Tetrahedron Letters No.24, pp. 1971-1975, 1965. Pergamon Press Ltd.
Printed in Great Britain.

REACTIONS OF cis, trans, trans-1,5,9-CYCLODODECATRIENE
III. THE STERIC COURSE OF NITROSYL CHLORIDE ADDITION (1)

Masaji Ohno, Masaru Okamoto and Norio Naruse
Basic Research Laboratories, Toyo Rayon Co. Ltd.,
Kamakura, Japan

(Received 15 April 1965)

The recent publications by Zakharkin (2), Wilke (3) and Metzger (4) on the nitrosyl chloride addition products of cyclododecatriene prompt us to report the results of our own investigations along similar lines.

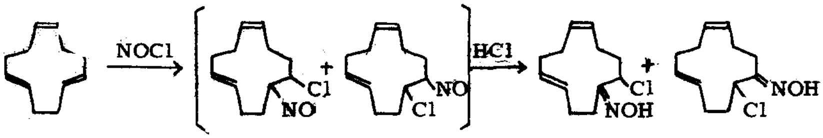
Addition of one mole equivalent of nitrosyl chloride in the presence of hydrochloric acid to cis, trans, trans-1,5,9-cyclododecatriene (I), in either methylene chloride at -10° or trichloroethylene at 10°C, was found to be exothermic and provided 2-chlorocyclododecadienone oxime (III) in nearly quantitative yields (Calcd. for $C_{12}H_{18}ClNO$: C, 63.3 ; H, 7.92 ; Cl, 15.6 ; N, 6.16 . Found : C, 63.15 ; H, 7.85 ; Cl, 15.79 ; N, 5.95).

It melted at 126 - 129°C even after several recrystallizations from ligroin and was easily hydrogenated into cyclododecanone oxime by catalytic reduction. Its infrared spectra showed that only the absorption intensity at 980 cm^{-1} characteristic of the trans double bond diminished and the one at 707 cm^{-1} characteristic of the cis double bond remained unchanged. Therefore, the product might be a mixture of 2-chloro-cis-5, trans-9-cyclododecadienone oxime (III $_a$) and 2-chloro-trans-5, cis-9-cyclododecadienone oxime (III $_b$).

The result clearly showed that the first attack by nitrosyl chloride took place at one of the trans double bonds and that there was a considerable difference in reactivity between the cis and trans double bonds of the cyclododecatriene.

Furthermore, Wilke (3) observed that the treatment of a mixture of trans- and cis-cyclododecene with nitrosyl chloride afforded only the chloronitroso dimer of the former, although the former is thermodynamically more stable than the latter (5).

No satisfactory explanation, however, for such competitive reactivities has been given.



I II III a III b

Various reactions utilizing the double bonds of the triene have been reported and are summarized in Table I. These facts show that addition mechanism is closely connected with the selectivity in the first attack to the double bonds of cis, trans, trans-1, 5, 9-cyclododecatriene. Generally, trans-addition reagents such as halogen, hydrogen chloride and acetic acid react with no selectivity in so far as the cis or trans configuration is concerned and cis-addition reagents such as diethylborane,

TABLE 1

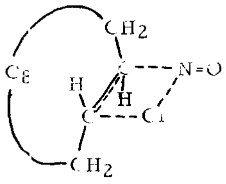
Reagent	mole	Product	addition mechanism	double bond preferentially attacked	Yield (%)	reference
Br_2	1	1-bromocyclododecatriene tetrabromocyclododecene	trans	no selectivity	61 20 - 30	6
"	2	tetrabromocyclododecene	"	cis and trans	20 - 40	6. 7
Cl_2	1	dichlorocyclododecadiene	"	no selectivity	70	6
$PhCO_3H$	1	monoepoxide	cis	trans	80 - 90	7
"	2	diepoxide	"	cis and trans	80	
H_2O_2-HCO_2H	1	monoepoxide	"	trans	76	8
Et_2BH	3	$(C_{12}H_{21})(BEt_2)_3$	"	*	80	9
$HCl/FeCl_3$	excess	mono- and dichloride	trans	no selectivity	20 - 40	10
$AcOH/BF_3$	"	monoacetate	"	"	50	10
OsO_4	1	glycol	cis	trans	89	11
$KMnO_4$	1	"	"	"	59	11
H-N=N-H	excess	cis-cyclododecene	"	"	60 - 82	1

* It was observed that the trans double bond reacted faster than the cis one.

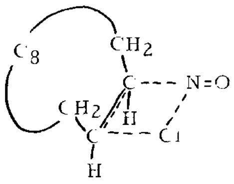
peracid, osmium tetroxide, potassium permanganate and diimide react with the trans double bond preferentially.

Meinwald (12) recently showed that the addition mechanism of nitrosyl chloride to double bonds is dependent upon the structure of olefins.

In case of cis, trans, trans-1, 5, 9-cyclododecatriene, the addition of nitrosyl chloride showed a remarkable selectivity for the trans double bonds like other cis-addition reagents as mentioned above. Such competitive reactivities might reasonably be explained in terms of conformational stability at four-center transition state or in cis-manner addition (1, 11). The transition state may be pictured as shown in IV for the trans double bond and V for the cis double bond, the former being more stable than the latter because of the difference of eclipsing effect. Thus the trans double bond reacts more rapidly than the cis one.



IV



V

After the addition of nitrosyl chloride, the chloronitroso monomer (II) may be rapidly isomerized into α-chlorooximes (III) by the action of hydrochloric acid, since the chloronitroso dimer or Wilke's compound is more slowly isomerized into α-chlorooxime in similar conditions. It should also be mentioned that the treatment of norbornene with nitrosyl chloride in the presence of hydrochloric acid easily afforded

3-chloronorcamphor oxime (13), which is known very difficult to obtain from 2-chloro-3-nitrosonorbornane dimer by hydrochloric acid (14).

References

(1) Part II, M. Ohno and M. Okamoto, *Tetrahedron Letters*, 2423 (1964)

(2) L. I. Zakharkin, *C. A.*, **56**, 5853b (1962).

(3) G. Wilke, *Angew. Chem.*, **75**, 10 (1963).

(4) H. Metzger, *Angew. Chem.*, **75**, 980 (1963).

(5) A. C. Cope, P. T. Moore and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960).

(6) H. Takahashi and M. Yamaguchi, *J. Chem. Soc. Japan*, **83**, 1042 (1962).

(7) L. I. Zakharkin and V. V. Korneva, *Doklady Akad. Nauk SSSR*, **132**, 1078 (1960).

(8) H. Takahashi and M. Yamaguchi, *Bull. Chem. Soc. Japan*, **36** 1390 (1963).

(9) R. Köster and G. Griaznov, *Angew. Chem.*, **73**, 171 (1961).

(10) L. I. Zakharkin, V. V. Korneva and A. V. Iogansen, *Doklady Akad. Nauk SSSR*, **138**, 373 (1961).

(11) M. Ohno and S. Torimitsu, *Tetrahedron Letters*, 2259 (1964).

(12) J. Meinwald, Y. C. Meinwald and T. N. Baker III, *J. Am. Chem. Soc.*, **86**, 4074 (1964).

(13) M. Ohno, N. Naruse, unpublished result.

(14) J. B. Miller, *J. Org. Chem.*, **26**, 4905 (1961).