A Convenient Synthesis of 1,6-Cycloundecadiene

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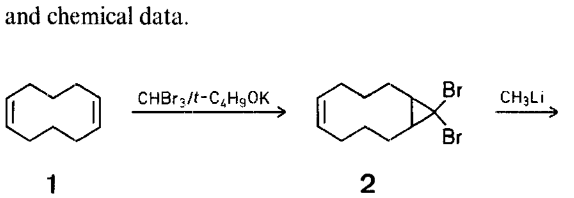
The sodium-ammonia reduction of allenes, in combination with an elegant synthesis of allenes has proved to be useful in synthesizing a homologue of an olefin or a diene in good yield[1-6]. In this communication, we report a further extension of this general method to provide a new synthesis the medium-ring diene 1,6-cycloundecadiene (**4**).

The reaction of a two-fold excess of the easily available *cis, cis*-1,6-cyclodecadiene (**1**) with bromoform and potassium *t*-butoxide followed by treatment of **2** with methyllithium at −40 to −45° in dry ether provides 1,2,7-cycloundecatriene (**3**) in good yield. Reduction of **3** with sodium in liquid ammonia yields the desired product, 1,6-cycloundecadiene (**4**), in excellent yield. The structure of the diene (**4**) was unequivocally established by physical and chemical data.



Our attempts to separate the possible isomeric dienes (*cis, trans*- and *cis,cis*-isomer) by G.L.C. analysis were not successful. The I.R. spectrum indicated the presence of a minor amount of *cis,trans*-isomer in the diene obtained. However, the relative amounts of *cis,trans*- and *cis,cis*-isomer were established by G.L.C. analysis of the products obtained after careful partial reduction of the mixture with diimide[7]. G. L. C. analysis showed a mixture of *cis*-cycloundecene and *cis,cis*-1,6-cycloundecadiene (**4**) in the ratio 28:72. The N.M.R. spectrum of **4** showed a multiplet at $\delta = 5.44$ corresponding to 4 olefinic H. The amount of unsaturation was established by microhydrogenation, whereas ozonolysis provided answer to the positions of the double bonds. Thus, the above procedure provides a convenient synthesis of 1,6-cycloundecadiene (**4**).

11,11-Dibromobicyclo[8.1.0]undec-6-ene (2):

Following the general procedure[8], from *cis,cis*-1,6-cyclodecadiene (27.2 g, 0.2 mol), bromoform (25.3 g, 0.1 mol) and freshly sublimed potassium *t*-butoxide (11.2 g, 0.1 mol) there was obtained 18.8 g (65%) of **2**; m.p. 62–63° (recrystallized from ethanol). T.L.C. showed it to be pure.

$C_{11}H_{16}Br_2$	calc.	C 44.15	H 3.90
	found	43.79	4.10

1,2,7-Cycloundecatriene (3):

11,11-Dibromobicyclo[8.1.0]undec-6-ene (18.0 g, 0.06 mol) was treated with methyllithium prepared from lithium (3.5 g, 0.5 g-atom) and methyl iodide (35 g, 0.25 mol) according to the procedure of Moore and Ward[8] at −40 to −45° in dry diethyl ether (300 ml); yield: 7.2 g (85%) of **3**; b.p. 57–58°/2 torr. The product was found to be homogeneous on a 10' × 1/4" Carbowax 20M column.

$C_{11}H_{16}$	calc.	C 89.19	H 10.81
	found	88.97	10.51

I.R. (neat): $\nu_{max} = 1620$ (w), 1950 (ms) cm^{-1}.

N.M.R. (CCl_4): δ 5.40 (m, 2H), 5.05 (m, 2H), 2.15 (m, 8H), 1.67 (m, 4H).

1,6-Cycloundecadiene (4):

1,2,7-Cycloundecatriene (7.2 g, 0.05 mol) was reduced with sodium (9 g, 0.4 g-atom) in liquid ammonia[3] (250 ml) to yield 7 g (95%) of **4**; b.p. 80°/8 torr. G.L.C. analysis on a 6' × 1/4" Carbowax 20M—$AgNO_3$ column showed two unresolved peaks. But G.L.C. analysis of the partial diimide reduction[8] products from 1,6-cycloundecadiene showed the presence of 28% *cis*-cycloundecene and 72% *cis,cis*-1,6-cycloundecadiene which were separated by preparative G.L.C. and identified by the usual procedure.

$C_{11}H_{18}$	calc.	C 88.00	H 12.00
	found	87.81	11.90

I.R. (neat): $\nu_{max} = 1620$ (w), 980 (w), 710 (s) cm^{-1}.

N.M.R. (CCl_4): δ 5.44 (m, 4H), 2.30 (m, 8H), 1.60 (m, 6H).

The authors gratefully acknowledge the financial support from C.S.I.R., New Delhi, India.

Received: May 23, 1972

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