Cyanoisopropyl Radical Induced Cyclization and Cyclopolymerization of *N*-Methyl-*N*-allyl-*N*-(2-alkylallyl)amines and *N*-Methyl-*NN*-bis-(2-alkylallyl)amines. A ^{13}C Nuclear Magnetic Resonance Study

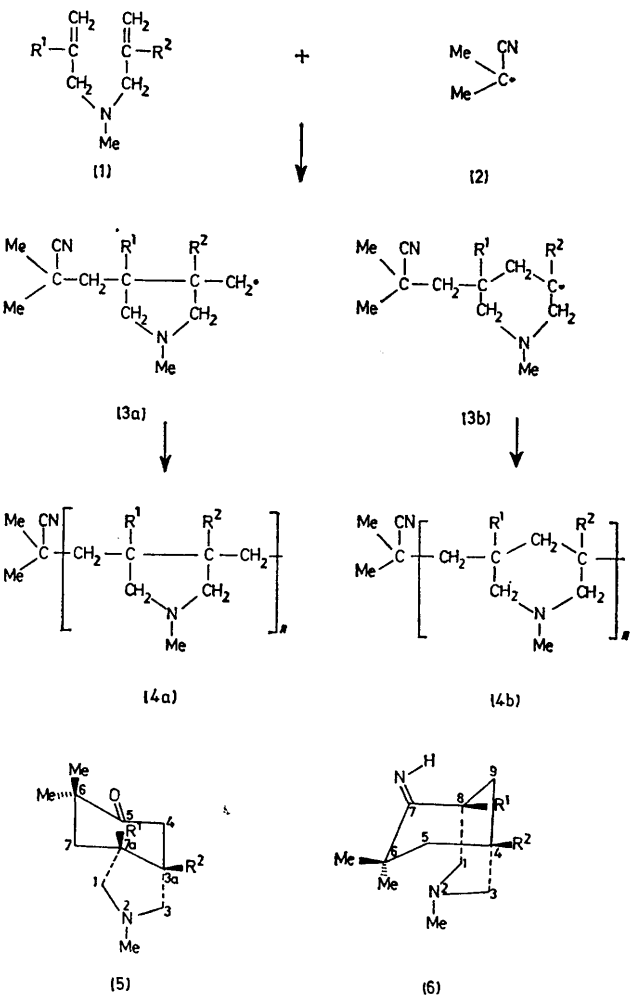
By DAVID G. HAWTHORNE, STANLEY R. JOHNS,* DAVID H. SOLOMON, and RICHARD I. WILLING
(*Division of Applied Organic Chemistry, CSIRO, P.O. Box* 4331, *G.P.O., Melbourne,* 3001, *Australia*)

Summary The structures of the cyclic products from the cyanoisopropyl radical induced cyclization and cyclopolymerization of *N*-methyl-*N*-allyl-*N*-(2-alkylallyl)amines and *N*-methyl-*NN*-bis-(2-alkylallyl)amines are shown by ^{13}C n.m.r. spectroscopy to be pyrrolidines and piperidines, the proportion of each depending upon the bulk of the 2-alkyl substituent.

THE structures of the polymers formed by free radical cyclopolymerization of 1,6-diene analogues have been the subject of considerable argument and discussion in the literature.[1] Five-, six- or seven-membered ring structures are possible depending upon the position of initial attack and upon the subsequent cyclization. E.s.r.[2] and ^{13}C n.m.r.[3] spectroscopy have shown that in cyanoisopropyl radical (**2**) induced cyclizations of *N*-methyl-*NN*-diallylamine (**1**; $R^1 = R^2 = H$) the resulting radical (**3a**; $R^1 = R^2 = H$) gives the polypyrrolidine (**4a**; $R^1 = R^2 = H$) and 2,6,6-trimethyl-*cis*-perhydroisoindol-5-one (**5**; $R^1 = R^2 = H$).

^{13}C n.m.r. spectroscopy has now been used to determine the structure of the polymers and bicyclic products obtained by reaction of the radical (**2**) with *N*-methyl-*N*-allyl-*N*-(2-alkylallyl)amines (**1**; R^1 = Me, Et, Pr^i; $R^2 = H$) and *N*-methyl-*NN*-bis(2-alkylallyl)amines (**1**; $R^1 = R^2$ = Me, Et, Pr^i). The proportions of the pyrrolidine (**4a**) and the piperidine (**4b**) units in the polymers are estimated from the relative intensity of the *N*-methyl signals, between 42—44 p.p.m. for (**4a**), and between 46—47 p.p.m. for (**4b**), in the ^{13}C spectra. The structures of the bicyclic products (**5**) and (**6**), formed under conditions of high initiator concentrations by an intramolecular cyclization of the radicals of (**3a**) and (**3b**) to the nitrile groups, by hydrogen abstraction to form an imine and by hydrolysis to the ketone in (**5**), are determined from the ^{13}C spectra (Table).

The introduction of a single 2-alkyl substituent *e.g.* (**1**; R^1 = Me, Et, Pr^i; $R^2 = H$) gives a polypyrrolidine polymer and a bicyclic fraction composed of a mixture of the isomers, 2,6,6-trimethyl-7a-alkyl-*cis*-perhydroisoindol-5-one, (**5**; R^1 = alkyl, $R^2 = H$) and 2,6,6-trimethyl-3a-alkyl-*cis*-perhydroisoindol-5-one (**5**; $R^1 = H$, R^2 = alkyl), the pro-



TABLE

^{13}C Chemical shifts (p.p.m.) of perhydroisoindol-5-ones and 2-azabicyclo[3,3,1]nonan-7-imines

Perhydroisoindol-5-one	C-1	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	2Me	6Me(ax)	6Me(eq)	3a-Me	7a-Me
(**5**); $R^1 = R^2 = H$	63·2	63·9	35·6	41·9	212·7	42·8	40·8	33·7	41·9	26·4	23·7	—	—
(**5**); $R^1 = R^2 = Me$	71·4	72·3	46·4	51·1	—	42·6	50·1	43·6	41·7	27·6	23·3	28·2	24·7
(**5**); $R^1 = Me$, $R^2 = H$ ..	72·1	63·6	46·1	41·8	217·7	43·1	49·4	40·6	41·8	29·6[a]	27·3[a]	—	28·2[a]
(**5**); $R^1 = H$, $R^2 = Me$ ..	63·7	71·9	40·8	49·1	218·3	42·9	42·7	41·9	42·1	27·4	23·9	28·9	—

2-Azabicyclo[3,3,1]nonan-7-imines	C-1	C-3	C-4	C-5	C-6	C-7	C-8	C-9	2Me	4Me	6Me(eq)	6Me(ax)	8Me
(**6**); $R^1 = R^2 = Me$	70·4	70·5	30·8	43·8	39·0	—	41·4	50·5	46·1	30·3	29·6	33·4	25·2
(**6**); $R^1 = R^2 = Et$	70·0	71·4	33·2	46·8	39·0	195·1	44·4	30·3	46·4	[b]	29·6	32·3	[b]
(**6**); $R^1 = R^2 = Pr^i$	69·1	69·4	35·2	43·5	39·2	195·5	47·0	29·4	46·8	[c]	29·7	31·8	[c]

[a] May be interchanged; [b] 4Et:CH_2 (34·8) Me (7·5), 8Et:CH_2 (37·0) Me (8·3); [c] 4Pr^i:CH (33·2) Me (18·6, 16·9), 8Pr^i:CH (36·5) Me (17·6, 16·9).

portion of the latter increasing with increasing bulk of R^2. The isomers are distinguished by loss of intensity of the C-4 signal in the ^{13}C n.m.r. spectrum after deuterium exchange of the C-4 methylene protons with KOH in [$^2H_4$]-methanol. The preferred initial radical attack is therefore at the 3-carbon of the least hindered allyl group and cyclization, as in the unsubstituted diallylamine, is to the 2-carbon of the second allyl residue.

The introduction of two 2,2′-alkyl substituents *e.g.* (**1**; $R^1 = R^2 =$ Me, Et, Pr^i) gives a polymer comprised of both pyrrolidine (**4a**) and piperidine (**4b**) units; the proportions of the piperidine groups increasing with increasing bulk of the alkyl substituent. The bicyclic fraction from (**1**; $R^1 = R^2 =$ Me) is a mixture of 2,3a,6,6,7a-pentamethyl-*cis*-perhydroisoindol-5-one (**5**; $R^1 = R^2 =$ Me) and 2,4,6,6,8-pentamethyl-2-azabicyclo[3,3,1]nonan-7-imine (**6**; $R^1 = R^2 =$ Me), but only (**6**; $R^1 = R^2 =$ Et) and (**6**; $R^1 = R^2 = Pr^i$) are obtained from (**1**; $R^1 = R^2 =$ Et) and (**1**; $R^1 = R^2 = Pr^i$) respectively. The size of the two 2,2′-alkyl substituents therefore correlates with the formation of the radicals (**3a**) and (**3b**); the larger the substituent the higher the proportion of (**3b**) which is formed by cyclization to the 3-carbon of the second allyl group. This effect is a steric one reflected not only in the structure but also in the rate of propagation which decreases with increasing bulk of 2,2′-alkyl substituent.

(*Received, 15th August* 1975; *Com.* 942.)

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