forces ^3p into a somewhat different range of twist from normal; this is illustrated schematically by the broken line in Figure 2. This distorted phantom triplet (represented by $^3p'$), if it were actually a complex between DTBN and ^3p, might well prefer a slightly cisoid conformation to reduce steric repulsion between the phenyl and *tert*-butyl groups.

Theoretical explanation for the rapid quenching is provided by the work of Hoytink[7] and Murrell.[8] In particular, Hoytink[7] has predicted that the rate of free-radical quenching of aromatic hydrocarbons should vary inversely with the E_T of the hydrocarbon, and that the quenching process involves essentially a vibronic relaxation of the triplet, which is made spin allowed by electron exchange with the radical. Since the ground-state potential energy curve for stilbene overlaps the triplet-state curve near $^3p,^{4d}$ the condition for rapid quenching by this mechanism is met admirably.

Finally, we wish to point out that preliminary quenching studies with various sensitizers, corrected for the changes in the stilbene decay ratio at different nitroxide concentrations, give linear Stern–Volmer plots from which reproducible quenching rate constants may be calculated. Assuming a diffusion-controlled rate constant of 5×10^9 M^{-1} sec^{-1} for energy transfer to stilbene in benzene, we find that DTBN quenches benzophenone triplets with $k_q = 3 \times 10^9$ M^{-1} sec^{-1}, while naphthalene triplets (sensitized by benzophenone)[9] are quenched with $k_q = 6 \times 10^8$ M^{-1} sec^{-1}. For perdeuterionaphthalene,[10] the observed value of $k_q = 3.7 \times 10^8$ M^{-1} sec^{-1} confirms the predictable[7] isotope effect on the quenching process and indicates that *DTBN quenching can be substantially slower than diffusion controlled* for triplets having relatively long nonradiative lifetimes.

(7) (a) G. J. Hoytink, *Mol. Phys.*, **3**, 67 (1960); (b) G. J. Hoytink, *Discuss. Faraday Soc.*, **45**, 14 (1968); (c) G. J. Hoytink, *Accounts Chem. Res.*, **2**, 114 (1969).

(8) J. N. Murrell, *Mol. Phys.*, **3**, 319 (1960).

(9) Full experimental and kinetic details will be published in the full paper.

(10) Obtained from Diaprep, Inc., in purity satisfactory for direct use.
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Selective Cyclooligomerization of Allene and Bis-π-allylnickel(0) Intermediates

Sir:

Nickel(0)-catalyzed oligomerization of allene leading to 1,2,4,6,9-pentamethylenecyclodecane (**1**)[1] is certainly a nonconcerted process as demonstrated by isolation of a linear allene trimer complex Ni(C$_9$H$_{12}$) (**2**) and its phosphine adduct Ni(C$_9$H$_{12}$)(PPh$_3$) (**3**).[2] Recently catalytic cyclotrimerization of allene with bis-
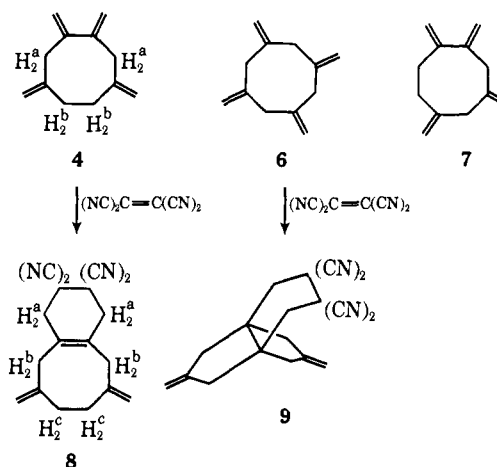
(1) (a) S. Otsuka, A. Nakamura, K. Tani, and S. Ueda, *Tetrahedron Lett.*, 297 (1969); (b) S. Otsuka, A. Nakamura, S. Ueda, and H. Minamida, *Kogyo Kagaku Zasshi*, **72**, 1809 (1969).

(2) S. Otsuka, A. Nakamura, S. Ueda, and K. Tani, *Chem. Commun.*, 863 (1971).

(tri-2-biphenylyl phosphite)nickel was briefly reported.[3] These results suggest the possibility of setting up an appropriate potential barrier controlling the growth reaction to particular oligoallenes. In fact this has been achieved. We wish to describe herein (1) a remarkable controlling effect of the phosphorus ligand in a nickel(0) complex catalyst, (2) a reexamination of the tetramer structure which previously has been erroneously assigned,[4] and (3) an allene tetramer nickel(0) complex which is related to the catalysis leading to the tetramer **4** and the pentamer **1**.

In the presence of Ni(C$_8$H$_{12}$)$_2$ (C$_8$H$_{12}$ = 1,5-cyclooctadiene) combined with 1–4 mol of *tert*-alkyl- or -arylphosphine as catalyst, allene produces a mixture of oligoallenes containing **4** as a main product, whereas with that containing triaryl phosphite, such as triphenyl, tri-2-tolyl, or tri-2-biphenylyl phosphite, one composed mainly of the trimer 1,2,4-trimethylenecyclohexane (**5**) is obtained regardless of the steric requirements of the ligand.[5] Higher phosphine–Ni ratios (>2) or higher catalyst concentrations (1.0–2.5 mol %) prefer formation of the tetramer **4** rather than the pentamer **1**. Similar tendency for the selectivity of oligomer formation was observed also with the Ni(0) triaryl phosphite system.[6]

The tetramer **4**, bp 40° (5 mm), m/e 160, shows ir and ^{1}H nmr spectra which are essentially identical with those of a sample prepared according to Lindsey's pre-

scription[4] using Ni(CO)$_2$[P(OPh)$_3$]$_2$ as a catalyst: ir (neat) 3080 (=C—H), 2960, 2920 (C—H), 1645 (C=C), 1628 (C(=CH$_2$)C(=CH$_2$)), and 885 (=CH$_2$) cm^{-1}; ^{1}H nmr (100 MHz, CCl$_4$) δ 4.90 (d, $J = 2.5$ Hz, 2 H, =CH$_2$), 4.75 (s, 6 H, =CH$_2$), 3.00 (s, 4 H, H^a), and 2.28 (sharp s, 4 H, H^b). The ^{13}C nmr enables us to assign it unambiguously as 1,2,4,7-tetramethylenecyclooctane **4**: δ (ppm from CS$_2$) 43.2 (2 C,-C(=C)-), 44.5 (2 C,-C-(=C)-), 80.1 (2 C, =CH$_2$), 80.5 (2 C, =CH$_2$), 114.8 (2 C, =CCH$_2$C=), and 155.6 (2 C, -CH$_2$CH$_2$-).[7]

(3) M. Englert, P. W. Jolly, and G. Wilke, *Angew. Chem.*, **83**, 84 (1971).

(4) R. E. Benson and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **81** 4247 (1959).

(5) C. A. Tolman, *ibid.*, **92**, 2956 (1970).

(6) A typical experiment carried out at 70° for 20 hr using 2.1 g of allene in 10 ml of benzene gave the following results: (a) the Ni(C$_8$-H$_{12}$)$_2$ (2.5 mol % based on allene)–4PPh$_3$ system (conversion, 93 %, selectivity: **5**, 28 %; **4**, 66 %; **1**, 6 %); (b) Ni[P(OPh)$_3$]$_4$ (1.2 mol %) catalyst (conversion, 81 %; selectivity: **5**, 72 %; **4**, 25 %; **1**, 3 %).

(7) The same conclusion concerning the structure of **4** was also obtained by G. S. Reddy and R. V. Lindsey, Jr., through ^{13}C nmr study (private communication from Dr. R. V. Lindsey, Jr.).

The addition of tetracyanoethylene (TCNE) to 4 takes place in tetrahydrofuran leading to a crystalline adduct 8, mp 220–222° (lit.[8] 222–223°), which shows a ^{1}H nmr spectrum (100 MHz, $(CD_3)_2CO$) identical with the reported one: δ 4.85 (s, 4 H, =CH_2), 3.32 (s, 4 H, H^a), 3.15 (s, 4 H, H^b), and 2.29 (s, 4 H, H^c). The TCNE addition was previously regarded as an unusual transannular 1,7 addition[8] leading to 9 on the basis of the structure 6 and was referred to as a [$_\pi2_s + _\pi2_s + _\pi2_s$] cycloadditon by Woodward and Hoffmann.[9] The addition reaction, however, is evidently an ordinary [$_\pi2_s + _\pi4_s$] process.

Treatment of $Ni(C_8H_{12})_2$ with excess allene at -30 to $-40°$ gives viscous red complexes, which showed air and thermal instability and could not be fully characterized, but on hydrogenation with PtO_2 catalyst yielded open-chain C_9 and C_{12} hydrocarbons. Addition of a n-hexane solution of 1 mol of PPh_3 to the red complexes in n-hexane at $-30°$ immediately gives an extremely air-sensitive orange-yellow powder, 10. When the reaction of PPh_3 with the red complexes was performed in toluene and followed by addition of n-hexane, the orange binuclear complex $Ni_2(C_{12}H_{16})(PPh_3)_3$ (11), whose ^{1}H nmr spectrum is not fully assignable,[10] crystallized slowly. Attempted recrystallization of 10 from a toluene–n-hexane mixture is unsuccessful owing to decomposition to give 11. The elemental analysis of 10 corresponds to the formula $Ni(C_{12}H_{16})(PPh_3)$.[11] Even in fresh C_6D_6 solution it shows an apparently complex ^{1}H nmr spectrum due to contamination by oligoallenes such as the tetramer 4 and by the binuclear complex 11, but the presence of uncoordinated exo-methylene groups can be recognized from the signals at δ 5.38 and 4.69. Both 10 and 11 upon treatment with CS_2 produce 4 and the known complex $[Ni(CS_2)(PPh_3)]_2$[12] implying that the $C_{12}H_{16}$ ligand should be identical in both complexes. When measured at room temperature immediately after sample preparation, the ^{1}H nmr spectra of 10 and 11 in CS_2 were the same and were rather simple, consisting of signals assignable to the C_{12}-bis-π-allylnickel(0) complex 12[13] at δ 1.50 (s, 4 H, H^a), 2.49 (s, 4 H, H^c), 2.71 (s, 4 H, H^b), 4.68 (m, 2 H, H^e), and 5.30 (d, $J = 2.0$ Hz, 2 H, H^d) together with the peaks due to 4. Nmr study showed that treatment of 10 with excess allene at 30° gave 4 and the complex 3. The nmr data and chemical reactions lead us to the structural assignment shown below for the complex 10. Further, it can be concluded that the un-

stable viscous red complexes contain the trimer complex 2 and the tetramer 12. There are two sites[14] in
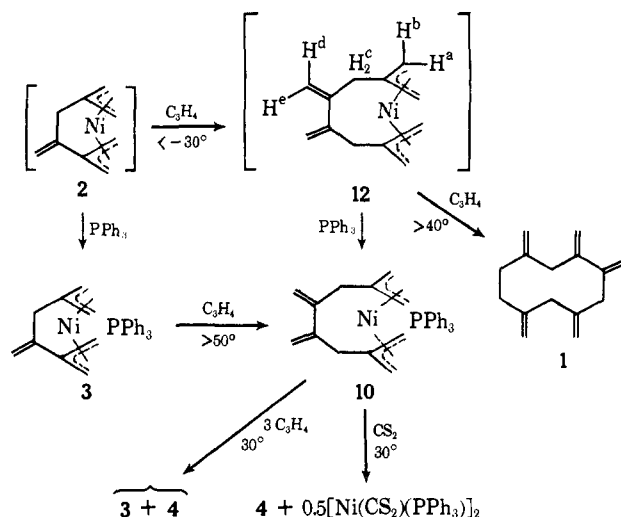
intermediates 2 or 3 for allene insertion. If a cyclic tetramer is to be formed from 3, the possible isomers are 4 or 7, depending on the insertion site. This feature also excludes the assignment of the tetramer as 6. The exclusive formation of 10 and 12 from 3 and 2, respectively, implies that there is a preferential site, namely the π-allyl moiety adjacent to the exo-methylene group.

The linear tetramer ligand in 12 offers two allylic sites for allene insertion but the sites are chemically equivalent. Therefore, if a cyclic pentamer is to be formed from an intermediate containing a linear tetramer of this structure, the only possible isomer for the pentamer is 1, not 1,2,4,6,8-pentamethylenecyclodecane as suggested previously.[15]

The effect of concentration of the catalyst and of ligand–Ni ratio on the distribution of the products can be explained by competitive coordination of allene and the ligand toward the complexes 2 and 12. These results lead us to the proposed reaction scheme giving 3, 4, and 1 as described above.

It is worth noting that all the allene oligomers obtainable by our method are of single component and free of other isomeric products. These results show how nickel(0) species act as templates for the oligomerization by forming bis-π-allylic intermediates.[16]

(8) J. K. Williams and R. E. Benson, J. Amer. Chem. Soc., 84, 1257 (1962).

(9) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 106.

(10) Anal. Calcd for $C_{66}H_{61}Ni_2P_3$: C, 74.54; H, 5.78; Ni, 10.95. Found: C, 75.04; H, 6.01; Ni, 10.66. The ^{1}H nmr (C_6D_6) shows the absence of uncoordinated exo-methylene groups and the ratio of area, aromatic protons vs. other ones ($\sim$45:16), also supports the formula. Further characterization will be described elsewhere.

(11) Anal. Calcd for $C_{30}H_{31}NiP$: C, 74.87; H, 6.36; Ni, 12.20. Found: C, 74.47; H, 6.36; Ni, 12.19.

(12) (a) M. Baird, G. Hartwell, Jr., R. Mason, A. I. M. Rae, and G. Wilkinson, Chem. Commun., 92 (1967); (b) M. C. Baird and G. Wilkinson, J. Chem. Soc. A, 865 (1967).

(13) The presence of coordinated CS_2 cannot be excluded from the nmr data alone.

(14) Note that the two carbon atoms in one π-allylic group are equivalent.

(15) F. W. Hoover and R. V. Lindsey, Jr., J. Org. Chem., 34, 3051 (1969).

(16) Note Added in Proof. After submission of this paper, a paper (P. J. De Pasquale, J. Organometal. Chem., 32, 381 (1971)) dealing with a similar allene oligomerization with Ni(0) catalysts appeared. The "allene monomer complex, $(PPh_3)_2Ni(C_3H_4)$," described in the paper seems to be identical with our allene trimer complex 3. Therefore, his mechanism appears to us questionable.

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