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Formal [2+2+1] and [4+1] Cycloadditions of Electron Poor Alkenes to Pentacarbonyl [(*N,N*-dimethylamino)methylene]chromium

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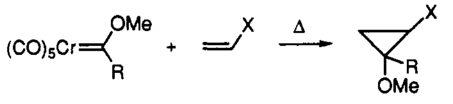
Summary: Methyl acrylate and acrylonitrile underwent a formal [2+2+1] cycloaddition with pentacarbonyl[(N,N-dimethylamino)methylene]chromium to give trisubstituted cyclopentanes in modest yield. Methyl sorbate underwent a formal [4+1] cycloaddition with the same complex to produce the trisubstituted cyclopentene. A number of other conjugated enones failed to undergo this cyclization.

Introduction

The thermal reaction of chromium alkoxycarbene complexes with electron deficient alkenes was one of the earliest "organic" reactions of Fischer carbenes studied (eq 1).[1] It has subsequently been developed into a practical procedure for the synthesis of donor–acceptor substituted cyclopropanes.[2] (Electron rich alkenes also undergo this cyclopropanation reaction, although under substantially different conditions.[3]) More recently, 1,3-dienes have been studied as substrates for this reaction, and a variety of vinylcyclopropanes have been prepared.[4] However, all of these studies have been restricted to the use of *alkoxy*-carbene complexes. Aminocarbene complexes have been much less studied in this regard,[5] although an intramolecular cyclopropanation of an *N*-butenylcarbene complex has been reported.[6] Reactions of alkynes with aminocarbene complexes having olefin groups on the nitrogen produce complex products resulting from cycloaddition/metathesis/cycloaddition/reductive elimination sequences.[7]



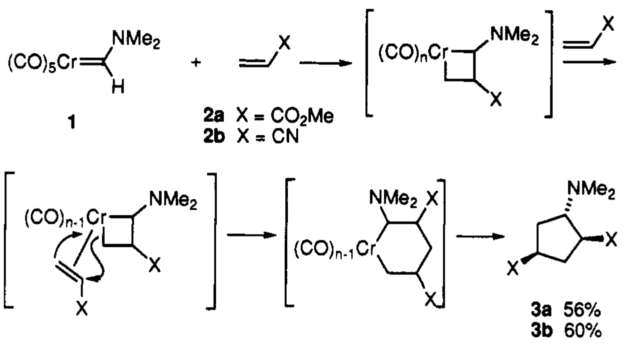
(1)

$X = CO_2R$, CN, etc.

With the development of efficient syntheses of pentacarbonyl[(amino)methylene]chromium complexes[8] and the report of their unusual cycloaddition chemistry with imines,[9] reactions of this class of carbenes with electron deficient olefins became of interest. The results of these studies are reported below.

Results and Discussion

The thermal reaction of pentacarbonyl[(*N,N*-dimethylamino)methylene]chromium (1) with methyl acrylate or acrylonitrile in acetonitrile as solvent produced *no* cyclopropane products. Rather, a single isomer of a 1,2,4-trisubstituted cyclopentane, resulting from a formal [2+2+1] cycloaddition was obtained in fair yield (eq 2).



(2)

The relative stereochemistry could not be unequivocally assigned from spectroscopic data. The thermodynamically most stable isomer is expected, since the compounds are formed in a polar solvent, and the amino group should be sufficiently basic to equilibrate the acidic α-positions. A possible route to the observed products is shown in eq 2 and parallels that thought operant in cyclopropanation.

Cycloaddition of the electron deficient alkene to the carbene complex, with the regiochemistry expected from the polarity of both the carbene complex and the alkene, produces the metallacyclobutane intermediate. The anticipated cyclopropane would result from reductive elimination from this intermediate. Instead, coordination and insertion of another alkene followed by reductive elimination would produce the observed products. The reasons for the difference between alkoxy- and aminocarbene complexes in their reactions with olefins **2a** and **2b** are not apparent.

Methyl sorbate also forms a five membered ring upon reaction with chromium carbene complex **1**, in a formal

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(2) For a review see: Ressig, H-U. *Topp. Curr. Chem.* **1988**, *144*, 73.

(3) (a) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966. (b) For cyclopropanation by *O*-acyl carbene complexes see: Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660.

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(5) For reviews on the reactions of chromium aminocarbene complexes see: Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381.

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(7) (a) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2701. (b) Chelain, E.; Goumont, R.; Hamon, L.; Parker, A.; Rudler, M.; Rudler, H.; Daran, J-C.; Vaissermann, J. *J. Am. Chem. Soc.* **1992**, *114*, 8088 and references therein.

(8) (a) Borel, C.; Hegedus, L. S.; Krebs, J.; Satoh, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1101. (b) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702. (c) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.

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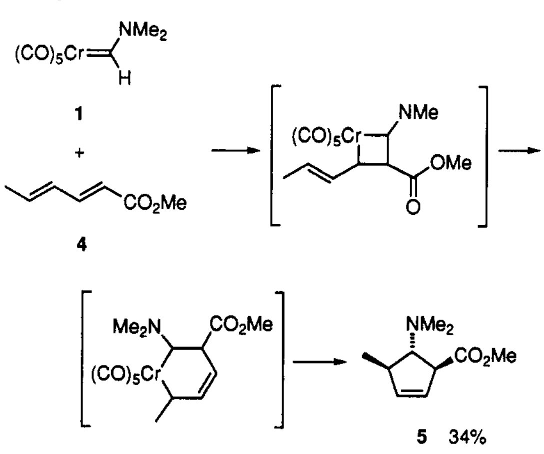
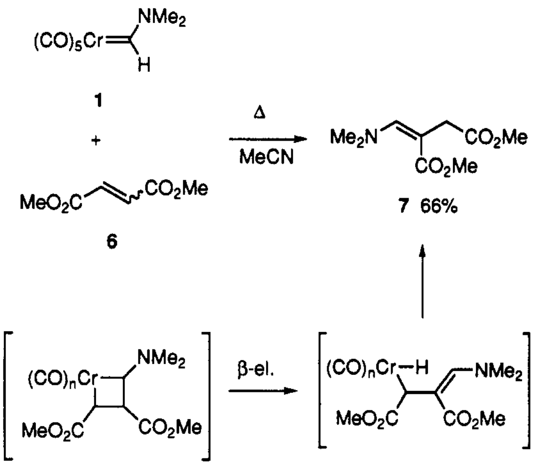
[4+1] cycloaddition (eq 3). This product can be rationalized by a "1,6" addition of the carbene to this enone,



(3)

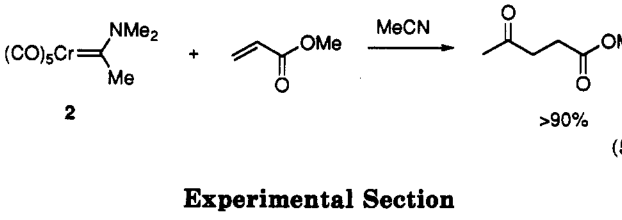
followed by reductive elimination. To our knowledge this is the first instance of a formal [4+1] cycloaddition of a chromium carbene to a diene.

Reaction of carbene complex 1 with dimethyl fumarate and dimethyl maleate takes yet a different course (eq 4). In this case, formal CH insertion (a common side reaction in alkoxycarbene complex cyclopropanation reactions) was observed.



(4)

Most striking was the range of closely related substrates that did *not* undergo productive reaction with carbene complex 1. These include methyl vinyl ketone, methyl crotonate, methyl methacrylate, cyclopentenone, cyclohexenone, methyl cinnamate, maleic anhydride, and styrene. In most cases, unreacted starting materials were recovered after long reaction times, although in a few cases (e.g. benzoquinone) decomposition occurred. The reaction was also restricted to carbene complex 1. When the [(dimethylamino)(methyl)carbene]chromium complex 2 was used, *only* insertion/hydrolysis products resulted (eq 5). Because of this the reaction is very limited in scope, although perhaps mechanistically interesting.



(5)

Experimental Section

Toluene, ethyl acetate, hexane (technical grade), and acetonitrile were distilled from CaH_2. Diethyl ether was predried over CaH_2 and distilled from benzophenone ketyl under a nitrogen atmosphere prior to use. All starting materials were commercially available (Aldrich) or synthesized. The carbene complexes 1 and 2 were prepared by literature procedures.[8b,c]

A Brüker ACS-300 NMR spectrometer was used for the 300-MHz ^1H NMR and the 75-MHz ^{13}C NMR. All NMR spectra were recorded in $CDCl_3$ and the chemical shifts are given in ppm relative to Me_4Si (0 ppm, ^1H and ^{13}C) and $CDCl_3$ (77 ppm, ^{13}C). IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer. Mass spectra were obtained on a VG Micromass Ltd. Model 16F spectrometer.

The products, although pure by NMR, were distilled (short path) prior to elemental analysis to remove decomposition products. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

2,4-Bis(carbomethoxy-1-(*N,N*-dimethylamino)cyclopentane (3a). A solution of 249 mg (1.00 mmol) of complex 1 and 198 μL (2.20 mmol) of methyl acrylate in 15 mL of MeCN was heated at reflux (48 h) and worked up as described below (air oxidation, 26 h) to give 127 mg (0.56 mmol, 56%) of **2a** as a colorless oil.

^1H NMR (300 MHz): δ 3.60 (s, 3H, OMe), 3.58 (s, 3H, OMe), 2.83 (q, 1H, J = 8.7 Hz), 2.75 (t, 1H, J = 7.7 Hz), 2.55 (dd, 1H, J = 14.5, 4.2 Hz), 2.45 (m, 2H), 2.33 (dd, 1H, J = 14.5, 9.0 Hz), 2.13 (s, 6H, NMe_2), 1.56 (q, 1H, J = 10 Hz). ^{13}C NMR (75 MHz): δ 174.44 (CO), 172.18 (CO), 69.48 (C1), 51.55 (OMe), 51.33 (OMe), 41.52 (2C, NMe_2), 39.30, 39.06, 32.88, 24.54. IR (film): ν 1725 (CO) cm^{-1}. MS (EI): m/z 229 (M^+). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 57.62; H, 8.35. Found: C, 57.59; H, 8.39.

2,4-Dicyano-1-(*N,N*-dimethylamino)cyclopentane (3b). A solution of 249 mg (1.00 mmol) of complex 1 and 146 μL (2.20 mmol) of acrylonitrile in 10 mL of MeCN was heated at reflux for 67 h under an argon atmosphere. The resulting green-brown precipitate was removed by filtration (Celite), and the filter cake was washed with 40 mL of Et_2O to give a brownish solution. The solution was diluted with 40 mL of hexane and air oxidized in a light-box (6 × 20-W Vitalite fluorescent bulbs) for 27 h. A brown precipitate was removed by filtration (Celite), and the filter cake was washed with Et_2O to give a pale yellow solution. The solvents were removed on a rotary evaporator at water aspirator pressure to give 97 mg (0.60 mmol, 60%) of **2b** as a pale yellow oil.

^1H NMR (300 MHz): δ 3.01 (t, 1H, J = 7.8 Hz), 2.78 (q, 1H, J = 9 Hz), 2.55–2.34 (m, 4H), 2.23 (s, 6H, NMe_2), 1.80 (q, 1H, J = 9 Hz). ^{13}C NMR (75 MHz): δ 120.39 (CN), 116.98 (CN), 70.25, 41.47 (2C, NMe_2), 34.26, 24.61, 22.15, 21.84. IR (film): ν 2940, 2860, 2820, 2770, 2225, 2220, 1935, 1445 cm^{-1}; MS (EI): m/z 163 (M^+). Anal. Calcd for $C_9H_{13}N_3$: C, 66.26; H, 7.98; N, 25.77. Found: C, 66.31; H, 7.91; N, 26.00.

2-(Carbomethoxy)-1-(*N,N*-dimethylamino)-5-methyl-3-cyclopentene (5). A solution of 249 mg (1.00 mmol) of complex 1 and 132 mg (1.05 mmol) of methyl sorbate in 15 mL of MeCN was heated at reflux (27 h) and worked up as described above (air oxidation, sunlight, 5 h) to give 63 mg (0.34 mmol, 34%) of 5 as a colorless oil.

^1H NMR (300 MHz): δ 5.69 (td, 1H, J = 5.8, 2.3 Hz), 5.53 (td, 1H, J = 5.8, 2.2 Hz), 3.67 (s, 3H, OMe), 3.50 (sextet, 1H, J = 6.4, 4.2, 2.3 Hz, H-2), 3.15 (t, 1H, J = 4.5 Hz, H-1), 2.67 (m, 1H, H-5), 2.21 (s, 6H, NMe_2), 1.11 (d, 3H, J = 7.0 Hz, Me). ^{13}C NMR (75 MHz): δ 175.10 (CO), 138.74, 126.06, 75.42 (C1), 51.97, 51.21, 45.67, 41.59 (2C, NMe_2), 20.72 (Me). IR (film): ν 1735 (CO) cm^{-1}. MS (NH_3-CI): m/z 184 (M + H^+). Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35. Found: C, 65.54; H, 9.19.

Methyl *trans*-3-(Carbomethoxy)-4-(*N,N*-dimethylamino)-3-butenoate (7). Thermal reaction of 249 mg (1.00 mmol) of complex 1 with 144 mg (1.00 mmol) of dimethyl maleate in 15 mL of MeCN for 45 h gave after standard workup (air oxidation, sunlight, 7 h) 136 mg of a pale yellow oil. Short path distillation gave 132 mg (0.66 mmol, 66%) of 7 as a colorless oil.

^{1}H NMR (300 MHz): δ 7.37 (s, 1H, H-4), 3.59 (s, 3H, OMe), 3.55 (s, 3H, OMe), 3.38 (s, 2H, H-2), 2.94 (s, 6H, NMe_2). ^{13}C NMR (75 MHz): δ 173.60 (CO), 170.25 (CO), 150.07 (C4), 89.14 (C3), 51.63 (OMe), 50.81 (OMe), 42.69 (2C, NMe_2), 30.83 (C2). IR (film): ν 1732 (CO) cm^{-1}. MS (EI): 201 (M^+). Anal. Calcd for $C_9H_{15}NO_4$: C, 53.70; H, 7.52. Found: C, 53.70; H, 7.39.

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