

Pyran-2-ylidene Carbene Complexes ¹

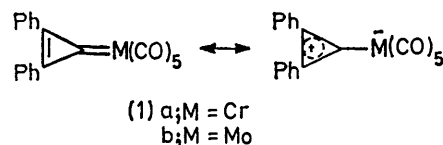
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Pentacarbonyl(diphenylcyclopropenyldiene)chromium(0) (1a) and the corresponding molybdenum complex (1b) have been synthesised and converted, by reaction with pyridinium ylides, into the pyran-2-ylidene complexes (2), a new type of carbene complex stabilised by 6 π -electron delocalisation. The 6-ethoxy-groups in the pyran-2-ylidene complexes (2b and e) are readily displaced by nucleophiles such as methanol, ammonia, ethylamine, morpholine, and phenyl-lithium. Pentacarbonyl-(6-ethoxy-3,4-diphenylpyran-2-ylidene)molybdenum(0) is converted into 4,5-diphenyl-2-pyrone by sodium hydroxide or by trifluoroacetic acid, and oxidised to 6-ethoxy-4,5-diphenyl-2-pyrone by lead tetra-acetate. Pentacarbonyl-(3,4,6-triphenylpyran-2-ylidene)molybdenum(0) reacts with *N*-phenacylpyridinium bromide and triethylamine to give 2-phenacylidene-3,4,6-triphenyl-2*H*-pyran (6). The complex also reacts with benzyne in a Diels-Alder reaction to give 1,2,4-triphenyl-naphthalene and hexacarbonylmolybdenum. The reactivity of the cyclopropenyldiene and pyran-2-ylidene complexes is compared with that of the corresponding carbonyl compounds.

MANY successful syntheses of transition metal-carbene complexes have been reported during the last few years, and it is clear that 'nucleophilic' carbenes can act as ligands in several types of complexes.² Most of these carbenes contain a heteroatom because the general methods of preparation of the complexes involve nucleophilic addition to carbon monoxide or isocyanide ligands. The cyclopropenyldiene complex (1a), first prepared by Öfele,³ is unusual in that the nucleophilic character of the carbene ligand is derived from the carboxylic π -electron system rather than from a lone pair on a heteroatom. Nucleophilic behaviour for such carbenes has been predicted by Gleiter and Hoffmann,⁴ and has been experimentally observed in reactions with electrophilic olefins.⁵

We have repeated the preparation of the chromium carbene complexes (1a) and have also prepared the molybdenum complex (1b), and have attempted to

assess their potential as synthetic intermediates, using the chemistry of diphenylcyclopropenone⁶ as a guide. The major outcome has been the preparation of a new class of carbene complexes, containing the pyran-2-ylidene system; the reactions of these complexes have been investigated.



Preparation of Pyran-2-ylidene Complexes.—Diphenylcyclopropenone has been shown to react with pyridinium ylides under mild conditions to give α -pyrone derivatives.⁷ The cyclopropenyldiene complexes (1a and b) both reacted with several pyridinium ylides in the same

⁵ S. D. McGregor and W. M. Jones, *J. Amer. Chem. Soc.*, 1968, **90**, 123.

⁶ D. Wendisch, in 'Methoden der Organischen Chemie (Houben-Weyl)', 1971, vol. 4/3, p. 741.

⁷ (a) Th. Eicher, E. von Angerer, and A.-M. Hansen, *Annalen*, 1971, **746**, 102; (b) Th. Eicher and E. von Angerer, *ibid.*, p. 120; (c) T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, 1971, **36**, 2451.

¹ Preliminary communication, C. W. Rees and E. von Angerer, *J.C.S. Chem. Comm.*, 1972, 420.

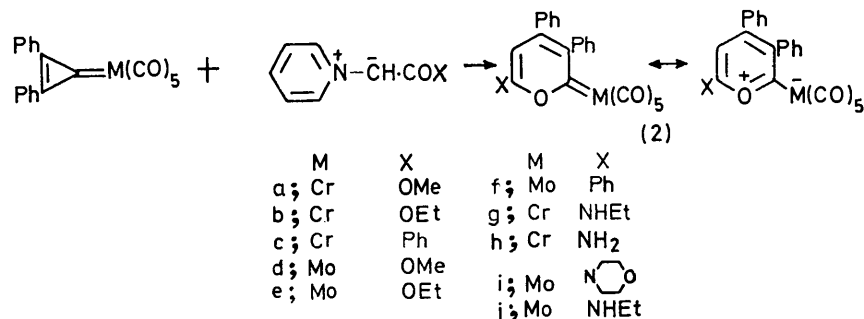
² D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

³ K. Öfele, *Angew. Chem. Internat. Edn.*, 1968, **7**, 950.

⁴ R. Gleiter and R. Hoffmann, *J. Amer. Chem. Soc.*, 1968, **90**, 5457.

manner, the products being the pyran-2-ylidene complexes (2) (Scheme 1). The air-stable purple, red, or orange complexes (2a—f) were isolated in good yields when the appropriate cyclopropenylidene derivatives (1) were treated with equimolar quantities of the pyridinium

was also isolated when the ethoxypyranylidene complex was treated with trifluoroacetic acid. A likely mechanism for the formation of the pyrone is shown in Scheme 2: nucleophilic displacement of the 6-ethoxy-group gives the 6-hydroxy-complex, which exists as its salt in

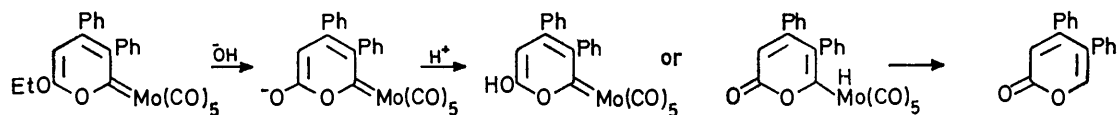


SCHEME 1

ylides at room temperature. The stability of the products can be attributed to the nucleophilicity of the carbene ligand, derived in this case from the aromaticity of the pyrylium system. The contribution of a dipolar pyrylium structure to the overall structure of the complexes was illustrated by some of their reactions.

Reactions of Pyran-2-ylidene Complexes.—The 6-ethoxy-groups of the complexes (2b and e) are very susceptible to nucleophilic displacement. For example,

sodium hydroxide solution. On acidification of the solution the anion is protonated and the complex undergoes dissociation to give the pyrone. It is not clear whether protonation will take place on the oxygen atom at the 6-position or on the metal. A similar reaction has been observed by Fischer and Maasböl⁸ in attempts to isolate the hydroxycarbene complex (4) by acidification of solutions containing the anionic complex (3). Benzaldehyde was detected as a product, and its formation was

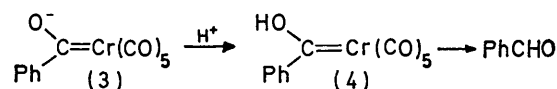


SCHEME 2

the molybdenum complex (2e) reacted with methanol containing a few drops of triethylamine at room temperature to give the corresponding 6-methoxy-complex (2d). Similar reactions of the complex (2e) were observed with phenyl-lithium, morpholine, and ethylamine; the products, which were isolated in good yields, were the 6-substituted derivatives (2f, i, and j). Reactions of the 6-ethoxypyranylidenechromium complex (2b) with methanol, phenyl-lithium, ethylamine, and ammonia gave the complexes (2a, c, g, and h), respectively. The displacement reactions take place much more readily than in the corresponding 2-pyrones; this presumably reflects the greater degree of dipolar character in the complexes.

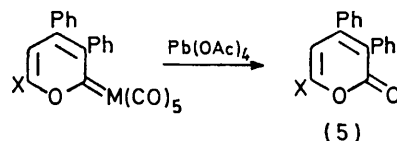
The reaction of the 6-ethoxypyranylidenemolybdenum complex (2e) with sodium hydroxide took a different course. A colour change was observed on adding aqueous sodium hydroxide to a solution of the complex in ethanol; the mixture was then acidified and the product extracted with ether. This product was identified as 4,5-diphenyl-2-pyrone, the hydrogen atoms at the 3- and 6-positions appearing as singlets in the n.m.r. spectrum at τ 3.64 and 2.52. The same product

ascribed to dissociation of the hydroxycarbene complex and rearrangement of the carbene (Scheme 3).



SCHEME 3

The overall reaction represents an efficient method of removing the carbenoid ligand from the metal. Another method was also found to be successful: oxidation of the pyranylidene complexes with lead tetra-acetate resulted in cleavage of the metal-carbon bond and introduction of an oxygen atom at the 2-position, giving the corresponding pyrones (5) (Scheme 4). The reaction proved to be

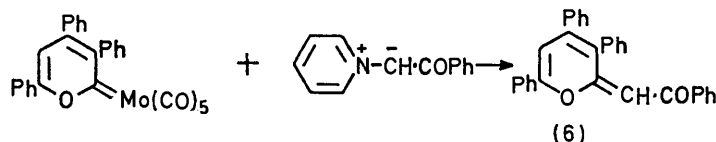


SCHEME 4

an efficient one for the 6-phenyl complexes but rather inefficient for the 6-ethoxy-complexes, probably because of competing nucleophilic attack at the 6-position.

⁸ E. O. Fischer and A. Maasböl, *Chem. Ber.*, 1967, **100**, 2445.

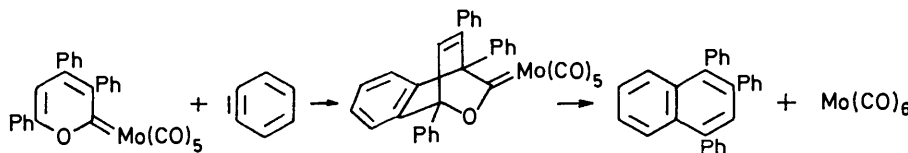
A third method of displacing the metal from the complex (2f) was discovered. When the complex was stirred with an equimolar amount of *N*-phenacylpyridinium bromide in the presence of triethylamine, it slowly reacted to give, in good yield, a single organic product, which was identified as 2-phenacylidene-3,4,6-triphenyl-2*H*-pyran (6) on the basis of analytical and spectroscopic data. The product, an orange crystalline solid, had a u.v. spectrum closely similar to that reported for some analogous methylenepyran derivatives.^{7a} The reaction (Scheme 5) is similar to those recently reported between



SCHEME 5

pentacarbonyl(phenylmethoxycarbene)tungsten and phosphorus ylides, which give vinyl ethers.⁹

One characteristic of α -pyrones is their ability to participate as the diene component in the Diels-Alder reaction. Carbon dioxide is extruded, and the product is aromatic, when an acetylene or benzyne is used as the two-electron component. We investigated the possibility that analogous reactions could occur with the pyranylidene complex: the complex (2f) was treated with benzyne (from benzenediazonium-2-carboxylate) and gave the Diels-Alder adduct, 1,2,4-triphenylnaphthalene, in moderate yield (Scheme 6). This reaction is unique in



SCHEME 6

that it involves the extrusion of a metal carbonyl, hexacarbonylmolybdenum, which was detected in the product mixture. 1,2,4-Triphenylnaphthalene was also prepared from 3,4,6-triphenyl-2-pyrone and benzyne under the same conditions, and there appeared to be little difference between the diene character of the pyrone and that of the molybdenum complex in this reaction.

Absorption Spectra.—The i.r. stretching frequencies of the pyranylidene complexes in the carbonyl region were similar for all the compounds studied; the spectra show two weak absorptions, at 2040–2060 and close to 1970 cm⁻¹, and a very strong absorption at 1930–1940 with a shoulder at 1920–1925 cm⁻¹.

In contrast, the u.v. and visible spectra vary markedly with the nature of the metal and of the 6-substituent. Solutions in hexane show an absorption above 500 nm, the position of which depends markedly on the substituents. For chromium complexes λ_{max} is 20–30 nm greater than for the corresponding molybdenum com-

plexes; its value is also greater for the 6-phenyl than for the 6-alkoxy-complexes. The band is solvent dependent; a shift to higher energy from 508 to 470 nm was observed in the spectra of the 6-ethoxy-pyranylidenemolybdenum complex (2e) in ethanol as compared with hexane as solvent.

Connor and Jones have observed similar long wavelength absorptions in the spectra of α -furylcarbene complexes, and have ascribed them to metal-to-ligand charge-transfer interactions.¹⁰ These were sensitive to the nature of the substituents; a decrease in the donor power

of the ligand corresponded to a decrease in the energy of the absorption. The long wavelength bands in the spectra of the pyranylidene complexes show the same trend, and may well have a similar origin.

Other Reactions of Cyclopropenylidene Complexes.—Attempts were made to apply other known reactions of diphenylcyclopropenone to the carbene complexes (1). The chromium complex (1a) reacted rapidly with diazomethane at room temperature, but gave a large number of products, none of which was isolated in a pure state. Irradiation of a solution of the complex (1a) in tetrahydrofuran gave diphenylacetylene (30%), also formed

under the same conditions from diphenylcyclopropenone. The complex (1a) was remarkably resistant to basic hydrolysis, however; it was unchanged after heating for 12 h in ethanolic sodium ethoxide. Diphenylcyclopropenone is readily hydrolysed in basic media.

Reactions of diphenylcyclopropenone with diazomethane and with pyridinium ylides are thought to involve initial attack at the carbon-carbon double bond, whereas the hydrolysis involves attack at the carbonyl group. Thus there appears to be some similarity between the reactions of diphenylcyclopropenone and those of the complexes when the initial attack is at the double bond, but not when the initial attack is at the carbonyl group or the carbon-metal bond.

EXPERIMENTAL

M.p.s were recorded on a Kofler hot-stage apparatus and are corrected. I.r. spectra were recorded on a Perkin-Elmer 125 spectrometer, u.v. spectra on a Unicam SP 800

⁹ C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, 1972, **94**, 6543.

¹⁰ J. A. Connor and E. M. Jones, *J. Chem. Soc. (A)*, 1971, 3368.

spectrophotometer, and n.m.r. spectra on a Varian HA-100 instrument at 100 MHz. Kieselgel G (Merck) was used for preparative layer chromatography.

Pentacarbonyl-(2,3-diphenylcyclopropenyliene)chromium(0) (1a).—(a) From 3,3-dichloro-1,2-diphenylcyclopropene.³ Disodium pentacarbonylchromate was prepared under nitrogen by heating under reflux for 5 h a solution of hexacarbonylchromium (4.4 g, 20 mmol) in dry, deoxygenated tetrahydrofuran (100 ml) with an amalgam prepared from mercury (11 ml) and sodium (1.38 g, 30 mmol). The yellow solution was added dropwise to a solution of 3,3-dichloro-1,2-diphenylcyclopropene (6.5 g, 25 mmol) in tetrahydrofuran (50 ml) at -70° . The mixture was allowed to attain room temperature, the solvent was distilled off, and the residue was applied to a chromatography column (silica). Elution with ether-petroleum (1:4) gave yellow crystals of pentacarbonyl-(2,3-diphenylcyclopropenyliene)chromium(0) (0.6–1.1 g, 8–14%), m.p. 199–200° (decomp.) [lit.³ 199–200° (decomp.)].

(b) From 3-ethoxy-1,2-diphenylcyclopropenylium tetrafluoroborate. Disodium pentacarbonylchromate (9 mmol) in dry, deoxygenated bis-(2-methoxyethyl) ether (90 ml) was added slowly under nitrogen to a stirred suspension of 3-ethoxy-1,2-diphenylcyclopropenylium tetrafluoroborate⁶ (2.84 g, 20 mmol) in bis-(2-methoxyethyl) ether (30 ml) at -50° . The mixture turned black, but as its temperature rose the dark colour disappeared and a precipitate appeared. The mixture was stirred at room temperature for 12 h and then poured into ether (250 ml); the solution was washed with water (5×150 ml), dried, and evaporated, and the residue was applied to a chromatography column (silica). Elution with ether-petroleum (1:4) gave the carbene complex (1a) (0.33 g, 10%), m.p. 199–200° (decomp.).

Pentacarbonyl-(2,3-diphenylcyclopropenyliene)molybdenum(0) (1b).—Disodium pentacarbonylmolybdate was similarly prepared from hexacarbonylmolybdenum (5.28 g, 20 mmol) and sodium amalgam (30 mmol) in tetrahydrofuran (200 ml). The red solution was added dropwise to a solution of 3,3-dichloro-1,2-diphenylcyclopropene (6.5 g, 20 mmol) in tetrahydrofuran (100 ml) at -70° . The mixture was then stirred at room temperature for 12 h, the solvent distilled off, and the residue applied to a chromatography column (silica). Elution with ether-petroleum (1:4) gave yellow crystals of *pentacarbonyl-(2,3-diphenylcyclopropenyliene)molybdenum(0)* (2.0 g, 24%), m.p. 180° (decomp.) (Found: C, 56.1; H, 2.6. $C_{20}H_{10}MoO_5$ requires C, 56.3; H, 2.3%; τ (CDCl₃) 2.30 (6H, m) and 1.73 (4H, m); m/e 426 (M^+), 398, 370, 342, 314, and 286 ($M^+ - 5CO$).

Pentacarbonyl-(6-methoxy-3,4-diphenylpyran-2-ylidene)chromium(0) (2a).—Pentacarbonyl-(2,3-diphenylcyclopropenyliene)chromium(0) (96 mg, 0.25 mmol) and *N*-(methoxycarbonylmethyl)pyridinium bromide (58 mg, 0.25 mmol) were stirred in dry methanol (10 ml) with triethylamine (0.2 g) for 12 h. The solvent was distilled off and the residue purified by layer chromatography (silica; $25 \times 25 \times 0.1$ cm) to give red crystals of *pentacarbonyl-(6-methoxy-3,4-diphenylpyran-2-ylidene)chromium(0)* (74 mg, 65%), m.p. 128–130° (Found: C, 60.7; H, 3.25. $C_{23}H_{14}CrO_7$ requires C, 60.8; H, 3.1%; v_{max} (cyclohexane) 2055w, 1967w, 1930vs, 1920m (C=O), and 1590 cm^{-1} ; λ_{max} (hexane) 258 (ϵ 23,000), 296 (11,500), 350 (4600), and 528 nm (5700); m/e 454 (M^+), 426, 370, 342, and 314 ($M^+ - 5CO$). By an analogous procedure, the following pyranylidene carbene complexes were prepared: *pentacarbonyl-(6-ethoxy-3,4-*

diphenylpyran-2-ylidene)chromium(0) (2b) (77%), red plates, m.p. 110–112° (Found: C, 60.8; H, 3.4. $C_{24}H_{16}CrO_7$ requires C, 61.5; H, 3.4%; v_{max} (cyclohexane) 2040w, 1960w, 1925vs (C=O), and 1588 cm^{-1} ; λ_{max} (hexane) 260 (ϵ 32,600), 297 (16,200), 352 (6500), and 528 nm (10,000); τ (CDCl₃) 8.40 (3H, t, J 7 Hz), 5.20 (2H, q, J 7 Hz), 3.84 (1H), and 3.10–2.78 (10H, m); m/e 468 (M^+), 440, 384, 356, and 328 ($M^+ - 5CO$); *pentacarbonyl-(3,4,6-triphenylpyran-2-ylidene)chromium(0)* (2c) (66%), purple crystals, m.p. 140–142° (Found: C, 67.4; H, 3.6; Cr, 10.6. $C_{28}H_{16}CrO_6$ requires C, 67.2; H, 3.2; Cr, 10.4%; λ_{max} (hexane) 247 (ϵ 43,000), 323 (21,500), 380 (8100), and 578 nm (6300); τ (CDCl₃) 3.0–2.7 (11H, m, Ph and vinyl H), 2.48–2.40 (3H, m), and 1.90–1.80 (2H, m); m/e 500 (M^+), 472, 416, 388, and 360 ($M^+ - 5CO$); *pentacarbonyl-(6-methoxy-3,4-diphenylpyran-2-ylidene)molybdenum(0)* (2d) (55%), red crystals, m.p. 122–124° (decomp.) (Found: C, 55.2; H, 3.0. $C_{23}H_{14}MoO_7$ requires C, 55.4; H, 2.8%; v_{max} (cyclohexane) 2050w, 1977w, 1927vs, and 1590 cm^{-1} ; τ (CDCl₃) 5.97 (3H), 3.72 (1H), and 3.10–2.75 (10H, m); m/e 498 (M^+), 470, 442, 414, 386, and 358 ($M^+ - 5CO$); *pentacarbonyl-(6-ethoxy-3,4-diphenylpyran-2-ylidene)molybdenum(0)* (2e) (78%), red crystals, m.p. 112–114° (decomp.) (Found: C, 56.2; H, 3.2. $C_{24}H_{16}MoO_7$ requires C, 56.25; H, 3.1%; v_{max} (cyclohexane) 2060w, 1977w, 1930vs (C=O), and 1590 cm^{-1} ; λ_{max} (hexane) 258 (ϵ 26,000), 295 (19,700), 362 (4900), and 508 nm (11,300); λ_{max} (EtOH) 257 (ϵ 30,000), 290 (21,200), 360 (6250), and 470 nm (10,200); τ (CDCl₃) 8.40 (3H, t, J 7 Hz), 5.18 (2H, q, J 7 Hz), 3.74 (1H), and 3.10–2.74 (10H, m); *pentacarbonyl-(3,4,6-triphenylpyran-2-ylidene)molybdenum(0)* (2f) (66%), purple crystals, m.p. 127–129° (Found: C, 62.1; H, 3.2. $C_{28}H_{16}MoO_6$ requires C, 61.8; H, 2.9%; v_{max} (cyclohexane) 2060w, 1979w, 1940vs (C=O), 1610, and 1580 cm^{-1} ; λ_{max} (hexane) 249 (ϵ 52,000), 321 (19,000), 372 (7000), and 553 nm (7700); τ (CDCl₃) 3.00–2.70 (10H, m), 2.66 (1H, vinyl H), 2.48–2.40 (3H, m), and 1.92–1.82 (2H, m); m/e 544 (M^+), 516, 488, 460, 432, 404 ($M^+ - 5CO$), 324, and 296.

Reactions of Pentacarbonyl-(6-ethoxy-3,4-diphenylpyran-2-ylidene)chromium(0) (2b).—(a) *With phenyl-lithium*. An ethereal solution of phenyl-lithium was added dropwise to a stirred solution of the complex (2b) (100 mg) in dry ether, until a colour change from red to purple was observed. Ethanol (5 ml) was added; layer chromatography gave pentacarbonyl-(3,4,6-triphenylpyran-2-ylidene)chromium(0) (2c) (58 mg, 60%), m.p. and mixed m.p. 138–140°.

(b) *With ethylamine*. A solution of the complex (2b) (50 mg) in aqueous ethylamine (70%; 5 ml) was poured into water (25 ml) and shaken with ether (20 ml). The ethereal solution was dried and evaporated; layer chromatography gave yellow crystals of *pentacarbonyl-(6-ethylamino-3,4-diphenylpyran-2-ylidene)chromium(0)* (2 g) (30 mg, 60%), m.p. 145–147° (Found: C, 61.7; H, 3.9; N, 3.1. $C_{24}H_{17}CrNO_6$ requires C, 61.7; H, 3.6; N, 3.0%; v_{max} (cyclohexane) 2050w, 1965w, 1925vs, and 1915 cm^{-1} (C=O); v_{max} (Nujol) 3400 cm^{-1} (NH); τ (CDCl₃) 8.60 (3H, t, J 7 Hz), 6.38 (2H, q, J 7 Hz), 4.30 (1H, NH), 4.12 (1H, vinyl H), and 3.10–2.80 (10H, m).

(c) *With ammonia*. The complex (2b) (50 mg) in ethanol (10 ml) was added to a saturated ethanolic solution of ammonia (5 ml). A colour change from red to yellow was observed. Evaporation of the solution to small volume gave orange crystals of *(6-amino-3,4-diphenylpyran-2-ylidene)pentacarbonylchromium(0)* (2h) (28 mg, 60%), m.p. 148–150° (decomp.) (Found: C, 60.2; H, 3.25; N, 3.25.

$C_{22}H_{13}CrNO_6$ requires C, 60.1; H, 3.0; N, 3.2%; ν_{max} (cyclohexane) 2050w, 1970w, 1935vs, and 1925m cm^{-1} C=O; ν_{max} (Nujol) 3460 and 3360 cm^{-1} (NH).

Reactions of Pentacarbonyl-(6-ethoxy-3,4-diphenylpyran-2-ylidene)molybdenum(0) (2e).—(a) *With methanol.* The complex (100 mg) was stirred for 24 h in dry methanol (10 ml) containing a drop of triethylamine. Evaporation gave pentacarbonyl-(6-methoxy-3,4-diphenylpyran-2-ylidene)-molybdenum(0) (2d) (66 mg, 68%) as red plates, m.p. and mixed m.p. 122—124°, identical (i.r., n.m.r.) with the specimen prepared earlier.

(b) *With phenyl-lithium.* To a solution of the complex (100 mg) in ether (30 ml), ethereal phenyl-lithium was added until the colour of the solution changed from red to purple. Ethanol (5 ml) was then added; the mixture was washed with water, dried, and evaporated to give pentacarbonyl-(3,4,6-triphenylpyran-2-ylidene)molybdenum(0) (2f) (80 mg, 75%), m.p. 127—129°, identical (n.m.r.) with the specimen prepared earlier.

(c) *With morpholine.* The complex (30 mg) was dissolved in morpholine (2 ml); the amine was then distilled off under reduced pressure and the residue purified by preparative layer chromatography, which gave red crystals of pentacarbonyl-(6-morpholino-3,4-diphenylpyran-2-ylidene)molybdenum(0) (2i) (19 mg, 59%), m.p. 150—152° (decomp.) (Found: C, 56.6; H, 3.7. $C_{26}H_{19}MoNO_6$ requires C, 56.4; H, 3.4%; ν_{max} (cyclohexane) 2055w, 1975w, 1935vs, 1920m (C=O), and 1592 cm^{-1} ; τ (CDCl₃) 6.18 (8H, m), 3.95 (1H), and 3.10—2.76 (10H, m).

(d) *With ethylamine.* The complex (50 mg) was dissolved in aqueous ethylamine (70%; 5 ml) and then poured into water (25 ml). The mixture was extracted with ether and the ethereal solution subjected to preparative layer chromatography. This gave orange crystals of pentacarbonyl-(6-ethylaminopyran-2-ylidene)molybdenum(0) (2j) (29 mg, 64%), m.p. 121—123° (Found: C, 57.1; H, 3.8. $C_{24}H_{17}MoNO_6$ requires C, 56.4; H, 3.4%; ν_{max} (cyclohexane) 2055w, 1973vs, 1933vs, 1920m (C=O), and 1610 cm^{-1} ; ν_{max} (Nujol) 3400 cm^{-1} (NH); τ (CDCl₃) 8.59 (3H, t, J 7 Hz), 6.39 (2H, q, J 7 Hz), 3.98 (1H, vinyl H), 3.90 (1H, exchanges with D₂O, NH), and 3.10—2.80 (10H, m).

(e) *Oxidation with lead tetra-acetate.* To the ethoxy-pyranylidene complex (2e) (100 mg) in dichloromethane (5 ml) was added lead tetra-acetate until the red colour of the solution had disappeared. The mixture was diluted with ether, washed with aqueous sodium carbonate, dried, and evaporated. The residue was subjected to layer chromatography. The major band gave pale yellow crystals of 6-ethoxy-3,4-diphenyl-2-pyrone (4 mg, 7%), m.p. 103—105° (lit.,^{7a} 104—106°), identical (i.r.) with an authentic specimen prepared from diphenylcyclopropenone.

(f) *With trifluoroacetic acid.* The complex (150 mg) was suspended in aqueous methanol (3 ml). Trifluoroacetic acid (8 ml) was added slowly, with stirring, until the complex dissolved. The mixture was then diluted with ether (50 ml) and washed with aqueous sodium carbonate, and the ether layer was separated and dried. Preparative layer chromatography gave crystals of 4,5-diphenyl-2-pyrone (42

mg, 56%), m.p. 115—116° (Found: C, 81.9; H, 4.8. $C_{17}H_{12}O_2$ requires C, 82.3; H, 4.8%; ν_{max} (Nujol) 1710s, 1625, and 1520 cm^{-1} ; τ (CDCl₃) 3.64 (1H), 3.15—2.70 (10H, m), and 2.52 (1H; *m/e* 248 (*M*⁺), 220, and 191.

(g) *With sodium hydroxide.* Ethanolic sodium hydroxide (0.2 g in 5 ml) was added dropwise to a stirred solution of the ethoxypyranylidene complex (150 mg) in ethanol (20 ml). The solution was then acidified (hydrochloric acid) and the mixture extracted with ether. Preparative layer chromatography of the residue gave 4,5-diphenyl-2-pyrone (50 mg), m.p. 115—116°.

Reactions of Pentacarbonyl-(3,4,6-triphenylpyran-2-ylidene)molybdenum(0) (2f).—(a) *With lead tetra-acetate.* To the complex (30 mg) in dichloromethane (3 ml), lead tetra-acetate was added in portions until the purple colour of the solution was discharged. The mixture was poured into ether (25 ml) and washed with aqueous sodium carbonate. Preparative layer chromatography of the organic fraction gave 3,4,6-triphenyl-2-pyrone (10 mg, 56%), m.p. 180—182° (lit.,^{7a} 183—184°), identical (i.r., t.l.c.) with an authentic specimen.

(b) *With N-phenacylpyridinium bromide and triethylamine.* The complex (2f) (72 mg, 0.13 mmol) and N-phenacylpyridinium bromide (37 mg, 0.13 mmol) were stirred in dry ethanol (10 ml) with triethylamine (0.2 g) at room temperature for 16 h. Column chromatography (silica) gave [with ether-petroleum (1:19)] 2-phenacylidene-3,4,6-triphenylpyran (6) (49 mg, 85%), as orange crystals, m.p. 200° (Found: C, 87.2; H, 5.2. $C_{31}H_{22}O_2$ requires C, 87.3; H, 5.2%; ν_{max} (Nujol) 1635 (C=O) and 1600 cm^{-1} (C=C); λ_{max} (CH₂Cl₂) 286 (ϵ 17,000), 335 (7500), 370 (7500), and 457 nm (7800); *m/e* 426 (*M*⁺), 349, 321, 105, and 77.

(c) *With benzenediazonium-2-carboxylate.* The complex (2f) (155 mg) was heated in 1,2-dichloroethane (25 ml) at 70°, and benzenediazonium-2-carboxylate¹¹ [from anthranilic acid (0.5 g)] was added as a slurry in 1,2-dichloroethane. The mixture was stirred and heated at 70° for 10 min, during which period the purple colour of the complex was discharged. Preparative layer chromatography of the product mixture gave hexacarbonylmolybdenum (40 mg, 53%) and 1,2,4-triphenylnaphthalene (40 mg, 39%), m.p. 161—162° (lit.,¹² 158—159°), identical with a specimen (62 mg, 28%) prepared from 3,4,6-triphenyl-2-pyrone (200 mg) and benzenediazonium-2-carboxylate.

Irradiation of Pentacarbonyl-(2,3-diphenylcyclopropenylidene)chromium(0) (1a).—The complex (1a) (100 mg) in tetrahydrofuran (50 ml) was irradiated (quartz; medium-pressure Hg lamp; 125 W) for 4 h. Diphenylacetylene (15 mg, 30%) was isolated by layer chromatography.

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¹¹ F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.* 1968, **48**, 12.

¹² O. Blum, *Ber.*, 1929, **62**, 881.