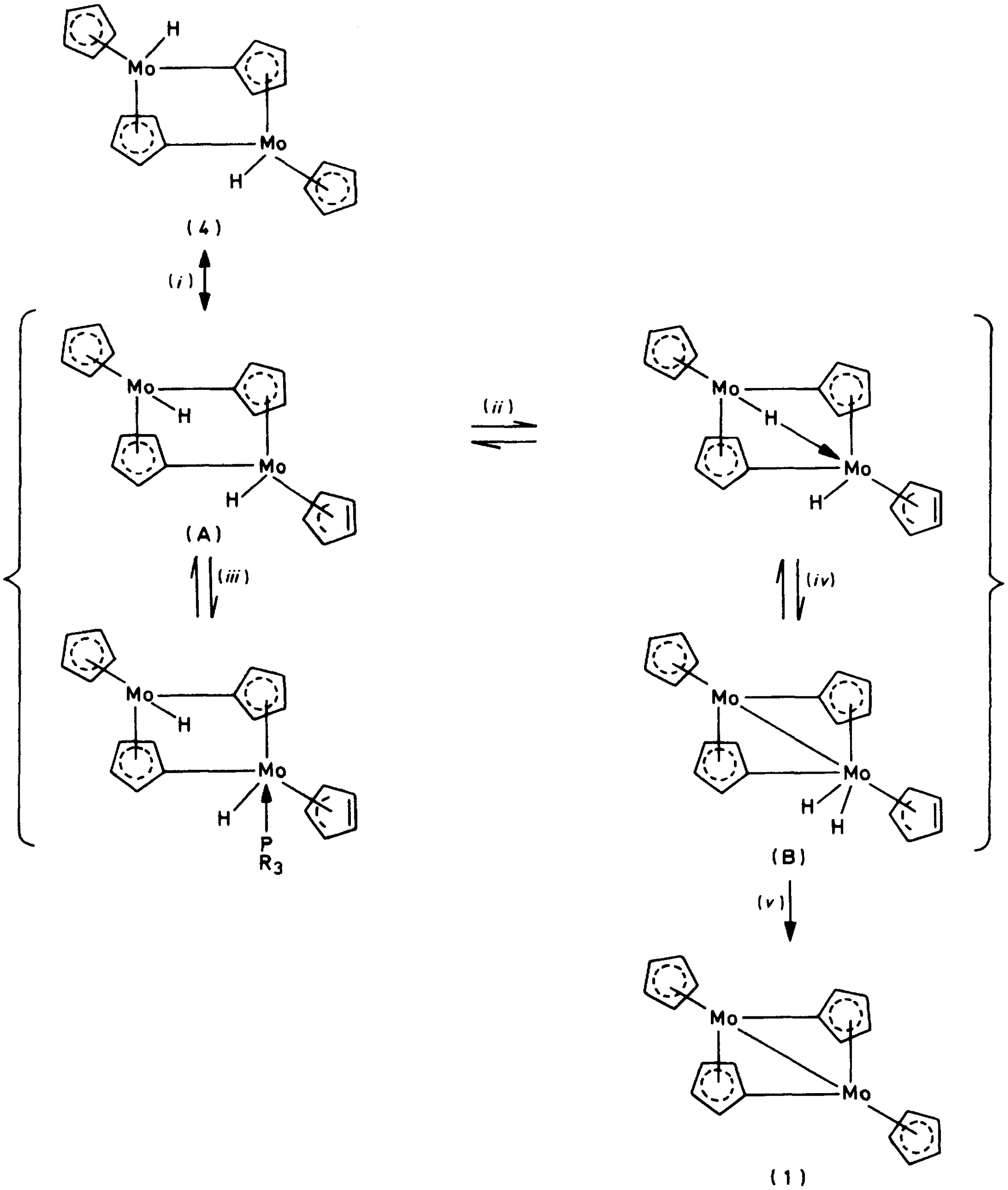
Scheme 1. (*i*) $Na[AlH_2(OCH_2CH_2OMe)_2]$ in toluene, 60%; (*ii*) iodomethane in toluene at r.t., 79%; (*iii*) photolysis in toluene, 20 h, 85%; (*iv*) hydrochloric acid or hydrogen chloride gas, 95%; (*v*) photolysis in toluene for 3 h, 80%; or photolysis in toluene and 1,2-bis(dimethylphosphino)ethane, 12 h, 70%; (*vi*) photolysis in toluene at −10 °C for 20 h, 80%; or photolysis in toluene in the presence of PPr^n_3 for 72 h, 30%; (*vii*) photolysis in toluene for 24 h, 75%; (*viii*) photolysis in toluene in the presence of PPr^n_3 for 12 h, 64%

500 W medium-pressure mercury lamps supplied by Hanovia Co. Ltd. Electronic spectra were determined at room temperature (r.t.), using a Perkin-Elmer 552 spectrophotometer. Microanalyses were performed by the microanalytical laboratory of this department. The compounds (3), (4), and (5) were prepared as recently described.[4]

Photolysis of $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (3).—Compound (3) (4.0 g, 11.23 mmol) in benzene (200 cm^3) was photolysed using a 500 W medium-pressure mercury lamp at r.t. for 24 h. A flocculent brown precipitate separated. The solution was filtered and then concentrated (to *ca.* 50 cm^3). A yellow-brown precipitate formed which was collected by filtration. The solid residue was washed with benzene and dried *in vacuo*. The i.r. spectrum showed it to be *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ (4) (0.25 g, 0.70 mmol). The filtrate was concentrated and light petroleum (b.p. 30—40 °C) added. After 12 h red crystals of $[\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ (1) separated, which were collected, washed with light petroleum (b.p. 30—40 °C), and dried *in vacuo* (2.3 g, 6.4 mmol), yield 57%.

Photochemical Studies.—Experiments were conducted in a 1-cm silica cell under argon or dinitrogen. Typically the concentration of the initial solutions of $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (3) was 0.006 mol dm^{-3}. The cell was held near (5 cm) a 40 W medium-pressure mercury lamp and the spectrum of the solution was monitored at approximately 30 min intervals. The maxima of the initial spectrum of $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ (3) ($\lambda_{max.}$ 587 nm, ε 323.51 $dm^3\ mol^{-1}\ cm^{-1}$) slowly reduced whilst the spectrum of *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ (4) became apparent. After *ca.* 9 h the spectrum was essentially identical to that of a pure solution of *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ (4) [a broad band in the region 520—570 nm with ε (estimated) 106.0 $dm^3\ mol^{-1}\ cm^{-1}$]. Further irradiation of the solution for 6 h caused the spectrum of the solution to change to that of essentially pure $[\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ (1) [$\lambda_{max.}$ 520 nm, ε (estimated) 263.0 $dm^3\ mol^{-1}\ cm^{-1}$]. The above experiment was repeated three times with identical results. The electronic spectra of solutions of the pure compounds (1), (3), and (4) were determined at *ca.* 0.006 mol dm^{-3} concentrations for the purposes of comparison.

Photolysis of $[H(\eta\text{-}C_5H_5)_2Mo(\mu\text{-}\sigma:C_5H_4)Mo(\eta\text{-}C_5H_5)]$ (5).—A suspension of (5) (0.30 g, 0.84 mmol) in toluene (200 cm^3) was irradiated with a 500 W lamp for 24 h. The solution became black-red and compound (4) could be isolated using the procedure described above (0.225 g, 0.63 mmol), yield 75%.



Scheme 2. Proposed mechanism for photoinduced conversion of (3) to (1). (*i*) Photoinduced η^5- to η^3-ring shift; (*ii*) migration of terminal H to a bridging position; (*iii*) trapping of the η^3-cyclopentadienyl intermediate which prevents formation of (A); (*iv*) migration of H to a terminal position giving (B); (*v*) photo- or thermally-induced loss of H_2 followed by an η^3- to η^5-ring shift

Photolysis of [$\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)$] (3) *in the Presence of Tri-n-propylphosphine.*—Compound (3) (0.140 g, 0.39 mmol) and tri-n-propylphosphine (1 cm^3) in toluene (200 cm^3) was irradiated for 3 h using a 500 W lamp. The initially green solution became orange. Filtration followed by concentration under reduced pressure separated yellow crystals. These were collected and shown to be the pure compound (4) (0.103 g, 0.29 mmol), yield 74%. A similar result was observed when tri-n-propylphosphine was replaced by 1,2-bis(dimethylphosphino)ethane.

Photolysis of [$H(\eta\text{-}C_5H_5)_2Mo(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)Mo(\eta\text{-}C_5H_5)$] (5) *in the Presence of Tri-n-propylphosphine.*—A suspension of (5) (0.35 g, 0.98 mmol) and PPr^n_3 (1 cm^3) in toluene (200 cm^3) was irradiated for 12 h using a 500 W lamp. The solution became orange and isolation, as described above, gave compound (4) (0.227 g, 0.63 mmol), yield 64%.

Photolysis of cis- *and* trans-[$\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2$] (4) *in the Presence of Tri-n-propylphosphine.*—Compound (4) (0.20 g, 0.56 mmol) and PPr^n_3 (1 cm^3) in toluene (200 cm^3) were irradiated for 3 d. The initially yellow solution darkened. Concentration under reduced pressure separated the unreacted compound (4). After removal of the solvent from the filtrate and crystallisation of the residue from benzene–light petroleum (b.p. 30—40 °C) red crystals of (1) were obtained (0.063 g, 0.178 mmol), yield 30%.

Reaction of [$\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2$] (1) *with Hydrochloric Acid.*—Compound (1) (0.3 g, 0.84 mmol) in acetone (100 cm^3) was treated with aqueous hydrochloric acid (2 cm^3 of a 5 mol dm^{-3} solution). After 30 min the initially red solution had become brown. The solvent was removed under reduced pressure giving the previously described compound [Mo(η-C_5H_5)$_2$Cl$_2$] (0.41 g), >90% yield. The same result was obtained when the acetone solution was treated with hydrogen chloride gas.

[Me(η-C_5H_5)Mo(μ-σ : η^5-C_5H_4)$_2$Mo(η-C_5H_5)I] (8).—Compound [{Mo(η-C_5H_5)}$_2$(μ-σ : η^5-C_5H_4)$_2$] (1) (1.0 g, 2.8 mmol) in benzene (150 cm^3) was treated with an excess of iodomethane (3.77 g). The initially red solution turned yellow-brown and a yellow-brown precipitate separated within a few minutes. The mixture was filtered and the filtrate was allowed to stand at r.t. for 14 h. Dark brown-red crystals separated. These were collected, washed with benzene, and dried *in vacuo* (1.10 g, 2.22 mmol), yield 79%. The product was virtually insoluble in all common solvents and the mass spectrum was indeterminate (Found: C, 42.1; H, 3.6. $C_{21}H_{21}IMo_2$ requires C, 42.5; H, 3.5%). The i.r. spectrum is closely similar to that of the bromo-analogue [partial i.r. data (mull): 833s, 805m, 772m, 680w, 616w, 599w, 585w, 488vw, 470vw, 405m, 395m, 367m, and 345m cm^{-1}].

Reaction of (8) *with* Na[AlH$_2$(OCH$_2$CH$_2$OMe)$_2$].—A suspension of (8) (0.37 g, 0.75 mmol) in toluene was treated with an excess of Na[AlH$_2$(OCH$_2$CH$_2$OMe)$_2$] and the mixture was stirred at r.t. for 3 h giving an orange solution. Ethanol (3 cm^3) then water (3 cm^3) were added and the solution became green. The organic layer was separated, filtered, and the solvent removed under reduced pressure. The green residue was identified as the green dimer (3) by comparison of the i.r. spectrum with that of an authentic sample (0.016 g, 0.45 mmol), yield 60%.

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References

1 M. Berry, S. G. Davies, and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1978, 99.
2 M. Berry, N. J. Cooper, M. L. H. Green, and S. J. Simpson, *J. Chem. Soc., Dalton Trans.*, 1980, 29.
3 N. J. Cooper, M. L. H. Green, C. Couldwell, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1977, 145.
4 M. L. H. Green, M. L. Poveda, J. Bashkin, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 30.

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