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PROPELLANES. XCIV. THE REACTION OF CYCLOPENTADIENYL COBALT COMPLEXES OF TETRAENIC PROPELLANES WITH 4-METHYL-3,5-DIOXO-TRIAZOLINEDIONE (MTAD)[**]

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Abstract - MTAD is able to replace CpCo moieties complexed to 1,3-dienes, affording the corresponding Diels-Alder adducts of these dienes.

Introduction. - We have shown that $Fe(CO)_3$ complexes of various propellanes containing cyclohexadiene rings are capable of interacting with 4-phenyl-3,5-dioxo-triazolinedione (PTAD). This reaction consisted of displacement of the iron tricarbonyl moiety by this very reactive dienophile and the configurations of the educts and products could be correlated. The ^1H-NMR spectra of the former were measured and permitted definition of the configuration of the respective $Fe(CO)_3$ groups.[2]

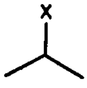
More recently CpCo-diethene was interacted with the same type of (tetraenic) propellane and a mixture of CpCo-complexes were shown to be present in the product mixture.[3] Owing to the C_{2v} symmetry of the starting materials 1 (—— x) represents a five-membered heterocyclic ring, e.g. ether or imide; other lines represent cyclohexadiene rings), in principle, one may obtain a mixture of five products 2a-e(M=$Fe(CO)_3$ or CpCo), 2 isomeric mono-complexes 2a,b and 3 isomeric bis-complexes (2c-e). Indeed five such products were isolated when M=$Fe(CO)_3$, 2e being found in ca 1% yield, presumably for reasons of steric repulsion between its M groups.[4a] This occurred when $Fe_2(CO)_9$ was reacted with 1 but when $Fe(CO)_5$ was used, only 2c was obtained, in high yield.[4a]

Discussion of Plans.- It is therefore not surprising that no 2e (M=CpCo) could be observed in the reaction mixture obtained using CpCo-diethene.[3] The steric repulsion of two CpCo moieties in the anti,anti bis-complex (frame of steric reference is the hetero-ring) is presumably responsible for the absence of this potential product.[3] Of course, one may not be certain from the ^1H-NMR spectrum of the reaction mixture that 2e is not present in an unobservable concentration but separation of the products also showed that no 2e could be isolated (see below).

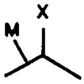
[**] Dedicated in friendship to an organocobaltophile, Professor Albert Eschenmoser, in honor of his seminal contributions to the chemistry of much more complex cobalt compounds.

Part XCIII. P. Ashkenazi, A.L. Gutman, Asher Mandelbaum, D. Muller, W.J. Richter, and D. Ginsburg, J. Amer. Chem. Soc., in press.

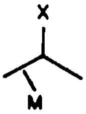
[♦] Deceased March 9, 1988.



1



2a



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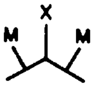
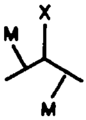
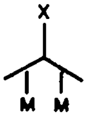


2c



2d



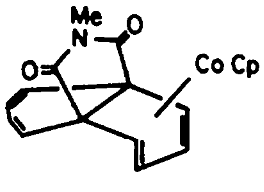
2e

After a lecture by P. Vollhardt including CpCo-complexes of various conjugated dienes, we suggested he try their reaction with a TAD following our earlier work on the Fe(CO)$_3$-complexes. In short order he informed us that the displacement reaction indeed occurs.[5] Since we had experience with the mono- and bis-Diels-Alder adducts of various tetraenic propellanes[1] it appeared worthwhile to study the interaction of their CpCo-complexes[3] with MTAD. Our Mulheim collaborators were kind enough to repeat for us the joint work reported earlier[3] so that we could attempt separation of product mixtures into their pure components. If we succeeded in such separation we could study the reactions of the pure mono- and bis-complexes with MTAD. MTAD was preferred to PTAD because of our experience in working with both triazolinediones; the methyl derivative was easier to workup.

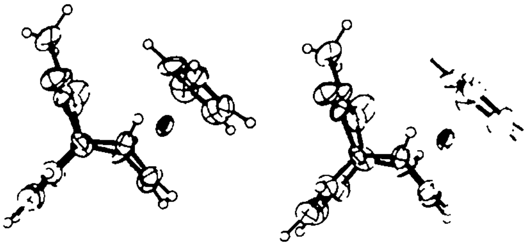
We were not looking forward happily to the need of working in an argon atmosphere during the separation and isolation stages but luckily the CpCo-complexes involved were sufficiently air-stable to make such a procedure unnecessary.

Results and Discussion.- The crude reaction mixtures prepared in Mulheim were chromatographically separated. Although the CpCo-complexes were less stable than the corresponding Fe(CO)$_3$ complexes it was possible both to isolate them and to react them with MTAD. Only 2c could not be isolated owing to its instability (see experimental section) and as mentioned before, no 2e was obtained.

Two sets of experiments were carried out with the pure CpCo-complexes. In one, the starting material was reacted with 1 eq MTAD, in the second with 10 eq so that a large excess of the latter dienophile was present throughout. Different results were obtained and these are summarized in the following schemes. In all the cases the mono- or bis-CpCo complex of the tetraenic propellane methyl imide was used, i.e. X=NMe imide, M=CpCo.



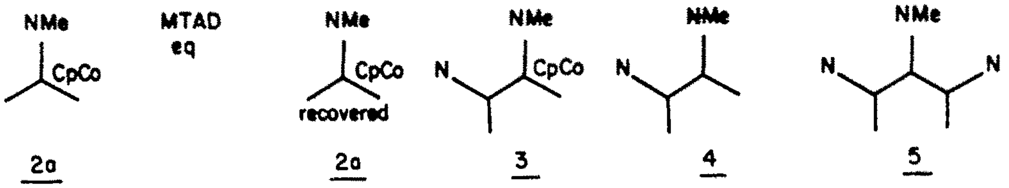
2a



ORTEP of 2a

The referee has suggested that we add a full structural formula to assure understanding of standard formulae used herein.

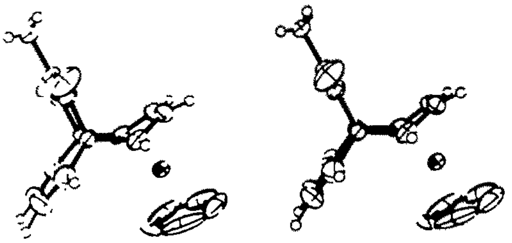
The first scheme shows the results for the corresponding mono-syn-complex, 2a, in % yield.



MTAD eq	2a recovered	3	4	5
		MTAD ADDUCTS		
1.1	29	66	5	—
10	—	31	24	40

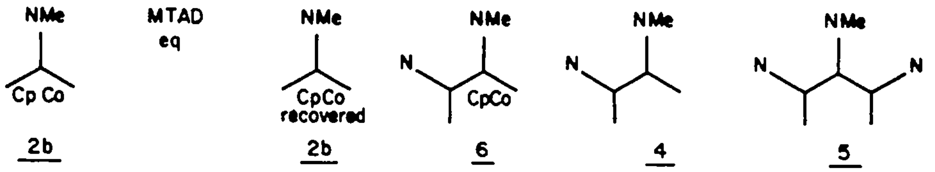
Scheme 1

Scheme 1 shows that for the same reaction time syn- starting material 2a (29%) may still be isolated when there is no excess of MTAD. But in both cases the first reaction step is attack of the naked (uncomplexed) cyclohexadiene ring. When an equivalent of MTAD is used, the major product 3 results from precisely such an attack (66%) but in some of this product loss of CpCo occurs leading to the syn-mono-Diels-Alder adduct 4 in 5% yield. When excess of MTAD is reacted with 2a the first step in the reaction sequence is again syn-attack of the naked cyclohexadiene ring (probably > 66%). But this time 3 is surrounded by a huge excess of MTAD molecules. Although the major product (40%) is then the syn,syn-bis-Diels-Alder adduct 5 for there is more than enough MTAD available, some 24% of the product is the cobalt-free syn-mono-Diels-Alder adduct, 4. Some CpCo is removed in either case, either at the very end of the reaction period or more likely during separation of products. CpCo is complexed less strongly to the propelladiene system than Fe(CO)$_3$ (where no such "spontaneous" loss of metallic moiety was earlier observed[1]) and it simply falls out, evidently via air oxidation. No intervention of Ce^{IV} is necessary. Another, more important, instance of similar behavior is discussed below.



ORTEP of 2b

Scheme 2 shows that the anti-mono-CpCo-complex, 2b, with 1.1 eq MTAD, permits 33% to be recovered. The major product 6 results from attack of the naked cyclohexadiene ring whilst the other two products are again 4 (11%) and 5 (5%) resulting from loss of some CpCo from 6 and little further reaction of 4 with MTAD, respectively.

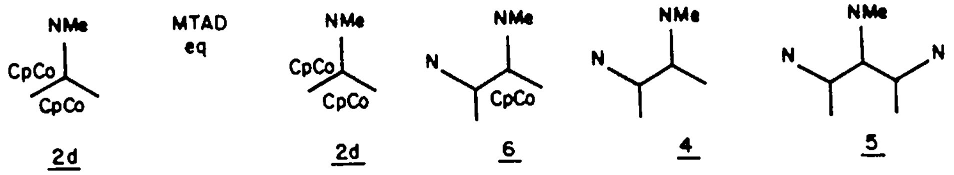


MTAD eq	2b	6	4	5
			MTAD ADDUCTS	
1.1	33	50	11	5
10	—	18	26	56

Scheme 2

However when an excess (10 eq) of MTAD is used, no 2b is recovered and 6, 4, and 5 are formed in 18%, 26%, and 50%, respectively.

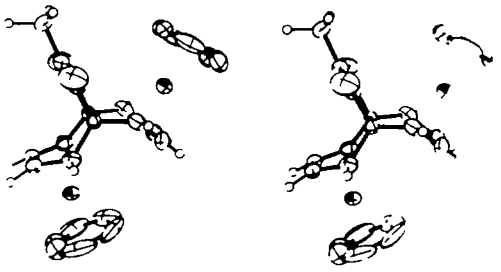
Scheme 3 shows the behavior of the syn,anti-bis-complex 2d.



MTAD eq	2d	6	4	5
1.1	76	12	11	1
10	44	1	22	32

Scheme 3

The same products are obtained in each case, in the relative amounts shown. Here recovery is the greatest, i.e. 2d is the stablest among type 2 products. There is clear indication that the syn-CpCo group is removed in preference to the anti one (Cf. 2d ⟶ 6). This is not in line with the behavior of the analogous syn,anti-Fe(CO)$_3$ complex of the tetraenic propellane imide where there is apparently no such selectivity.[1b]



ORTEP of 2d

Albeit we know the ^{1}H-NMR spectrum of the syn,syn-bis-CpCo-complex[3] upon chromatography of the crude reaction mixture only 2a, 2b, and 2d were isolated. The fourth component 2c does not survive the separation procedure. Again a syn-CpCo moiety is rather easily removed but the unsymmetrical bis-complex 2d is stable under the same treatment during separation and isolation.

When 2d is treated with ceric ammonium nitrate (3 eq) removal of CpCo is not as selective as compared with the syn,anti-bis-Fe(CO)$_3$ analog.[2] Nevertheless, in addition to completely cobalt-less material 1, the syn CpCo group is removed as compared to the anti-group by a factor of $>$ 4:1. Thus, here also, it is easier to remove the syn-moiety.

None of the anti,anti-CpCo-complex 2e was observed in the NMR spectrum of the crude reaction mixture, nor was any observed on the chromatographic plate nor otherwise isolated.

Acknowledgments.- We are grateful to Professor P. Vollhardt for his private communication[5] and to Prof. Dr. G. Wilke for his kind agreement to prepare for us enough crude reaction mixtures of tetraenic propellane imides with CpCo-diethene and to Herr L. Stehling for these preparations. Again one of us (D.G.) owes royal hospitality to Professor Wilke during an additional stay at Mulheim/Ruhr in the summer of 1986.

Experimental.- UV spectra were measured in EtOAc on a Carey 15 spectrometer. IR spectra were measured in CHCl$_3$ using a Perkin Elmer 298 spectrometer. NMR spectra were measured in CDCl$_3$ on a Bruker 400 MHz spectrometer. Mass spectra were measured on a Varian MAT 711 spectrometer. All mp's (from EtOAc) are uncorrected.

Separation.- a) The crude reaction mixture of the methylimide and CpCo-diethene (2.1 g) was separated on dry columns of silica (Woelm 100-200) followed by preparative silica plates with EtOAc (3): hexane (7) as eluent. 2d (1.23 g), 2b (0.23 g), and 2a (0.33 g) and 1 (25 mg) were isolated. On the basis of our knowledge of the ^{1}H-NMR spectrum of 2c[3] it is clearly unstable under the separation conditions (in solution and/or with SiO$_2$). b) Rapid trituration of the same crude mixture (48 mg) with EtOAc, in the dark, gave a ppt of 2d (17 mg). Evaporation of mother liquor and treatment with benzene gave a ppt of decomposition products. Hexane added to evaporated mother liquor gave solid (16 mg) and a part (11 mg) was hexane-soluble. This fraction appeared to contain 2c but when this stood in solution and particularly if SiO$_2$ was then used, this decomposed into 2a. The relative amounts of the three pure products isolated were very similar in both separation procedures. On the other hand, the isomer 2d, remained unchanged in solution or over SiO$_2$.

2a: M.p. 200-202°C. UV: 388 sh (2.98), 338 (3.3), 266 (4.25), nm (log e). IR: 1780, 1708, 1440, 1385, 1295, 1018 cm^{-1}. ^{1}H-NMR (400 MHz): 5.72 (dd, 2H, $J_{3,4}$=7.5, $J_{2,3}$=2.6, vinylic), 5.57 (dd, 2H, same J's, vinylic), 4.83 (dd, 2H, $J_{3,4}$=4.3, $J_{2,3}$=2.4, Co-vinylic), 4.72 (s, 5 Cp H), 3.74 (dd, 2H, same J's, Co-vinylic), 3.09 (s, $3NC\underline{H}_3$). ^{13}C-NMR (100 MHz): 126.59, 118.43, 80.21, 74.94, 60.89, 59.45, 24.89. MS: 337, M$^+$(78), 335 (32), 272 (5.4), 252 (42), 187 (8), 128 (47), 124 (100). MW: $C_{18}H_{16}NO_2Co$: Calc. 337.0513, found 337.0534.

2b: M.p. 226-230°C (dec). UV: 388 (2.86), 334 (3.2), 264 (4.16). IR: 1770, 1708, 1435, 1382, 1290, 1010. ^{1}H-NMR: 5.94 (dd, 2H, $J_{3,4}$=7.8, $J_{2,3}$=2.1, vinylic), 5.64 (dd, 2H, same J's, vinylic), 5.05 (d, 2H, J=2.02, Co-vinylic), 4.83 (s, 5 Cp H), 2.95 (d, 2H, J=2,2 Co-vinylic), 2.74 (s, $3NC\underline{H}_3$). ^{13}C-NMR (100 MHz): 125.68, 121.68, 80.19, 76.42, 56.28, 55.37, 24.56. MS: 337, M$^+$(100), 335 (46), 252 (88), 128 (34). MW: Calc. 337.0512, found 337.0543.

2d: M.p. 247-248°C. UV: 388 (3.13), 332 (3.46), 268 (4.40); no fluorescence. IR: 1768, 1700, 1435, 1380, 1295, 1010. ^{1}H-NMR: 5.32 (dd, 2H, $J_{3,4}$=4.4, $J_{2,3}$=2.4,Co-vinylic), 4.80 (dd, 2H, same J's, Co-vinylic), 4.69 (s, 5 Cp H), 4.58 (s, 5 Cp H), 3.07 (dd, 2H, $J_{3,4}$=4.4, $J_{2,3}$=2.3, Co-vinylic), 2.88 (s, 3 $NC\underline{H}_3$), 2.82 (dd, 2H, same J's, Co-vinylic). ^{13}C-NMR: 178.43, 80.37, 79.58, 76.03, 75.82, 58.65, 56.53, 53.98, 24.28. MS: 461, M$^+$(88), 376 (9), 337 (7), 310 (6), 272 (6), 252 (53), 189 (100), 187 (9), 128 (7), 124 (52). MW: $C_{23}H_{21}NO_2Co_2$: Calc. 461.0235, found 461.0221.

Reactions with MTAD. - General procedure: **2a**, 2b, or **2d** was each treated with MTAD (1.1 eq and 10 eq, respectively) in EtOAc solution and allowed to stand for 48h. The whole was filtered, the solvent evaporated and separation effected on prep SiO_2 plates using EtOAc (7): hexane (3) as eluent. In all cases Co-less products were identical to authentic samples.[1]

MTAD (1.1 eq) and 2a (38 mg) gave recovered 2a (11 mg; 29%), 3, (33 mg; 66%), 4 (2 mg; 5%) (see Scheme 1). 4 and 5 were identical to authentic specimens.[1]

3: M.p. 270-274°C (dec). UV: 388 (2.64), 332 (2.88), 262 (4.09). IR: 1790, 1720. ^{1}H-NMR: 6.01 (t, J=3.4, 2 vinylic H), 4.97 (dd, 2H, $J_{3,4}$=4.2, $J_{2,3}$=2.2, Co-vinylic), 4.78 (t, J=3.4, 2H, $C\underline{H}$-N), 4.68 (s, 5 Cp H), 3.20 (s, $3NC\underline{H}_3$), 3.04 (dd, 2H, same J's, Co-vinylic), 2.86 (s, $3NC\underline{H}_3$). ^{13}C: 128.14, 80.16, 76.51, 55.41(q), 55.10, 49.06, 25.50, 25.11. MS: 450, M^+(1.4), 337 (13), 285 (69), 252 (13), 189 (41), 165 (34), 161 (100), 128 (5), 124 (66). MW: $C_{21}H_{19}N_4O_4Co$: Calc. 450.0738, found 450.0765. Scheme 1 shows the products when 10 eq MTAD are used.

2b gave the products shown in Scheme 2.

6: M.p. > 280°C. UV: 406 (2.63), 328 (2.94), 270 (4.08). IR: 1785, 1725. ^{1}H-NMR: 6.64 (t, J=3.4, 2 vinylic H), 5.09 (dd, 2H,$J_{3,4}$=4.2, $J_{2,3}$=2.3, Co-vinylic), 4.95 (t, J=3.4, 2H, $C\underline{H}$-N), 4.71 (s, 5 Cp H), 2.92 (m, $3NC\underline{H}_3$ + 2H, Co-vinylic), 2.76 (s, $3NC\underline{H}_3$). ^{13}C: 175.88, 127.85, 81.91, 75.42, 57.56, 54.79, 49.39, 25.47, 24.83. MS: 450, M^+(16), 337 (28), 285 (8), 252 (13), 189 (13), 165 (66), 161 (100), 128 (30), 124 (56).

4 and 5 were identical to authentic specimens.[1]

Scheme 3 summarizes the results of the reactions of **2d** with different amounts of MTAD. 2d is the most stable to MTAD (see amounts recovered). 6 was identical to that described above, 4 and 5 were identical to authentic specimens.[1]

Treatment of products with Ce^{IV}. - 2d (200 mg) with ceric ammonium nitrate (474 mg, 3 eq) gave in MeOH after separation on a prep SiO_2 plate using EtOAc(4): hexane(1) as eluent gave completely demetalated 1 (23 mg, 27%), 2a (18 mg, 13.5%), and 2b (80 mg, 59.5%).

3 (27 mg) with ceric salt (68 mg) in EtOAc(3): MeOH(1) (10 ml) using EtOAc(7): hexane(3) as eluent gave 4 (18 mg; 92%) identical to an authentic specimen.[1]

6 (21 mg) with ceric salt (58 mg), as above gave identical 4 (15 mg; 98%).

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