Metal Carbonyl Chemistry. Part XXV.[1] Reactions of Acetyl- and Benzoyl-pentacarbonylmanganese with Dicyclopentadiene

By **Brian L. Booth, Michael Gardner,** and **Robert N. Haszeldine,*** Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Dicyclopentadiene reacts with $[(RCO)Mn(CO)_5]$ (R = Me or Ph) in hexane or benzene to give the known 1 : 1 adduct $[(RCO{\cdot}C_{10}H_{12})Mn(CO)_4]$ as the major product, with low yields of the 2 : 1 adduct $[(RCO{\cdot}C_{10}H_{12})Mn(CO)_4(C_{10}H_{12})]$ and a novel lactone $[(C_{10}H_{12}{\cdot}CO{\cdot}O{\cdot}CR)Mn(CO)_4(C_{10}H_{12})]$. When the reaction between $[(MeCO)Mn(CO)_5]$ and the diene is carried out in acetonitrile the lactone is one of the major products. An acyl derivative of a similar lactone complex, namely, $[(C_{10}H_{12}{\cdot}CO{\cdot}O{\cdot}CMe)CO{\cdot}Mn(CO)_5]$ is obtained when the 1 : 1 adduct (R = Me) is carbonylated. The formation of these various products is discussed and compared with the formation of the lactone complexes $[(CH_2{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CMe)Mn(CO)_5]$ and $[(CH_2{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CMe)CO{\cdot}Mn(CO)_5]$ from reaction between $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$ and $Na[Mn(CO)_5]$.

MANY transition-metal catalysed carbonylation reactions of olefins and dienes result in the formation of lactones as by-products, as, for example, in the palladium-catalysed, high-pressure carbonylation of hexa-1,4-diene.[2] In some reactions, such as the $[Ni(CO)_4]$-catalysed reactions of acetylenes and carbon monoxide with alkyl, allyl, or acyl halides,[3,4] or the similar reaction of an aryl halide with styrene,[5] lactones are often the major reaction products. In all these reactions unstable acyl metal carbonyl intermediates are believed to be responsible for lactone formation. We now report the isolation of acyl and lactone intermediates from the reactions between acylmanganese carbonyls and dicyclopentadiene which clearly illustrate the various mechanistic steps involved in the formation of lactones in carbonylation reactions.

Acetylpentacarbonylmanganese reacts with dicyclopentadiene at 20 °C in hexane during 14 days to give the previously reported[1] compounds (Ia) and (IIa) in 68 and 5% yields respectively, together with a mixture containing compound (III) and a compound thought to be the lactone (IVa) isolated in 12% yield. This mixture could not be separated into its pure components despite repeated chromatography. When this reaction was repeated under similar conditions in acetonitrile the yield of (Ia) was only 25%, and the major products were (III) and (IVa) which again could only be isolated as a mixture in 53% yield. A small amount of (IIa) (9% yield) was also isolated from this reaction. Benzoylpentacarbonylmanganese reacts similarly with dicyclopentadiene at room temperature during 10 days to give the known[1] compounds (Ib) and (IIb) in 69 and 7% yields respectively, and the lactone complex (IVb) in 13% yield; no compound analogous to (III) was detected in this reaction.

The i.r. spectrum of (IVb) shows a weak band at 1 610 cm^{-1} for the cyclopentene double-bond, and a medium–strong band at 1 791 cm^{-1} typical of the ν(CO) band of a lactone, *cf.* a band at 1 805 and 1 782 cm^{-1} in the previously reported compounds $[(O{\cdot}CO{\cdot}CH_2{\cdot}CH{:}C)Mn(CO)_5]$ and $[O{\cdot}CO(CH_2)_2CH{:}CMn(CO)_5]$ respectively.[6] The metal carbonyl region of the spectrum (solution in CCl_4) is complex and shows bands at 2 083m, 2 078m—w (sh), 1 993s, 1 987vs, 1 983vs, 1 955s, and 1 947m—s cm^{-1}. The simple compound (IVb) having C_s symmetry should show only four bands ($3A' + A''$) in this region, and the observed pattern appears to be one arising from two sets of four such bands which are near co-incident. One explanation of the observed spectrum is that (IVb) is a mixture of enantiomers, although other compounds (*vide infra*) which contain a similar asymmetric carbon atom appear to prefer one configuration. The mixture of (III) and (IVa) shows bands of medium intensity in the i.r. region at 1 800 cm^{-1} [ν(CO) lactone], 1 715 cm^{-1} [ν(CO) of an unco-ordinated CH_3CO group], and a metal–acyl band at 1 620 cm^{-1}. With the exception of the band at 1 800 cm^{-1} the spectrum is almost identical to that of pure (III) prepared from the reaction between $[MeMn(CO)_5]$ and dicyclopentadiene as described previously.[1] Only four bands at 2 078m, 1 988s, 1 974s, and 1 937s cm^{-1} are apparent in the metal carbonyl region indicating that the bands due to (III) are coincident with those of (IVa), and while it is possible that (IVa) is also a mixture of enantiomers, no evidence for this could be obtained. ^1H N.m.r. spectra were not obtainable as these compounds have poor solubility in most of the common organic solvents. An attempt to convert the mixture of (III) and (IVa) into (IVa) alone by heating at 80 °C for 7 days resulted only in extensive decomposition to $[Mn_2(CO)_{10}]$ and a trace of a white solid which could not be positively identified, but which had an i.r. spectrum similar to a compound

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[1] Part XXIV, B. L. Booth, M. Gardner, and R. N. Haszeldine, *J.C.S. Dalton*, preceding paper.

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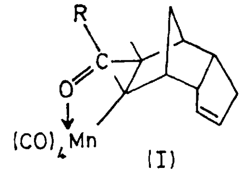
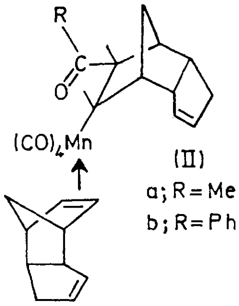
[5] E. Yoshisato, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, 1969, **34**, 1500.

[6] C. S. Kraihanzel and L. G. Herman, *J. Organometallic Chem.*, 1968, **15**, 397.

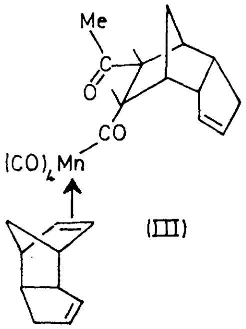
$C_{14}H_{16}O_3$ previously isolated in low yield from the reaction of $[MeCo(CO)_4]$ and dicyclopentadiene.



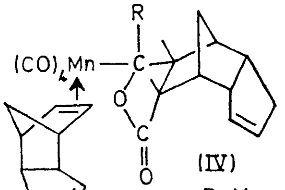
(I)
a; R=Me
b; R=Ph



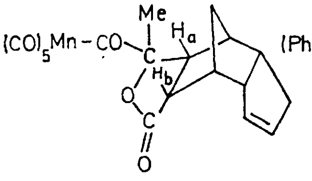
(II)
a; R=Me
b; R=Ph



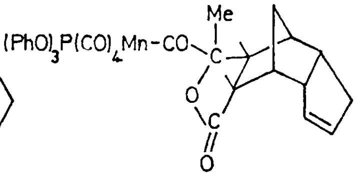
(III)



(IV)
a; R=Me
b; R=Ph



(V)



(VI)

Compound (Ia) may be carbonylated using 100 atm of carbon monoxide at 65 °C in hexane to afford the lactone complex (V) in 64% yield, together with some $[Mn_2(CO)_{10}]$. This compound has been characterised by analysis, molecular weight, and i.r., ^1H n.m.r., and mass spectroscopy. Its i.r. spectrum shows five bands ($2A_1 + B_1 + 2E$) in the metal carbonyl region at 2 116m, 2 050vw, 2 031s, 2 014s, and 2 005s as expected for an $Mn(CO)_5$ group attached to an unsymmetrical alkyl group.[7] Bands of medium intensity at 1 795 and 1 645 cm^{-1} are assigned to the lactone and metal acyl carbonyl groups respectively. It is possible that (V) is a mixture of enantiomers, but there is no spectroscopic evidence for this assumption. The ^1H n.m.r. spectrum (CCl_4 solution) shows a characteristic absorption at τ 4.40 for the two olefinic protons, and a singlet at τ 8.86 for the CH_3 group. The bridging methylene protons are coincident at τ 8.53 which suggests that the lactone group is *endo* to the methylene bridge. This assumption is supported by a singlet at τ 6.88 for an *exo* H atom (H_b) and the absence of any bands in the region of τ 4.80—5.0 for *endo* hydrogens.[8] Reaction of (V) with $P(OPh)_3$ in ether at 50 °C affords the mono-triphenyl phosphite derivative (VI) in 60% yield. Its i.r. spectrum shows the expected four bands ($3A' + A''$) in the metal carbonyl region at 2 086m, 2 013s, 2 000s, and 1 982s cm^{-1} for a *cis*-$[RMn(CO)_4L]$ structure. Other bands at 1 775 cm^{-1} [ν(CO) lactone] and 1 620 cm^{-1} [ν(CO) metal-acyl] fully support the structure assigned. Attempts to decarbonylate (V) to give the corresponding alkyl complex by heating the solid above its melting point, or by refluxing a solution in benzene for several hours, resulted only in decomposition with the formation of $[Mn_2(CO)_{10}]$.

The carbonylation of (Ia) in cyclohexane has been followed by removing samples from the autoclave at intervals throughout the reaction and examining these by i.r. spectroscopy. After 5 h the spectrum was mainly that of unchanged starting material {bands at 2 074m, 1 982s, 1 977s, 1 943s cm^{-1} [ν(Mn–CO)]; 1 640m—w (co-ordinated CH_3·CO)}, but the appearance of a new band at 1 710 cm^{-1} (unco-ordinated CH_3·CO) indicates the formation of an intermediate, (VIII) (see Scheme). The complexity of the metal carbonyl region which shows bands at 2 120, 2 059, 2 020, 2 010, 2 007, and 2 000 cm^{-1} in addition to those of (Ia) suggests the presence of a third component, which is probably (VII). After 15 h the major compound present was (VIII) and there was little (Ia) left after this period as evidenced by the low intensity of the characteristic terminal metal carbonyl bands. Nevertheless, the band at 1 640 cm^{-1} was still quite intense indicating that an appreciable concentration of (VII) was now present in the mixture. It is probable that this band at 1 640 cm^{-1} comprises two overlapping absorptions from the co-ordinated CH_3CO group and the metal acyl group since both these absorb in approximately the same region. Examination of the spectrum after 36 h still showed the presence of compounds (VII) and (VIII), but there were also new bands at 1 715 and 1 625 cm^{-1} attributed to the unco-ordinated CH_3CO group and metal acyl group respectively of (IX). In addition there was a band at 1 795 cm^{-1} attributed to the lactone carbonyl group of (X). After two days the spectrum resolved into a mixture of the bands for compounds (X) and (V), and after a further two days only compound (V) was present. It is clear from these results that the formation of lactones in these reactions arises by the insertion of a vicinal keto-group into an acyl–manganese σ-bond and no lactone formation occurs until both the metal acyl group and an unco-ordinated keto-group are present in the same molecule. Further confirmation of these conclusions has been obtained by an investigation of the reaction of $Na[Mn(CO)_5]$ with levulinoyl chloride, CH_3·CO·CH_2·CH_2·COCl. Levulinoyl chloride was obtained in 24% yield by the standard reaction of levulinic acid with an excess of thionyl chloride. The chloride is not very stable and appreciable decomposition to a black tar occurs on distillation *in vacuo*. Even after distillation the colourless, readily hydrolysable, liquid darkens appreciably during several days in a sealed flask. Its reaction with $Na[Mn(CO)_5]$

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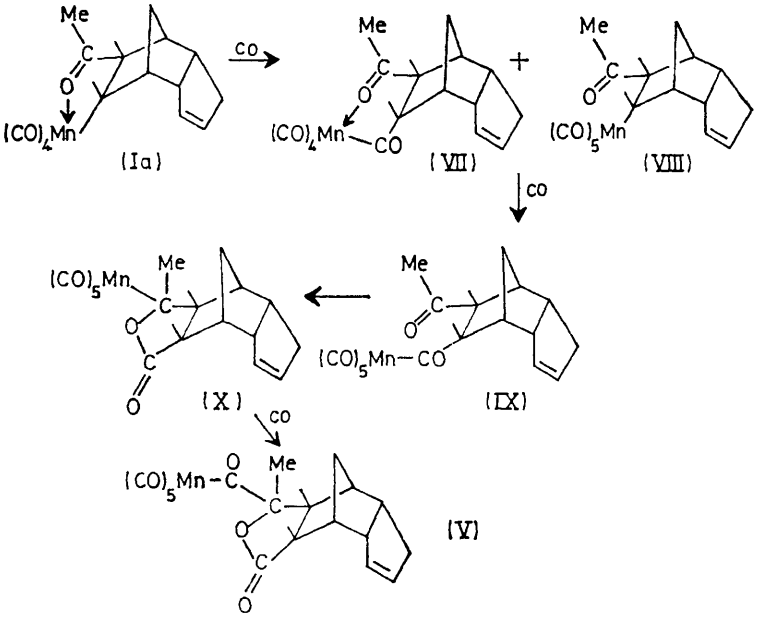
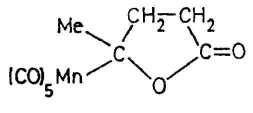
[7] K. Noack, U. Schaerer, and F. Calderazzo, *J. Organometallic Chem.*, 1967, **8**, 517.

[8] L. F. Hines and J. K. Stille, *J. Amer. Chem. Soc.*, 1972, **94**, 485.

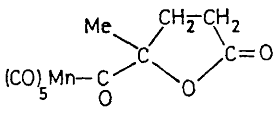


SCHEME

occurs readily at room temperature in ether to afford compounds (XI) and (XII) in 12 and 17% yields respectively. The i.r. spectrum of (XI) shows bands in the metal carbonyl region at 2 128m—w (A_1), 2 054m—w (B_1), 2 038s (E), 2 021vs (E), and 1 990w,sh (A_1) typical of an Mn(CO)$_5$ group,[7] and a band of medium intensity at 1 785 cm^{-1} [ν(CO) lactone]. The ^{1}H n.m.r. spectrum (CCl$_4$ solution) shows an ABCD multiplet centred at τ 7.73 for the methylene protons and a singlet at τ 8.68 for the CH$_3$ group in the relative intensities of 4 : 3, in agreement with the assigned structure. This compound appears to be a single enantiomer from the spectroscopic data. The i.r. spectrum of (XII) shows a similar band pattern in the metal carbonyl region [ν(Mn–CO) 2 126m—w, 2 062w,sh, 2 037vs, 2 022vs, and 1 990w,sh cm^{-1}] and bands at 1 800 cm^{-1} [ν(CO) lactone] and 1 635 cm^{-1} [ν(Mn•CO•R)] in good agreement with the proposed structure. It is evident that in the intermediate, [(CH$_3$•CO•CH$_2$•CH$_2$•CO)Mn(CO)$_5$], presumed to be formed initially in this reaction, the same characteristics defined above for lactone formation are present. The relatively low yields obtained from this reaction may, in part, be accounted for by the instability of the acyl halide, but also some decomposition of (XI) or its precursor, must occur during the reaction in order to account for the formation of (XII).

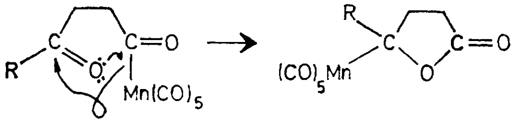


(XI)



(XII)

This present work has demonstrated that a carbonyl group can insert into the carbon–metal σ-bond of a metal acyl complex. The detailed mechanism of this insertion step awaits further clarification. However, an analogy has recently been drawn between the chemistry of acyl transition-metal carbonyl compounds and organic acyl compounds, particularly amides.[9] Extending this analogy further it seems reasonable to suggest that this insertion reaction occurs by nucleophilic attack of the ketonic carbonyl group on the acyl carbon atom, followed by an intramolecular migration of the leaving group [Mn(CO)$_5$]$^-$ to the electron-deficient carbon atom of the ketone group.



The oxygen atom of a carbonyl group is not usually regarded as a strong nucleophile and it is probable that the favourable geometry of the system is largely responsible for the occurrence of this reaction.

EXPERIMENTAL

I.r. spectra were recorded as mulls on a Perkin-Elmer 257 grating instrument; the metal carbonyl region was examined using solutions in CCl$_4$ or cyclohexane. ^{1}H N.m.r. spectra were recorded on a Varian HA 100 spectrometer and molecular weights were determined on a Mechrolab vapour-pressure osmometer. Except where stated chromatographic separations were carried out on deactivated alumina, and light petroleum had a boiling range

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[9] R. W. Johnson and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 2091.

of 40—60 °C. All reactions were carried out under an atmosphere of dry nitrogen. Acetyl- and benzoyl-pentacarbonylmanganese were prepared by a previously reported procedure.[10] Dicyclopentadiene and levulinic acid were commercial samples.

Reactions with Dicyclopentadiene.—(a) [(MeCO)Mn(CO)$_5$] *in hexane.* Acetylpentacarbonylmanganese (3.0 g, 12.6 mmol) and dicyclopentadiene (4.0 g, 30.3 mmol) in hexane (25 ml) were kept for 14 days in a sealed tube at room temperature. Carbon monoxide (5.9 mmol) was evolved during the reaction. Removal of the solvent and chromatography of the residue gave (Ia) (2.9 g, 8.50 mmol, 68%) on elution with light petroleum. Further elution with a 1 : 1 mixture of light petroleum–dichloromethane gave (IIb) (0.30 g, 0.63 mmol, 5%) as a viscous oil. Final elution with a 1 : 3 mixture of the same eluants gave a yellow solid (0.70 g, 1.39 mmol, 11%) identified by i.r. spectroscopy as a mixture of (III) and (IVa) (Found: C, 64.2; H, 5.7. $C_{27}H_{27}MnO_6$ requires C, 64.4; H, 5.4%).

(b) [(MeCO)Mn(CO)$_5$] *in acetonitrile.* When a solution of [(MeCO)Mn(CO)$_5$] (1.7 g, 7.14 mmol) and dicyclopentadiene (2.5 g, 19.0 mmol) in acetonitrile (20 ml) was kept under similar conditions to those used in the previous experiment, CO (1.2 mmol) was evolved. Chromatography (Florisil; light petroleum eluant) gave decacarbonyldimanganese (0.20 g, 0.51 mmol) and (Ia) (0.60 g, 1.75 mmol, 25%). Elution with a 1 : 1 light petroleum–dichloromethane mixture gave (IIa) (0.30 g, 0.63 mmol, 9%) and further elution with a 1 : 3 mixture of these solvents gave a yellow solid mixture of (III) and (IVa) (1.9 g, 3.79 mmol, 53%). Final elution with acetone gave a viscous yellow oil (0.2 g) which could not be identified.

(c) [(PhCO)Mn(CO)$_5$]. A solution of [(PhCO)Mn(CO)$_5$] (4.0 g, 13.3 mmol) and dicyclopentadiene (6.0 g, 45.4 mmol) in benzene (40 ml), kept at 20 °C for 10 days in a tube sealed under vacuum, gave carbon monoxide (6.2 mmol). Chromatography on Florisil, after removal of the solvent, gave (Ib) (3.8 g, 9.15 mmol, 69%) with light petroleum, (IIb) (0.50 g, 0.93 mmol, 7%) with a 1 : 1 light petroleum–dichloromethane mixture, and (IVb) (1.0 g, 1.77 mmol, 13%) with a 1 : 2 mixture of the same solvents. This last compound was isolated as a yellow solid, m.p. 130 °C (decomp.), after recrystallisation from a mixture of hexane–dichloromethane [Found: C, 68.2; H, 5.4%; *M* ($ClCH_2{\cdot}CH_2Cl$), 559. $C_{32}H_{29}MnO_6$ requires C, 68.1; H, 5.2%; *M*, 564]. Final elution with acetone gave an oil (0.2 g) of unknown composition.

Carbonylation of (Ia).—When a solution of (Ia) (4.0 g, 11.7 mmol) in hexane (100 ml) was heated at 65 °C for 7 days in a 200-ml stainless-steel autoclave pressurised to 100 atm with carbon monoxide, chromatography of the products, after removal of solvent, gave decacarbonyldimanganese (0.4 g, 1.03 mmol) with light petroleum. Further elution with a 1 : 1 mixture of light petroleum–dichloromethane gave (V) (3.2 g, 7.50 mmol, 64%) as an off-white solid, m.p. 104—106 °C, which was recrystallised from dichloromethane–hexane [Found: C, 53.3; H, 3.8%; *M* (C_6H_6), 400. $C_{19}H_{15}MnO_8$ requires C, 53.5; H, 3.5%; *M*, 426]. Its u.v. spectrum in hexane showed an absorption at $\lambda_{max.}$ 219.5—221 nm (ε 33 000). Its mass spectrum (A.E.I. model MS 902 spectrometer) showed a parent ion at *m/e* 426.

Reaction of (V) *with Triphenyl Phosphite.*—A solution of (V) (0.3 g, 0.71 mmol) and triphenyl phosphite (0.3 g, 0.97 mmol) in diethyl ether (20 ml) was kept in a sealed tube at 50 °C for 4 days. Carbon monoxide (0.45 mmol) was evolved. Removal of the solvent and chromatography of the residual oil with a 1 : 1 mixture of light petroleum–dichloromethane as eluant gave (VI) (0.30 g, 0.42 mmol, 60%) as a white solid, m.p. 124 °C (decomp.), which was recrystallised from diethyl ether (Found: C, 61.2; H, 4.6. $C_{36}H_{30}MnO_{10}P$ requires C, 61.0; H, 4.3%).

Reaction of Levulinoyl Chloride with Na[Mn(CO)$_5$].—Levulinoyl chloride (5.6 g, 41.7 mmol, 24%) was prepared by the slow addition of thionyl chloride (45.0 g, 378 mmol) during 1 h to levulinic acid (20.0 g, 173 mmol) at 20 °C, and stirring of the mixture at this temperature for 7 days. Removal of the excess of thionyl chloride under high vacuum at 20 °C and vacuum distillation of the residue gave the acyl chloride as a colourless liquid, b.p. 45 °C/0.5 mmHg (Found: C, 44.9; H, 5.0. $C_5H_7ClO_2$ requires C, 44.6; H, 5.2%). In a separate experiment when the mixture was refluxed at 80 °C for 1 h after complete addition of the thionyl chloride, a black tar was the only product.

Levulinoyl chloride (3.0 g 22.3 mmol) was added to a solution of sodium pentacarbonylmanganate (4.5 g, 20.6 mmol) in diethyl ether (100 ml) and the mixture was stirred at room temperature for 4 h. Removal of the solvent and chromatography gave decacarbonyldimanganese (0.40 g, 1.03 mmol) with light petroleum, and (XI) (0.70 g, 2.38 mmol, 12%) with a 3 : 2 mixture of light petroleum–dichloromethane. Compound (XI) was recrystallised from diethyl ether–hexane as a yellow solid, m.p. 114 °C [Found: C, 41.1; H, 2.7%; *M* ($ClCH_2{\cdot}CH_2Cl$), 294. $C_{10}H_7MnO_7$ requires C, 40.8; H, 2.4%; *M*, 294]. Further elution with a 2 : 3 mixture of light petroleum–dichloromethane gave (XII) (1.1 g, 3.42 mmol, 17%) as a pale yellow solid, m.p. 128 °C (decomp.), which was recrystallised from dichloromethane–hexane [Found: C, 40.9; H, 2.4%; *M* ($ClCH_2{\cdot}CH_2Cl$), 319. $C_{11}H_7MnO_8$ requires C, 41.0; H, 2.2%; *M*, 322]. Final elution with methanol gave a yellow solid (0.8 g) whose analysis (Found: C, 3.5; H, 2.7%) and i.r. spectrum indicated that it was an impure hydrated inorganic manganese compound.

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[4/2107 *Received*, 14*th October*, 1974]

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[10] T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, 1957, **22**, 598.