INTERACTION OF CUMULENE SYSTEMS WITH ORGANOMETALLIC π-COMPLEXES

II. FERROCENYLBUTATRIENES AND RELATED COMPOUNDS

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INTRODUCTION

In a previous report[1] we have investigated direct interaction of cumulene systems with various organometallic compounds. We now describe some related studies on ferrocenylbutatrienes including an interesting example of the stabilization of cumulene systems by neighboring ferrocenyl groups. Among various cumulene systems, aryl-substituted butatrienes have been most extensively investigated and their preparation seemed to be most easily accomplished. A number of substituted butatrienes with varying stability have been prepared in the past. Among substituted butatrienes, tetra-arylbutatrienes are known to be very stable. However, only a few examples are known for di- and tri-substituted compounds and there have been no example of mono-substituted compounds[2].

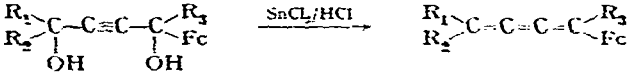
We were interested in the stability order of the ferrocenyl butatrienes and have attempted to prepare tetra-, tri- and di-substituted butatrienes containing one or two ferrocenyl groups as substituents. We unexpectedly found that di- and tri-substituted butatrienes are more stable than a similar tetra-substituted butatriene. In the course of this study, 1,4-diferrocenylbutatriene was reported by Schlögl *et al.*[3] without analytical data. We have also prepared the same compound according to their method. It gave poor elemental analyses and its visible spectrum was similar to that of 1,4-diferrocenyl-1,3-butadiene. We therefore questioned the presence of the butatriene system. However, by an improved method for the preparation of the butatriene, we obtained a compound giving reasonable elemental analyses and infrared and ultraviolet spectra.

RESULT AND DISCUSSION

Preparation of ferrocenylbutatrienes

The most convenient and widely used method for the preparation of butatriene systems is dehydroxylation of a substituted 2-butyne-1,4-diol. A variety of modifications and of reagents for this reaction have been known[2]. Among such reagents, the stannous chloride and hydrochloric acid system was found to be best suited for the preparation of ferrocenylbutatrienes. As the starting materials, 1,4-diferrocenyl-2-butyne-1,4-diol (Ia), 1,1-diphenyl-4-ferrocenyl-2-butyne-1,4-diol (Ib), 1,1,4-triphenyl-

4-ferrocenyl-2-butyne-1,4-diol (Ic), and 1-(9-hydroxy-9-fluorenyl)-3-ferrocenyl-1-propyne-3-ol (Id) were prepared. The dehydroxylation of these ferrocenylbutynediols at room temperature always gave material having poor elemental analyses, and the presence of a butatriene system was questioned from the infrared and visible spectra. Therefore, a modified low temperature method, which is described in detail in EXPERIMENTAL, was used for the dehydroxylation. The products obtained by the low temperature method had properties quite different from those obtained by the room temperature method.



(Ia): $R_1 = R_2 = H,\ R_2 = Fc$

(Ib): $R_1 = R_2 = Ph,\ R_3 = H$

(Ic): $R_1 = R_2 = R_3 = Ph$

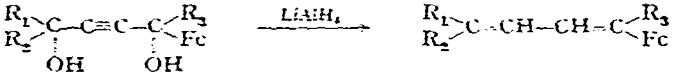
(IIa): $R_1 = R_3 = H.\ R_2 = Fc$

(IIb): $R_1 = R_2 = Ph.\ R_3 = H$

(IIc): $R_1 = R_2 = R_3 = Ph$

1,4-Diferrocenylbutatriene (IIa), prepared and purified at low temperatures under nitrogen, had the expected properties and gave the correct elemental analyses. Once prepared and purified at low temperatures, the compound was stable at room temperature and in air for a month. Hydrogenation of this compound over Raney nickel catalysts gave 1,4-diferrocenyl-*n*-butane quantitatively. An infrared absorption band near 2032 cm^{-1} is generally known as an evidence for the presence of a butatriene system[1-6]. The absorption band near 2032 cm^{-1} was absent in 1,4-diferrocenylbutatriene (IIa) because of its symmetry around the butatriene system. 1,1-Diphenyl-4-ferrocenylbutatriene (IIb) was prepared in the similar way from the corresponding butynediol (Ib). The product showed a strong infrared band at 2035 cm^{-1} indicating the presence of the butatriene system. 1,1,4-Triphenyl-4-ferrocenylbutatriene (IIc) was prepared also in the similar manner. The product, nicely red crystalline at low temperature, could not be isolated in a pure state owing to rapid decomposition to black amorphous intractable materials at room temperature.

For the comparison of the electronic spectra with those of the ferrocenylbutatrienes, the corresponding ferrocenylbutadienes were prepared.



(Ia): $R_1 = R_3 = H,\ R_2 = Fc$

(Ib): $R_1 = R_2 = Ph,\ R_3 = H$

(Ic): $R_1 = R_2 = R_3 = Ph$

(IIIa): $R_1 = R_3 = H,\ R_2 = Fc$

(IIIb): $R_1 = R_2 = Ph,\ R_3 = H$

(IIIc): $R_1 = R_2 = R_3 = Ph$

These compounds (IIIa–c) were obtained in good yields by the method of Schlögl *et al.*[7].

Preparation of (tetraphenylallene)- and (tetraphenylbutatriene)chromium tricarbonyl

The preparation of cumulene complexes of chromium was attempted in order to elucidate the interaction of the cumulene systems with neighboring organometallic *π*-complexes. Tetraphenylallene was refluxed with chromium hexacarbonyl in di-*n*-

butyl ether to give a yellow complex in 4.7% yield. It was shown to contain one chromium tricarbonyl group attached to one of the phenyl groups. Tetraphenylbutatriene was reacted with chromium hexacarbonyl in exactly the same way to give red crystals in 6% yield. The complex was shown to be of similar type with that of the allene complex. These chromium tricarbonyl complexes are stable in air and soluble in benzene and in acetone. Attempts to prepare the molybdenum analog of the butatriene complex failed and only a rearrangement to give 1-(diphenylmethylene)-3-phenylindene was observed.

TABLE 1

ELECTRONIC SPECTRA OF FERROCENYLBUTATRIENES, -BUTADIENES AND RELATED COMPOUNDS

Compounds	λ_{max} (mμ) (ε)		λ_{max} (mμ) (ε)	
1,4-Diferrocenylbutatriene (IIa)[a]	370	(27100)	510	(5300)
1,4-Diferrocenyl-1,3-butadiene (IIIa)[a]	330	(30400)	463	(3600)
1,1-Diphenyl-4-ferrocenylbutatriene (IIb)[a]	390	(22300)	525	(3100)
1,1-Diphenyl-4-ferrocenyl-1,3-butadiene (IIIb)[a]	338	(28000)	460	(2000)
1,1,4-Triphenyl-4-ferrocenylbutatriene (IIc)[a,e]	335	—	480	—
1,1,4-Triphenyl-4-ferrocenyl-1,3-butadiene (IIIc)[a]	352	(27600)	470	(2500)
(Tetraphenylbutatriene)chromium tricarbonyl (IV)[a]	402	(26900)	493	(13800)
1,1,4,4-Tetraphenylbutatriene[b]	420	(33000)	—	—
(2,2-Dicyanovinyl)ferrocene[c]	316	(22600)	518	(6600)
	377	(4200)		
(1-Methyl-2,2-dicyanovinyl)ferrocene[c]	312	(17400)	508	(4600)
	375	(sh.[d])		

[a] In tetrahydrofuran. [b] In benzene: *cf.* ref. 4. [c] In cyclohexane: *cf.* ref. 9. These compounds slowly decomposed in polar organic solvents. Therefore it was impossible to measure the spectrum in tetrahydrofuran. [d] Shoulder. [e] The electronic spectrum of this compound was measured in a specially cooled cell because of the instability of the compound.

Electronic spectra

The visible and ultraviolet spectra of ferrocenylbutatrienes and the closely related chromium tricarbonyl complex are shown in Table 1 and Figs. 1 and 2. The most interesting point in these electronic spectra is the appearance of strong bands near 450–550 mμ region. These bands can be ascribed to the charge transfer from the ferrocenyl group or chromium tricarbonyl group to the butatriene system*. A comparison of the spectrum of (tetraphenylbutatriene)chromium tricarbonyl (IV) with the corresponding metal-free compound clearly shows this (*cf.* Fig. 2). The metal-free compound shows a band at 420 mμ and this band persists in its chromium complex in a somewhat modified way, appearing at 402 mμ. In addition to this band, another longer-wave-length band was observed in the complex at 493 mμ. Similar bands appeared in the spectra of ferrocenylbutatrienes near 510 mμ (*cf.* Fig. 1). Strong bands near 510 mμ appeared also in some conjugated ferrocenes such as (2,2-dicyanovinyl)-ferrocenes. These bands have been assigned as charge transfer bands[10]. Among the three ferrocenylbutatrienes, (IIa), (IIb), and (IIc), the extent of the red shift of the charge transfer bands of (IIa) and (IIb) is greater when the comparison was made.

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* A molecular orbital calculation of tetraphenylbutatriene showed an antibonding level of considerably low energy[8]. This was supported by formation of mono- and di-anions on reaction with alkali metals[8].

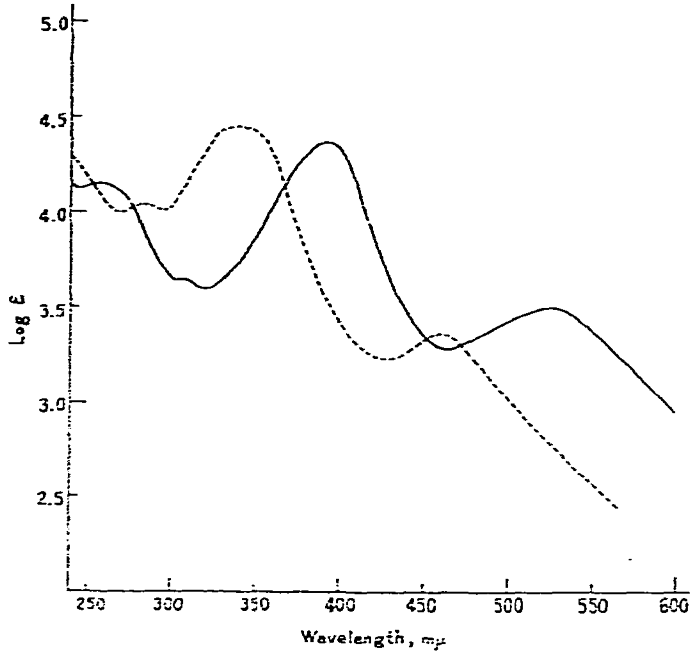


Fig. 1. Electronic spectra of 1,1-diphenyl-4-ferrocenylbutatriene ((IIb) (——) and 1,1-diphenyl-4-ferrocenyl-1-3-butadiene (IIIb) (– – – –) in tetrahydrofuran.

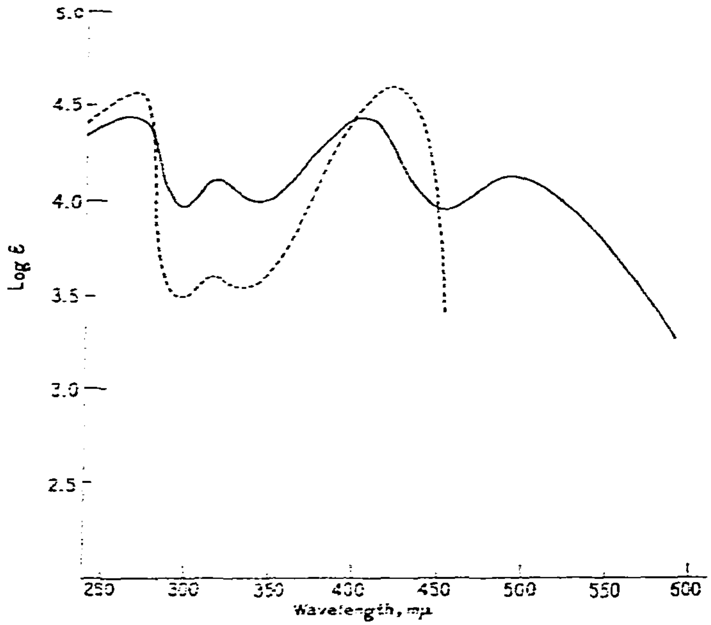
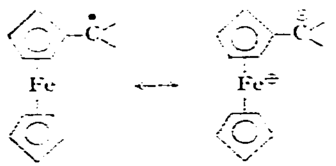


Fig. 2. Electronic spectra of (tetraphenylbutatriene)chromium tricarbonyl (IV) (——) in tetrahydrofuran and tetraphenylbutatriene (– – – –) in cyclohexane.

The intensity of the band is greater in (IIa) than in (IIb). This spectral behavior could be explained as follows: The non-bonding orbitals of the two terminal ferrocenyl groups, such as the *hag* molecular orbital of the Moffitt's description, of (IIa) easily overlaps with the anti-bonding molecular orbital of the butatriene system to give rise to the greatest charge transfer. In the butatriene system of (IIb) the charge transfer occurs only on one terminal. In the tetra-substituted compound, (IIc), the overlap for the charge transfer is sterically disturbed owing to the phenyl group adjacent to the ferrocenyl group. These band positions and intensities are then seen to be related with the stability of the ferrocenylbutatrienes.

Stability of the butatriene systems

The instability of butatriene systems, in general, has been related with the ease of formation of the corresponding di-radical species. Although tetraarylbutatrienes are stabilized by an extensive conjugation with the aryl groups, the corresponding di- and tri-substituted compounds are not stable enough to guarantee their easy isolation[10]. On the other hand, the stability of the butatriene systems is improved through introduction of bulky substituents. In the case of 1,4-diferrocenylbutatriene (IIa), a di-substituted butatriene, without extensive conjugation with aryl groups and without very bulky substituents, a third stabilizing factor must be operative. We believe the third factor to be the charge transfer caused by the ferrocenyl groups. α-Carbonium ion stabilization in ferrocene derivatives is well-known[11]. Therefore, the following electronic interaction seems possible and reasonable. Thus, the diradical



species of 1,4-diferrocenylbutatriene (IIa) can be stabilized by the supply of electrons from the ferrocenyl groups to the butatriene system. Actually, this electron supply is manifested in the strong charge transfer absorptions in the region of 510 mμ. The decreased stability of 1,1,4-triphenyl-4-ferrocenylbutatriene (IIc) is perhaps due to its greater steric hindrance to supply an electron from the ferrocenyl group to the butatriene system and to the concurrent disturbance of conjugation of the system with the phenyl group at C_4.

In summary, the stabilization of butatriene systems by neighboring ferrocenyl groups is thus an interesting and unique property of the ferrocenyl group. The similar stabilization of cumulene systems by neighboring organometallic π-complexes seems possible and it may be one of the characteristic properties of the π-complexes.

EXPERIMENTAL

All melting points are uncorrected and measured by a micro-melting point apparatus made by Yanagimoto Company. Polarized light was sometimes used to examine crystallinity. Infrared spectra were obtained by a Hitachi Model EPI-2 and a Jasco Model IR-S spectrophotometer. Visible and ultraviolet spectra were measured by a Beckman DK-2 spectrophotometer. Alumina used for chromatography had activity grade I and was of 200–300 mesh size. Elemental analysis was performed by Messrs. T. SHISHIDO and T. SHIBANO of this Institute.

Materials

Ferrocene[12], formylferrocene[13], benzoylferrocene[14], ethynylbenzhydrol[15], 1-ferrocenyl-2-propyn-1-ol[7], 1,4-diferrocenyl-2-butyne-1,4-diol[7], 1,4-diferrocenyl-1,3-butadiene[7], tetraphenylallene[16], tetraphenylbutatriene[8], 1-(diphenylmethylene)-3-phenylindene[17], chromium hexacarbonyl[18] were prepared by the method described in literature.

1,1-Diphenyl-4-ferrocenyl-2-butyne-1,4-diol (Ib)

A solution containing about 0.048 mole of phenyllithium in 86 ml of anhydrous diethyl ether was added over 5 minutes period to a solution of 5 g (0.024 mole) of ethynylbenzhydrol in 75 ml of anhydrous tetrahydrofuran with stirring under nitrogen. After the exothermic reaction was ceased in 10–30 minutes, a solution of 5.15 g (0.024 mole) of formylferrocene in 35 ml of anhydrous tetrahydrofuran was added. The reaction mixture was refluxed for 1 h with stirring, cooled and poured over crushed ice. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with water, and dried over sodium sulfate. After the removal of the organic solvent at reduced pressure, the remaining yellow semi-solid was crystallized from benzene. Pale yellow needles were obtained, m.p. 148–53°; yield 4.3 g (42.4 %). (Found: C, 73.91; H, 5.29. $C_{26}H_{22}O_2Fe$ calcd.: C, 73.94; H, 5.25 %.)

1,1,4-Triphenyl-4-ferrocenyl-2-butyne-1,4-diol (Ic)

By the analogous method mentioned above, from benzoylferrocene and ethynylbenzhydrol, the title compound was obtained as yellow needles; m.p. 160–66° (dec.); 34.3 % yield. (Found: C, 77.21; H, 5.40. $C_{32}H_{26}O_2Fe$ calcd.: C, 77.12; H, 5.26 %.)

1-(9-Hydroxy-9-fluorenyl)-3-ferrocenyl-1-propyn-3-ol (Id)

A solution of 1.4 g of 1-ferrocenyl-2-propyn-1-ol in 100 ml of diethyl ether was added to a suspension of lithium amide (prepared from 0.2 g of lithium in liquid ammonia by ferric nitrate catalyst) in 200 ml of liquid ammonia with stirring. After 30 minutes, a solution of 1.44 g of fluorenone in 100 ml of diethyl ether was added with stirring. The reaction mixture was stirred for 4 hours at −35° and poured over crushed ice. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with water, and dried over sodium sulfate. After the removal of the organic solvent at reduced pressure, the remaining solid was washed with benzene. Pale yellow crystals were obtained (420 mg, 17.2 % yield). It was recrystallized twice from tetrahydrofuran/petroleum ether giving pale yellow needles; m.p. 204–11°. (Found: C, 73.73; H, 4.97. $C_{26}H_{20}O_2Fe$ calcd.: C, 74.30; H, 4.80 %.)

1,4-Diferrocenylbutatriene (IIa)

A solution of 300 mg of stannous chloride dihydrate in 1.5 ml of concentrated hydrochloric acid and 0.8 ml of tetrahydrofuran was added to a solution of 230 mg of 1,4-diferrocenyl-2-butyne-1,4-diol in 8 ml of tetrahydrofuran at —30 ~ —40° under nitrogen. The red-purple solution was left standing for 18 h, with occasional stirring, at —30 ~ —40° under nitrogen and then 60 ml of 20 % hydrochloric acid, which had been previously cooled to —30 ~ —40°, was added. Red-purple precipitates were filtered, washed with 20 % hydrochloric acid with cooling at —30 ~ —40°, then with ice-water and a mixture of diethylamine and *n*-hexane (1:1) near 0°. The precipitates were dried over phosphorus pentoxide under reduced pressure. Red-purple powder (190 mg) was obtained which contained no halogen (Beilstein test). This powder was dissolved in dry benzene and filtered and the filtrate was evaporated *in vacuo*. Thus, red-purple powder was sufficiently analytically pure. Decomposition began from about 200° in air. (Found: C, 67.96; H, 5.02. $C_{24}H_{20}Fe_2$ calcd.: C, 68.61; H, 4.80 %.)

1,4-Diferrocenyl-n-butane

1,4-Diferrocenylbutatriene (211.4 mg) in 100 ml of tetrahydrofuran was hydrogenated in the presence of Raney nickel catalyst during 40 minutes. After the removal of the catalyst, the filtrate was evaporated and the residue was recrystallized from petroleum ether (b.p. 40°) to give 209.0 mg of yellow crystals; m.p. 106–8° (lit. m.p. 105–111°). Infrared spectrum was consistent with the structure of the title compound. (Found: C, 68.20; H, 6.41. $C_{24}H_{26}Fe_2$ calcd.: C, 67.65; H, 6.15 %.)

1,1-Diphenyl-4-ferrocenylbutatriene (IIb)

A solution of 1 g of stannous chloride dihydrate in 2.5 ml of concentrated hydrochloric acid and 1.5 ml of tetrahydrofuran was added to a solution of 1,1-diphenyl-4-ferrocenyl-2-butyne-1,4-diol in 15 ml of tetrahydrofuran at —30 to —40° in nitrogen. The resulting solution was kept for 26 h with occasional stirring at —30 ~ —40°, and then 80 ml of 20 % hydrochloric acid, which had been previously cooled at —30 ~ —40°, was added. The deep-purple precipitates were filtered, washed with 20 % hydrochloric acid, water, 28 % aqueous ammonia and water consecutively and dried over phosphorus pentoxide under reduced pressure. The deep-purple powder thus obtained contained no halogen (Beilstein test). This powder was dissolved in petroleum ether (b.p. 38–41°), and the filtrate was evaporated. Deep-purple solid was obtained which gave reasonable analyses. Decomposition began from about 180° in air. (Found: C, 79.78; H, 5.84. $C_{26}H_{20}Fe$ caldc.: C, 80.48; H, 5.19 %.)

1,1,4-Triphenyl-4-ferrocenyl-butatriene (IIc)

A solution of 500 mg of stannous chloride dihydrate in 1.2 ml of concentrated hydrochlorid acid and 1 ml of tetrahydrofuran was added to a solution of 500 mg of 1,1,4-triphenyl-4-ferrocenyl-2-butyne-1,4-diol in 7 ml of tetrahydrofuran at —50 ~ —70° in nitrogen. It was kept for 3 h with occasional stirring at —50 ~ —70° and 50 ml of petroleum ether (b.p. 38–41°), cooled previously below —50°, was added. The reaction mixture was well shaken in order to extract the product in petroleum ether. The pink-red colored petroleum ether layer was decanted and concentrated under reduced pressure below —30°, giving nicely crystalline, red prisms. Elemental analysis of the compound was unsuccessful owing to the decomposition on warming to give intractable materials. The mother liquor was also concentrated in the similar manner to give red crystals, which also decomposed to black materials on warming. The electronic spectrum of the red petroleum ether solution showed maxima at 335 mμ and 480 mμ in the cold. Hydrogenation of this red solution has been unsuccesful. The reason for this is not clear.

1,1-Diphenyl-4-ferrocenyl-1,3-butadiene (IIIb)

A solution of 423 mg of 1,1-diphenyl-4-ferrocenyl-2-butyne-1,4-diol in 100 ml of anhydrous diethyl ether was added over 5 minutes to a suspension of 2.0 g of lithium aluminum hydride in 200 ml of anhydrous diethyl ether with stirring. The mixture was refluxed for 4 h, cooled, and ethyl acetate was added to decompose an excess of the lithium aluminum hydride. The mixture was filtered and the residue was washed with diethyl ether, the combined filtrate was dried over sodium sulfate and concentrated under reduced pressure. A semi-solid was obtained quantitatively and was recrystallized from ethyl acetate to give red prisms; m.p. 130–6°, 131 mg. (Found: C, 80.18; H, 5.97. $C_{26}H_{20}Fe$ calcd.: C, 80.01; H, 5.68 %.)

1,1,4-Triphenyl-4-ferrocenyl-1,3-butadiene (IIIc)

By the analogous method mentioned above, from 1,1,4-triphenyl-4-ferrocenyl-2-butyne-1,4-diol, the title compound was obtained as red prisms, m.p. 203–6°, quantitatively. (Found: C, 82.36; H, 5.63. $C_{32}H_{26}Fe$ calcd.: C, 82.41; H, 5.62 %.)

(Tetraphenylallene)chromium tricarbonyl

Tetraphenylallene (2.0 g) and chromium hexacarbonyl (2.0 g) were placed in a flask with a mixture of 8 ml of di-*n*-butyl ether, 3 ml of tetrahydrofuran and 2 ml of *n*-hexane. The use of the tetrahydrofuran and *n*-hexane was to prevent the sublimation of the chromium hexacarbonyl during the reaction. The mixture was heated at reflux for 28 h under nitrogen. Evolution of gas was measured to show the extent of the reaction. A total of *ca.* 130 ml of gas was evolved. The filtered yellow solution was evaporated at room temperature *in vacuo* and chromatographed on alumina. Elution with *n*-hexane/benzene (1:3 to 1:5) gave yellow eluate which on evaporation and crystallization from hot acetone/ethanol (1:3) gave the title compound in 4.7 % yield as yellow crystals; m.p. 188–89°, dec. 210–30° in air. UV: λ_{max} 258 mμ (log ε 4.14), 320 mμ (log ε 3.35); IR: $\nu_{C\equiv O}$ 1908, 1982 cm^{-1}. (Found: C, 74.75; H, 4.51. $C_{30}H_{20}CrO_3$ calcd.: C, 74.99; H, 4.20 %.)

(Tetraphenylbutatriene)chromium tricarbonyl (IV)

The analogous reaction using tetraphenylbutatriene (1.0 g) in place of tetraphenylallene and chromium hexacarbonyl (1.2 g) for 20 h gave a deep red solution, while evolution of 130 ml of gas was observed. Chromatography of the evaporated solution gave red eluate with benzene/*n*-hexane (1:3 to 1:1), which on evaporation and crystallization from benzene/*n*-hexane gave the title compound as red needles in 6 % yield (83 mg), m.p. 185–87° in air (dec. at 220°). IR: $\nu_{C\equiv O}$ 1913, 1984 cm^{-1}. (Found: C, 75.00; H, 4.28. $C_{31}H_{20}CrO_3$ calcd.: C, 75.60; H, 4.09 %.) Deep-violet solid was obtained in very poor yield (0.2 %) from the violet eluate which followed the red one. Recrystallization from benzene further decreased the amount of the violet product. No analysis of this product was attempted. However, the observation that thermal decomposition at 200° gave yellow crystals melting at 244–45° (tetraphenylbutatriene), together with the visible (λ_{max} at 512, 396 mμ) and the infrared spectra (strong bands at 1902, 1988 cm^{-1}), suggested that the product most likely was (tetraphenylbutatriene)bis(chromium tricarbonyl).

Attempts to prepare (tetraphenylbutatriene)molybdenum tricarbonyl

Tetraphenylbutatriene (1.8 g) and molybdenum hexacarbonyl (1.32 g) were heated in 80 ml of decalin at 110–20° for 20 h. The reaction gave yellow crystals, m.p. 203–4°, identified as 1-(diphenylmethylene)-3-phenylindene by mixed melting point test and by comparison of infrared spectra. A similar reaction using di-*n*-butyl ether as solvent at 140° gave only a trace of the expected compound.

SUMMARY

Ferrocenylbutatrienes, $R_1R_2C{=}C{=}C{=}CR_3Fc$, where $R_1 = R_3 = H$, $R_2 = Fc$ (IIa), $R_1 = R_2 = Ph$, $R_3 = H$ (IIb), $R_1 = R_2 = R_3 = Ph$ (IIc) and corresponding butadiene derivatives were prepared and their electronic spectra were measured. There was considerable difficulty in obtaining pure samples. However, (IIa) and (IIb) were obtained in analytically pure state. The stability order was found to be (IIa) ~ (IIb) > (IIc). (Tetraphenylallene)- and (tetraphenylbutatriene)chromium tricarbonyls were also prepared. Absorption bands due to a charge transfer from the metal into the butatriene system were observed and thought to be in a close relatonship to the stabilization of the butatriene system by neighboring ferrocenyl groups.

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