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PROPELLANES. PART LXXXVII[†]. THE REACTION OF SEVERAL TETRAENIC PROPELLANE-IMIDES WITH CYCLOPENTADIENYL-COBALT-DIETHENE

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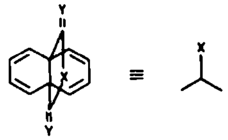
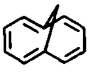
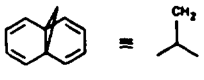
Abstract.- Reaction of the title compounds gives a mixture of products whose configurations have been established by NMR spectroscopy. In two cases single products were isolated, one of which analyzed by X-ray crystallography.

It has long been of interest to extend the work on the reaction of the tetraenic ether 1a with several iron carbonyls[4] to the reaction of tetraenic propellanes with organometallic cobalt or nickel reagents. Since recently the reaction with 1,6-methano[10]annulene 2a, (a compound whose bis-norcaradiene valence tautomer is also a tetraenic propellane), 2b, with cyclopentadienylcobalt-bisethene 3 has been studied[5] we chose to react the tetraenic imides 1b and 1c with the same reagent.



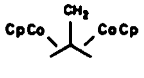
1a X = O , Y = H_2
b X = NMe , Y = O
c X = NPh , Y = O


2a



2b

In the case of 2 the syn, syn- and the syn,anti-bis-products 4 and 5 were obtained exclusively[2]. In the case of 1a with $Fe(CO)_5$ only the syn,syn-bis-product 6 was obtained in high yield[1a] and its structure determined by X-ray crystallography[1b]. When, however, $Fe_2(CO)_9$ was used 1a gave all the possible isomers, 2 mono-$Fe(CO)_3$ derivatives, the syn- and the anti-, and the 3 possible bis-adducts, syn,syn-, 6, syn,anti-, 7, and anti,anti-, 8, albeit the last in very low yield[1a]. The structure of the syn,anti-bis-$Fe(CO)_3$ compound 7 also had its structure determined[1c], showing a configuration greatly influenced by stereoelectronic effects. Although crystals were grown of the anti,anti-bis-derivative at College Station, the crystals were twinned and the material available did not suffice for recrystallization from a series of solvents[1d]. Therefore it is not yet known how this compound accommodates both of the anti-Fe(CO)$_3$ groups so as to be able to exist. As we will show below, no anti,anti-bis-CpCo-products could be observed in our case.



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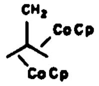

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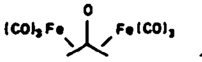

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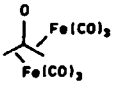

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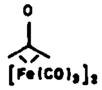

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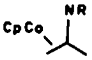
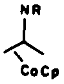
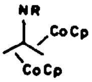
The tetraenic imides, 1b and 1c, afforded by reaction with 3 in each case four of the five possible products: syn-, 9, anti-, 10, syn,anti- 11 (of type 5) and syn,syn- 12 (of type 4). No isomer at all of type 8 was observed in the NMR spectrum of the mixture.



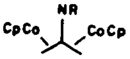
9b R=Me
c R=Ph



10b R=Me
c R=Ph



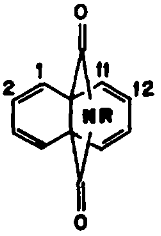
11b R=Me
c R=Ph



12b R=Me
c R=Ph

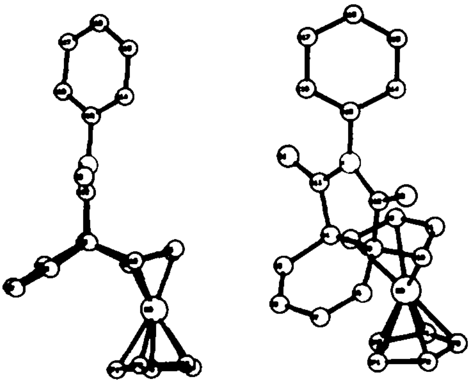
The Table gives the composition of the product mixture in each case as determined by NMR spectroscopy and the chemical shifts.

		1:3 .1:1 or 1:2 % Product		^{1}H-Chemical Shift ppm					
				H_{Cp}	H_{CH_3}	H_1	H_{11}	H_2	H_{12}
9b	syn	21	17	4.40	2.72	3.65	5.36	4.41	5.81
10b	anti	63	57	4.49	2.43	2.81	5.63	4.69	5.65
11b	syn/anti	12	20	4.44 4.41	2.74	3.11	2.82	4.87	4.56
12b	syn/syn	4	6	4.31	3.21	2.82		4.72	
9c	syn	21		4.50		3.75	5.42	4.46	5.89
10c	anti	57		4.53		2.91	5.70	4.79	5.72
11c	syn/anti	14	63	4.53 4.45		2.91	3.19	4.63	4.89
12c	syn/syn	8	37	4.38		2.91		4.76	



Underlined values: Shifts of protons at complexed C=C bonds.

One of the products crystallized from the reaction mixture of 1c and 3 was shown by X-ray crystallography to be the anti-mono-adduct 10c (Figure).



Figure

Acknowledgement.- This work was carried out in Mülheim. One of us (D.G.) is grateful for the very kind hospitality and support. We thank the Minerva Komitees für die wissenschaftliche Zusammenarbeit zwischen deutschen und israelischen Forschungsinstituten for additional support to D.G.

EXPERIMENTAL PART

Solutions of the reactants in d_8-toluene were mixed in ratios 1:3 = 1:1 and 1:2 at 213°K and the 400 MHz ^{1}H-NMR spectra taken at ca. 213°K without separation of the resulting products. All lines of the product spectra listed in the Table were assigned. Details may be obtained from R.B. In some experiments solid or crystalline products were isolated and analyzed.

9b + 10b : 11b + 12b = 84:16. Calc. C, 63.42; H, 4.75; N, 3.98; Co, 18.76. Found C, 63.96; H, 5.0; N, 4.40; Co, 18.57.

According to the NMR spectra (see table) the 1c : 3 = 1:1 product would give the following values of the elemental analysis.

9c + 10c : 11c + 12c = 78:22. Calc. C, 68.10; H, 4.51; N, 3.32; Co, 16.46.

The values found prove the product isolated in crystalline form to be a mono-CpCo adduct, according to the X-ray structural analysis 10c. Its detailed crystal structure data may be obtained from R.G.

10c: $C_{23}H_{18}NO_2Co$: Calc. C, 69.18; H, 4.54; N, 3.51; Co, 14.76. Found C, 68.72; H, 5.18; N, 3.46; Co, 14.97.

The 1c:3 = 1:2 product 12c was also isolated in crystalline form.

12c: $C_{28}H_{23}NO_2Co_2$: Calc. C, 64.26; H, 4.43; N, 2.68; Co, 22.52. Found C, 63.72; H, 5.18; N, 2.75; Co, 22.26.

REFERENCES

1. M. Kapon, P. Ashkenazi, and D. Ginsburg, *Tetrahedron*, in press.
2. NMR Spectroscopy.
3. X-ray structural analysis.
4. a) J. Altman, E. Cohen, T. Maymon, J.B. Petersen, N. Reshef, and D. Ginsburg, *Tetrahedron*, *25*, 5115 (1969). b) K.B. Birnbaum, *Acta Cryst.*, *B28*, 161 (1972). c) G.I. Birnbaum, *J. Am. Chem. Soc.*, *94*, 2455 (1972). d) F.A. Cotton, private communication.
5. P. Mues, R. Benn, C. Krüger, Y.-H. Tsay, E. Vogel, and G. Wilke, *Angew. Chem.*, *94*, 879 (1982); *Angew. Chem. Suppl.*, 1891 (1982).