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[2+4] Cycloaddition of η^6-(styrene)chromium tricarbonyl and conjugated dienes

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Cycloaddition of η^6-(styrene)chromium tricarbonyl to hexa-2,4-diene or cyclopentadiene afford the Diels—Alder adducts with retention of the $Cr(CO)_3$ group, whereas cyclohexa-1,3-diene undergoes aromatization to give η^6-(benzene)chromium tricarbonyl. The counter synthesis of these (arene)chromium tricarbonyl derivatives from uncoordinated adducts of the Diels—Alder reaction and chromium hexacarbonyl was carried out.

Key words: Diels—Alder reactions, η^6-(styrene)chromium tricarbonyl, chromium complexes.

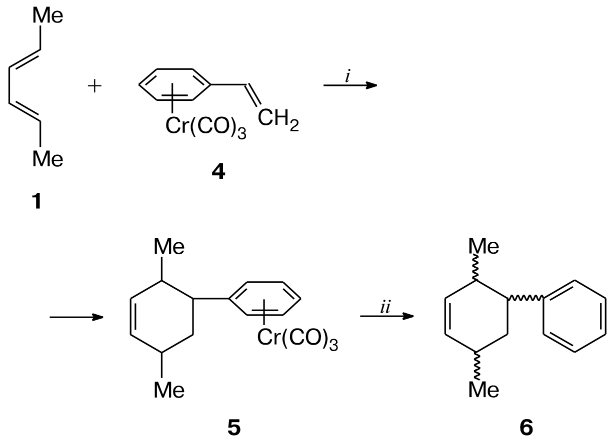
Among diverse synthetic methods of contemporary organic chemistry, diene-based synthesis plays one of the leading roles.[1—4] Styrene and its derivatives are efficient dienophiles, which in the Diels—Alder reactions with dienes give phenyl-substituted cyclohexenes or bicyclic compounds.

The use of unsaturated (arene)chromium tricarbonyl complexes in the reactions of diene synthesis of various types is known[5—11]; however, the reactions of (styrene)chromium tricarbonyl with linear and cyclic dienes have not been described to the recent time. The purpose of the present work is to study the possibility of the Diels—Alder reaction to occur involving hexa-2,4-diene (**1**), cyclopentadiene (**2**) or cyclohexa-1,3-diene (**3**), and (styrene)chromium tricarbonyl complex (**4**), which acts in this reaction as a dienophile. The reactions were carried out in sealed glass ampules with a twofold excess of diene in the inert solvent (octane).

Diene **1** (a mixture of isomers) reacted with complex **4** at 150 °C for 5 h to yield a mixture of products from which compound **5** was isolated in 40% yield as a dark yellow liquid congealed on cooling (Scheme 1).

The IR spectrum of compound **5** contains absorption bands of C—H stretches in the region of 3050—2820 cm^{-1}, giving two characteristic bands at 1967 and 1886 cm^{-1} belonging to the CO groups of the $Cr(CO)_3$ moiety. The decomposition of the obtained adduct upon UV irradiation of its ethyl acetate solution in air gives a mixture of *cis*- and *trans*-isomers of hydrocarbon **6**. Two substances were found by GC/MS analysis. They have closely lying peaks on the chromatogram and similar mass spectra with molecular ion peaks at m/z 186. Note that the retention times and mass spectra are entirely identical to the corresponding data for product **6**, which was obtained from the counter synthesis by the Diels—Alder reaction between **1** and uncoordinated styrene (see below).

Scheme 1



i. Octane, 150 °C, 5 h; *ii.* $h\nu$, O_2.

The reaction of cyclopentadiene **2** with **4** at 120 °C within 5 h affords η^6-[(bicyclo[2.2.1]hept-2-en-5-yl)benzene]chromium tricarbonyl (**7**) as pale yellow crystals with the melting point 50—52 °C (Scheme 2).

The synthesized compound was characterized by IR spectroscopy and ^1H NMR spectroscopy. The IR spectrum of compound **7** exhibits two characteristic bands of CO stretching vibrations at 1900 and 1878 cm^{-1} and bands characteristic of bicyclic alkene.

Unlike previous examples, cyclohexadiene **3** reacted with compound **4** yielding a yellow substance readily sub-

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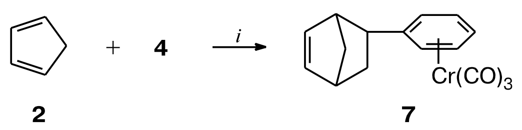
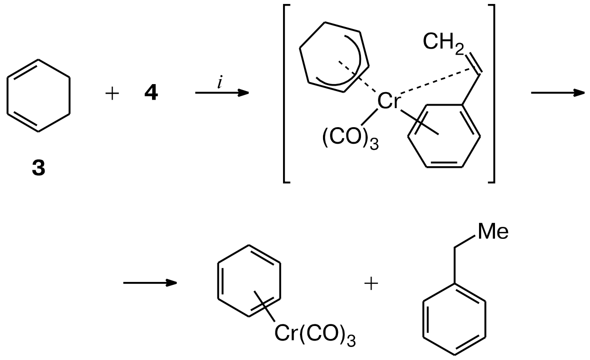
Scheme 2



i. Octane, 120 °C, 5 h.

limated *in vacuo*. The analysis by HPLC, IR spectroscopy, and mass spectrometry[12] showed that this substance was η^6-(benzene)chromium tricarbonyl (m.p. 160—162 °C, *cf*. Ref. 13: 162 °C) (Scheme 3).

Scheme 3



i. Octane, 150 °C.

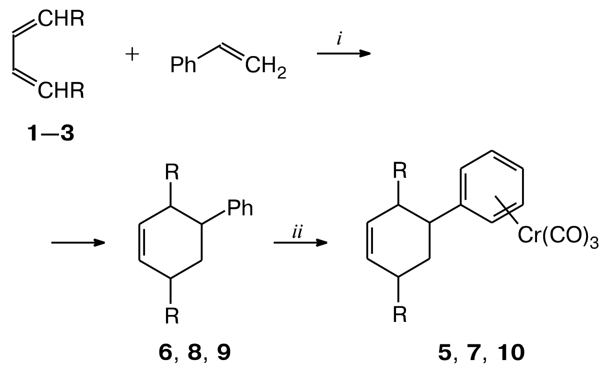
The tendency of cyclohexa-1,3-diene to undergo aromatization under the action of chromium carbonyl complexes is well known[14,15] and, therefore, the benzene complex is presumably formed at the stage of an intermediate, whose decomposition results in the aromatization of the hexadiene ring to form η^6-(benzene)chromium tricarbonyl and ethylbenzene. The appearance of these products and the absence of free styrene in the reaction mixture confirm the reaction equation presented above.

Thus, our studies revealed that unsaturated (arene)chromium tricarbonyl complexes, such as η^6-(styrene)chromium tricarbonyl (**4**), can be involved in the cycloaddition reactions to give the corresponding adducts, although in low yields.

In order to additionally confirm the structure of the (arene)chromium tricarbonyl adducts formed, we carried out the independent synthesis, which involved preliminary preparation of the Diels—Alder adducts between the corresponding dienes **1**—**3** and styrene (160—200 °C, 30 h) and subsequent complexation of the latter with chromium hexacarbonyl (Scheme 4).

The reaction of hydrocarbon **6** with chromium hexacarbonyl leads to complex **5** in 64% yield as a dark yellow oil. The decomposition of this complex under UV irradiation in air gives compound **6**, being a mixture of *cis*- and *trans*-stereoisomers in the same ratio that was in the substrate subjected to complexation.

Scheme 4



i. Hydroquinone, 160 °C, 30 h; *ii*. $Cr(CO)_6$, 120—160 °C, 5—18 h.

R = Me (**1**, **5**, **6**); R + R = CH_2 (**2**, **7**, **8**), $(CH_2)_2$ (**3**, **9**, **10**)

The reaction of phenylnorbornene **8** with chromium hexacarbonyl in refluxing diglyme—octane (1 : 1) gives complex **7** in 57% yield. Complex **7** is identical to that obtained following Scheme 2. Decomposition of this complex **7** gives the product exhibiting one peak on the GC/MS chromatogram, and its mass spectrum completely coincides with the spectrum of hydrocarbon **8** (see Ref. 12).

The reaction of compound **9** with chromium hexacarbonyl proceeds similarly to form yellow crystalline substance **10** with m.p. 92—94 °C in 40% yield. This compound gives one peak on the HPLC chromatogram, whereas its IR and NMR spectra exhibit all characteristic signals, whose positions correspond to the assumed structure. The decomposition of compound **10** under UV irradiation in air affords the product, whose mass spectrum contains the molecular ion peak with m/z 184. The mass spectrum of the decomposition product is identical to that of the starting hydrocarbon **9**.

To conclude, [2+4] cycloaddition between the (styrene)chromium tricarbonyl and conjugated dienes have been studied for the first time and can serve as an efficient route to chromium tricarbonyl derivatives of phenyl-substituted mono- and bicyclic hydrocarbons. Complexation of the pre-synthesized phenyl-containing Diels—Alder adducts can be regarded as an alternative way for their preparation. The fact of cyclohexadiene aromatization when attempting to involve it into the Diels—Alder reaction with compound **4** was established.

Experimental

All solvents were distilled above sodium metal under atmospheric pressure.[16] To remove the stabilizer, styrene was washed with 10% aqueous sodium hydroxide and then with water, dried, and distilled (b.p. 48—49 °C (10 Torr)). Cyclopentadiene (**2**) was obtained from its dimer by decomposition at 180 °C and collecting the fraction boiling at 40—42 °C (see Ref. 17). Cyclohexa-1,3-diene (**3**) and hexa-2,4-diene (**1**) were distilled under atmospheric pressure, collecting the fractions with b.p. 79—82 and 81—83 °C, respectively.

Gas chromatographic analysis was carried out on a Tsvet-500M chromatograph with a packed column with 15% Apiezon on Chromaton N-AW-DMCS (column length 2 m, flow rate of helium 26 mL min^{-1}). HPLC was carried out on a Knauer Smartline 5000 instrument with an S 2600 PDA detector (column Diaspher-110-S16, 5 μm, 4.6×250 mm, isocratic elution mode, acetonitrile—water (84 : 16) as eluent). IR spectra were recorded on an Infralyum-FT-801 instrument in the range from 480 to 4600 cm^{-1} in a suspension with KBr. ^1H and ^{13}C NMR spectra were measured on a Bruker Avance 400 spectrometer (working frequencies 400 and 101 MHz, respectively). GC/MS studies were carried out on an Trace GC Ultra/MS QII instrument in the mode of positive ion detection with electron impact ionization (70 eV) in the range *m/z* 28—500 (capillary column TR5MS 60 000×0.25 mm, helium flow rate 1 mL min^{-1}, temperature programming from 60 to 300 °C at a heating rate of 15 deg min^{-1}).

η^6-(Styrene)chromium tricarbonyl (4) was synthesized by the Rausch method.[18]

Synthesis of the Diels—Alder adducts of diene hydrocarbons with styrene 6, 8, and 9 (general procedure). A 100-mL glass ampule was filled with the corresponding diene (0.25 mol), styrene (0.25 mol), and hydroquinone (0.25 g). The ampule was freezed with liquid nitrogen, deaerated *in vacuo*, and sealed. The reaction mixture was heated in a thermostat for 30 h at 160 °C, then the ampule was opened, and the products were twice distilled *in vacuo*.

3,6-Dimethyl-4-phenylcyclohexene (6). The yield was 65%, b.p. 121—125 °C (3 Torr) (*cf.* Ref. 19: b.p. 124—128 °C (3 Torr)), n_D^{20} 1.5093 (*cf.* Ref. 19: n_D^{20} 1.50916). GC/MS (EI, 70 eV), τ/min: 16.4, 16.8; *m/z* (I_{rel} (%)): 186 $[M]^+$ (37), 118 $[M - C_5H_8]^+$ (21), 104 $[M - C_6H_{10}]^+$ (12), 82 $[M - C_8H_8]^+$ (100), 68 $[M - C_9H_{10}]^+$ (24).

5-Phenylbicyclo[2.2.1]hep-2-ene (8).[20,21] The yield was 72%, b.p. 82—95 °C (3 Torr) (*cf.* Ref. 20: b.p. 114—116 °C (14 Torr)), n_D^{20} 1.5504 (*cf.* Ref. 20: n_D^{20} 1.5510). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 170 $[M]^+$ (21), 115 $[M - C_2H_4]^+$ (9), 104 $[M - C_5H_6]^+$ (100), 91 $[C_6H_5CH_2]^+$, 78 $[C_6H_6]^+$ (26).

5-Phenylbicyclo[2.2.2]oct-2-ene (9).[22,23] The yield was 83%, b.p. 105—111 °C (3 Torr) (*cf.* Ref. 22: 94—97 °C (1—2 Torr)), n_D^{20} 1.5432 (*cf.* Ref. 22: n_D^{20} 1.5430). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 184 $[M]^+$ (100), 154 $[M - C_2H_6]^+$ (19), 142 $[M - C_3H_6]^+$ (23), 115 $[M - C_5H_{10} - H]^+$ (73), 104 $[M - C_6H_8]^+$ (100), 91 $[C_6H_5CH_2]^+$ (88), 80 $[M - C_8H_8]^+$ (100).

η^6-[(3,6-Dimethylcyclohexen-4-yl)benzene]chromium tricarbonyl (5). ***A.*** A 10-mL glass ampule was filled with complex **4** (0.24 g, 0.001 mol), diene **1** (0.32 g, 0.004 mol), and octane (3 mL). The ampule was heated in a thermostat for 5 h at 150 °C. Then the ampule was cooled down and centrifuged, and yellow solution was decanted, the solvent from which was evaporated *in vacuo*, and the products were extracted with hot hexane. The target product was isolated as a yellow viscous liquid congealed in a refrigerator. The yield was 40%.

B. A glass ampule with an all-sealed reflux condenser and a device for mechanical return of sublimed chromium hexacarbonyl was filled with hydrocarbon **6** (1.8 g, 0.0096 mol), chromium hexacarbonyl (2.6 g, 0.0115 mol), and a diglyme—octane (1 : 1) mixture (70 mL). The mixture was refluxed at 160 °C for 18 h under argon. Then the mixture was filtered through a glass filter with the Al_2O_3 layer, and the solvent was evaporated *in vacuo*. The yield was 64%. IR (KBr), ν/cm^{-1}: 3050 (ν(C_{Ar}—H)); 2962, 2911, 2826 (ν(C—H)); 1967, 1886 (CrC=O); 1632 (C=C); 1602 (ν(C—C_{Ar})); 1454, 1371 (ν(C—C)); 1199, 1106, 856, 741 (skeletal vibrations); 662, 621 (ω(C_{Ar}—H)).

η^6-[(Bicyclo[2.2.1]hept-2-en-5-yl)benzene]chromium tricarbonyl (7). ***A.*** A solution of cyclopentadiene **2** (0.26 g, 0.004 mol) and complex **4** (0.5 g, 0.002 mol) in octane (3 mL) was refluxed for 5 h at 120 °C. The product was recrystallized from an ethyl acetate—hexane mixture. The yield was 21%, m.p. 50—52 °C. According to the NMR spectroscopy and HPLC data, the purity of the product was 92%.

B. Compound **7** was also obtained by the complexation of hydrocarbon **8** (4.6 g, 0.027 mol) with chromium hexacarbonyl (6 g, 0.027 mol) in diglyme—octane (1 : 1) similarly to the synthesis of compound **5**, method ***B***. The yield was 57%. ^1H NMR (acetone-d_6), δ: 6.34 (dd, 1 H, =CH, *J* = 5.3 Hz, *J* = 3.1 Hz); 5.84 (dd, 1 H, =CH, *J* = 5.4 Hz, *J* = 2.6 Hz); 5.77—5.53 (m, 4 H, $ArCr(CO)_3$); 5.21 (d, 1 H, *o*-$ArCr(CO)_3$, *J* = 6.4 Hz); 3.26—3.08 (m, 1 H, CH—Ar); 3.02 (s, 1 H, $C\underline{H}—CH_2$); 2.92 (s, 1 H, $C\underline{H}—CH_2$), 2.14 (td, 1 H, $C\underline{H}_2$—CHAr, *J* = 12.6 Hz, *J* = 9.4 Hz, *J* = 3.6 Hz); 1.46 (td, 2 H, CH_2, *J* = 19.8 Hz, *J* = 8.5 Hz); 1.11 (d, 1 H, $C\underline{H}_2$—CHAr, *J* = 10.5 Hz). ^{13}C NMR (101 MHz, acetone-d_6), δ: 138.17, 131.78 (=CH); 95.43, 95.03, 92.26, 92.42 ($ArCr(CO)_3$); 43.16 ($C\underline{H}$—Ar); 49.56, 43.14 ($\underline{C}H—CH_2$); 31.71 ($\underline{C}H_2$—CHAr); 50.35 (CH_2); 31.73 ($\underline{C}H_2$—CHAr). ^1H-^1H COSY (400 MHz, acetone-d_6), δ: 1.11 (1.46, 2.14, 3.17); 1.46 (1.11, 2.92, 3.02); 2.14 (1.11, 2.92, 3.17); 2.92 (1.46, 2.14, 6.33); 3.02 (1.44, 5.83); 3.17 (1.46, 2.14, 3.02); 5.21 (5.60); 5.60 (5.21); 5.83 (3.02; 6.34); 6.34 (2.92, 5.83). ^1H-^{13}C COSY NMR (400—101 MHz, acetone-d_6), δ: 1.10—31.73; 1.47—50.35; 2.14—31.72; 2.92—43.14; 3.02—49.56; 3.17—43.16; 5.22—92.42; 5.45—92.26; 5.61—95.03; 5.83—131.78; 6.34—138.17. IR (KBr), ν/cm^{-1}: 3064 (ν(C_{Ar}—H)); 2966, 2921, 2852 (ν(C—H)); 1970, 1878 (CrC=O); 1632 (C=C); 1608 (ν(C—C_{Ar})); 1458, 1335 (ν(C—C)); 1152, 1106, 882, 725 (skeletal vibrations); 691, 630 (ω(C_{Ar}—H)).

η^6-[(Bicyclo[2.2.2]oct-2-en-5-yl)benzene]chromium tricarbonyl (10) was synthesized from hydrocarbon **9** (5 g, 0.027 mol) and chromium hexacarbonyl (6 g, 0.027 mol) in a diglyme—octane (1 : 1) mixture similarly to the synthesis of compound **5**, method ***B***. The yield was 40%, m.p. 92—94 °C. IR (KBr), ν/cm^{-1}: 3064 (ν(C_{Ar}—H)); 2963, 2923, 2851 (ν(C—H)); 1965, 1857 (CrC=O); 1631 (C=C); 1601 (ν(C—C_{Ar})); 1445, 1335 (ν(C—C)); 1152, 1106, 882, 725 (skeletal vibrations); 691, 635 (ω(C_{Ar}—H)). ^1H NMR (acetone-d_6), δ: 6.41 (t, 1 H, =CH, *J* = 7.3 Hz); 6.13 (t, 1 H, =CH, *J* = 7.3 Hz); 5.76—5.33 (m, 4 H, $ArCr(CO)_3$); 5.24 (d, 1 H, *o*-$ArCr(CO)_3$, *J* = 6.4 Hz); 2.63 (s, 1 H, C=C—CH); 2.03 (dd, 1 H, ≡C—H, *J* = 15.9 Hz, *J* = 6.9 Hz); 1.86—1.61 (m, 1 H, ArC—H); 1.67—1.45 (m, 2 H, $ArCHC\underline{H}_2$), 1.45—1.12 (m, 4 H, $CH_2—CH_2$).

η^6-(Benzene)chromium tricarbonyl was obtained by the reaction of compounds **4** and **5**. The yield was 85%, m.p. 160—162 °C (*cf.* Ref. 13: 162 °C). IR (KBr), ν/cm^{-1}: 3056 (ν(C_{Ar}—H)); 2987, 2916, 2848 (ν(C—H)); 1975, 1858 (CrC=O); 1599 (ν(C—C_{Ar})); 1018, 787. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 214 $[M]^+$ (16); 186 $[M - CO]^+$ (2); 158 $[M - 2 CO]^+$ (3); 130 $[M - 3 CO]^+$ (35), 77 $[C_6H_5]^+$ (14), 52 $[Cr]^+$ (100), 28 $[CO]^+$ (27).

Decomposition of (arene)chromium tricarbonyl compounds was carried out in a quartz beaker equipped with a magnetic stirrer in an ethyl acetate solution under UV irradiation with a high-pressure mercury lamp in air for 10 h. The precipitate of chromium oxide that formed was filtered off. The reaction products were analyzed using physicochemical methods.

References

1. A. S. Onishchenko, *Dienovyi sintez* [*Diene Synthesis*], Izd-vo Izv. Akad. Nauk SSSR, Moscow, 1963, 650 pp. (in Russian).
2. A. Wasserman, in *Diels Alder Reactions. Organic Background and Physico-Chemical Aspects*, Elsevier Publ. Co., Amsterdam—London—New York, 1965.
3. W. Carruthers, *Cycloaddition Reaction in Organic Synthesis*, Pergamon Press, Oxford, New York, 1990, 373 pp.
4. M. C. Kloetzel, in *Organic Reactions*, vol. **4**, John Wiley and Sons, New York, 1949.
5. G. R. Knox, D. G. Leppard, P. L. Pauson, W. E. Watts, *J. Organomet. Chem.*, 1972, **34**, 347.
6. J. W. Hull, W. L. Gladfelter, *Organometallics*, 1982, **1**, 264.
7. D. Mohring, M. Nieger, B. Lewall, K. H. Dotz, *Eur. J. Org. Chem.*, 2005, 2620.
8. J. Li, L. Xie, M. Guzel, S. B. Heaton, D. Ma, A. E. Kallmerten, G. B. Jones, *J. Organomet. Chem.*, 2007, **692**, 5459.
9. M. Prokešova, E.Solčaniova, S. Toma, K. W. Muir, A. A. Torabi, G. R. Knox, *J. Org. Chem.*, 1996, **61**, 3392.
10. C. Baldoli, S. Maiorana, E. Licandro, G. Zinzalla, M. Lanfranchi, A. Tiripiccho, *Tetrahedron: Asymmetry*, 2001, **12**, 2159.
11. M. Joudot, J. Rouzanud, A. Castel, F. Delpech, P. Riviere, H. Gomitzka, S. Massou, *Inorg. Chim. Acta*, 2004, **357**, 259.
12. *NIST Mass Spectral Library*, version 2005.
13. W. Strohmeier, *Chem. Ber.*, 1961, **94**, 2490.
14. E. O. Fischer, H. Werner, *Metall π-Complexes*, Elsevier, Amsterdam—London—New York, 1966.
15. E. O. Fischer, H. J. Rähle, *Anorg. Allgem. Chem.*, 1965, **341**, 137.
16. A. Weissberger, E. Proskauer, J. A. Riddick, E. E. Toops Jr., *Organic Solvents; Physical Properties and Methods of Purification*, Intersci. Publ Inc., New York—London, 1955, 552 pp.
17. B. A. Kazanskii, E. M. Terent´eva, in *Sintezy organicheskikh soedinenii* [*Syntheses of Organic Compounds*], Izd-vo Akad. Nauk SSSR, Moscow, 1950, Vol. **1**, 158 pp. (in Russian).
18. M. D. Rausch, G. A. Moser, E. J. Zaiko, A. L. Lipman, *J. Organomet. Chem.*, 1970, **23**, 185.
19. O. Korverl, T. L. Kwa, C. Boelhouwer, *Tetrahedron*, 1968, **24**, 1025.
20. K. Alder, H. F. Richert, *Ber. Deutsch. Chem. Ges.*, 1938, **71**, 379.
21. W. Mitlesics, P. J. Wheatley, H. Zeiss, *J. Am. Chem. Soc.*, 1962, **84**, 2327.
22. A. N. Akopyan, V. S. Aslamazyan, S. G. Kon´kova, *Arm. Khim. Zh.* [*Armenian Chemical Journal*], 1975, **28**, 101 (in Russian).
23. J. J. Eisch, S. J. Y. Liu, *J. Organomet. Chem.*, 1970, **21**, 285.

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