Journal of Organometallic Chemistry, 93 (1975) C31—C33

Preliminary communication

BINUCLEAR π-COMPLEXES OF TETRAMETHYLENEETHANE DIMERS: 1,4-BIS(DIMETHYLENEMETHYLENE)CYCLOHEXANEDIIRON HEXACARBONYL

SHOSHANA SADEH and YEHIEL GAONI*

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot (Israel)

(Received May 7th, 1975)

Summary

The reaction of 2,3-bis(bromomethyl)-1,3-butadiene with diiron enneacarbonyl yields two isomeric binuclear complexes of bis(dimethylenemethylene)-cyclohexane, besides the known complex of tetramethyleneethane.

2,3-Bis(bromomethyl)-1,3-butadiene (I) and several of its derivatives [1, 2] are potential precursors of the tetramethyleneethane biradical II, postulated as an intermediate in allene dimerization or in thermal rearrangement of dimethylenecyclobutane [3]. Like other unstable organic species, biradical II may be stabilized by the formation of complexes with transition metals [4], and this has been demonstrated in particular in the reaction of allene with triiron dodecacarbonyl to give complex III [5], or of substituted allenes, yielding analogous complexes [4, 6].

We have now found that the reaction of I with diiron enneacarbonyl in hexane offers an alternative route to III (formed in 11% yield), and at the same time yields two isomeric binuclear complexes of a dimer of II, identified as the trimethylenemethane-type complexes IV and V (7.5 and 2% yield, respectively).

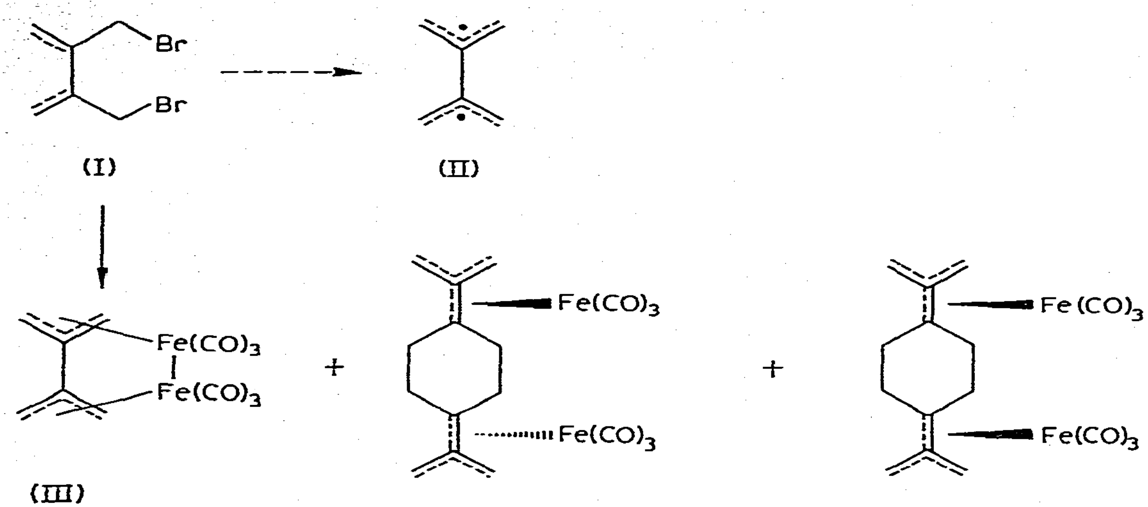
The more abundant isomer showed a centrosymmetric molecular structure**, space group $P2_1/a$, with unit cell parameters: $a = 12.99$, $b = 11.35$, $c = 7.14$ Å, $\beta \sim 100°$. $\rho = 1.41$ g/cm^3, for $Z = 2$. Based on this result and on the additional physical data (see Table 1), this isomer was assigned structure IV, while the spectroscopically very similar minor isomer was assigned the cisoid structure V.

Carbon-13 NMR of IV showed four types of skeletal carbons at δ 37.5, 49.1 (terminal and cyclic methylenes), 96.1 and 100.4 ppm (downfield from TMS; tertiary carbons) with an approximate ratio of 2/2/1/1.

---

*To whom correspondence should be addressed.

**Preliminary X-ray measurements were performed in the Department of Structural Chemistry of this Institute by Mr. J. Halfon.



(I) (II)

(III) (IV) (V)

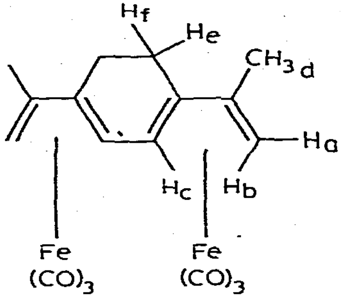
Treatment of IV with 85% sulfuric acid, followed by dilution with water and extraction with ether [7] yielded a 1/1 mixture of the bis-diene complexes VI and VII (81% yield of purified compounds). The proton NMR spectra (see Table 1) made possible a distinction between the conjugated complex VI, where the H_c proton appeared as a sharp singlet, and the unconjugated VII, where it appeared as a double doublet (*X*, part of an *ABX* system formed with H_e and H_f).

The mass-spectral fragmentation of all four complexes IV-VII is very similar, with a molecular peak at *m/e* 440 and with peaks corresponding to the consecutive loss of six CO units (or combination of CO and Fe). The parent peak is at *m/e* 270 ($M^+ - H_2Fe(CO)_4$?) for three out of the four compounds and at 298 and 214 (equal intensity) for VI.

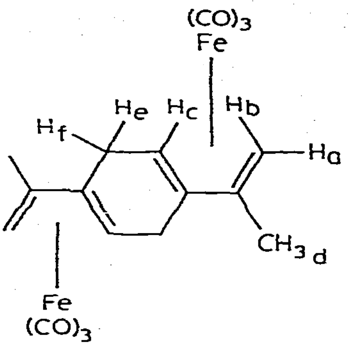
TABLE 1

PHYSICAL PROPERTIES OF BINUCLEAR COMPLEXES

Compound	M.p. (°C)	$\delta(CDCl_3)$	isooctane		IR ν(CO) cm^{-1}
			λ_{max} (nm)	ϵ	
IV	210	1.85 s (4) 1.91 s (8) 2.31 s (4)	275(sh)	2480	2045, 1985, 1970, 1960
V	203	1.82 s (4) 1.87 s (8) 2.26 s (4)	275 (sh)	2200	2055, 2000, 1987(sh) 1980, 1973, 1964
VI	208	0.30 d, H_a, J_{ab} 2.5 1.46 s, H_c 1.77 d, H_b, J_{ab} 2.5 2.19 s, H_d 3.00 AB-q, H_eH_f, J_{ef} 10 Hz	265(sh) 330	14000 8700	2030, 1960(sh), 1950
VIII	170	0.13 d, H_a, J_{ab} 2.5 1.21 dd, H_c, J_{ce} 2.5 J_{cf} 6.5 1.71 d, H_b, J_{ab} 2.5 2.19 s, H_d 3.27 dq, H_eH_f, $J_{ef} \simeq$ 20 Hz	300	6350	2030, 1976, 1951

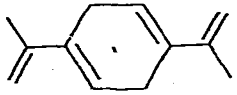


(VI)



(VII)

Finally, oxidation of VII with ceric ammonium nitrate in methanol yielded a mixture of two hydrocarbons, in a ratio of ~ 1/8 (total yield 95%). These were separated by preparative GLC and identified as 1,4-diisopropenylbenzene (VIII) (minor component, identical with an authentic sample prepared according to [8]) and 1,4-diisopropenyl-1,4-cyclohexadiene (IX), m.p. 115 °C (lit. [9]: 117-117.5 °C), δ ($CDCl_3$) 1.97, 3.03, 4.97 and 6.03, broad singlets, ratio 3/2/2/1. High resolution mass spectrum: M^+ at *m/e* 160.1264 (calcd. mol. wt.: 160.1252).



(IX)

Oxidation of VI in similar conditions yielded mainly polymeric material, but GLC showed the formation of the corresponding hydrocarbons.

The cyclodimerization reaction encountered here is reminiscent of two coupling reactions which have been observed before and which involved bromomethylbutadiene [7] or 2-bromomethylnaphthalene [10], the latter formally comprising a bromomethylbutadiene unit. It seems that in all these cases the formation of a four-electron trimethylenemethane ligand (from one double bond and from, say, a C—Br bond) over four carbons, makes available a pair of electrons on the fifth carbon for C—C bond formation. In the case of I this process is repeated twice, back and forth, leading to a cyclic product. This view will be elaborated on in our full report of this work.

References

1 Y. Gaoni, Tetrahedron Lett., (1973) 2361.
2 S. Sadeh and Y. Gaoni, Tetrahedron Lett., (1973) 2365.
3 T. Beetz and R.M. Kellogg, J. Amer. Chem. Soc., 95 (1973) 7925 and leading references therein.
4 I.I. Kritskaya, Russ. Chem. Rev., 41 (1972) 1027.
5 A. Nakamura, Bul. Chem. Soc. Jap., 39 (1966) 543.
6 R.B. King and C.A. Harmon, J. Organometal. Chem., 86 (1975) 239.
7 K. Ehrlich and G.F. Emerson, J. Amer. Chem. Soc., 94 (1972) 2464.
8 N.V. Meiya and A.F. Nikolaev, J. Org. Chem. USSR, 1 (1965) 286.
9 M.T. Taylor and C.P. Harris, J. Amer. Chem. Soc., 41 (1919) 1676.
10 A.N. Nesmeyanov, I.S. Astakhova, G.P. Zol'nikova, I.I. Kritskaya and Yu.T. Struchkov, Chem. Commun., (1970) 85.