demonstrate the successful nature of competition between substitution and elimination channels for gas-phase anion-molecule reactions.

Acknowledgment. We gratefully acknowledge financial support of this work by a National Science Foundation Presidential Young Investigator Award (Grant CHE-8552742).

Registry No. Hydroxide, 14280-30-9; dimethyl sulfite, 616-42-2; diethyl sulfite, 623-81-4; amide, 17655-31-1; ethylmethyl sulfite, 10315-59-0.

Nickel(0)-Catalyzed Reaction of Diynes with Aldehydes

Tetsuo Tsuda,* Takao Kiyoi, Toshiki Miyane, and Takeo Saegusa*

Department of Synthetic Chemistry
Faculty of Engineering, Kyoto University
Yoshida, Kyoto, Japan

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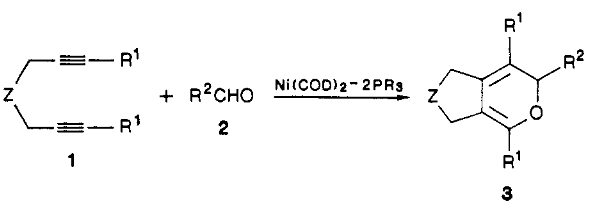
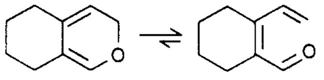
Transition-metal-catalyzed cycloaddition of diynes with unsaturated compounds is useful for the synthesis of polycyclic compounds and is actively studied recently.[1] The cycloaddition of diynes with a carbonyl group, however, has not been reported except in our recent study of the Ni(0)-catalyzed cycloaddition of diynes with carbon dioxide to bicyclic α-pyrones.[2] Here we investigated the Ni(0)-catalyzed cycloaddition of diynes **1** with aldehydes **2** to bicyclic α-pyrans **3** (eq 1).

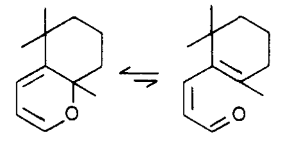


(1)

Dihydro- and tetrahydro-α-pyrans are well-known compounds.[3] Those substituted with functional groups, in particular, are important intermediates in the synthesis of natural products.[4] On the contrary, examples of the α-pyran ring system are limited because the α-pyran ring consisting of a dienolic ether structure undergoes electrocyclic ring opening to a dienone. Several monocyclic α-pyrans bearing alkyl and heteroatom substituents are known.[5] It is suggested that the alkyl substituent causes the steric destabilization of the dienone tautomer.[6] The literature on bicyclic α-pyrans is sparse except for 1-benzo-α-pyrans stabilized by the fusion of the benzene ring.[5] The bicyclic α-pyran **4a** exists at room

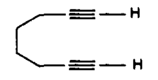
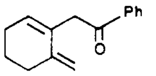
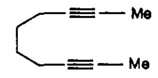
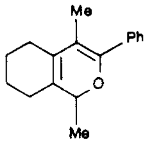
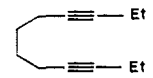
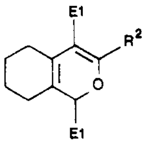
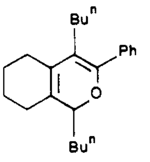
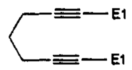
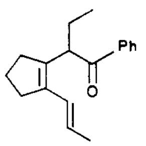
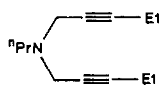
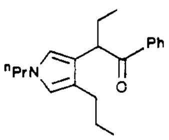


4a **4b**
(2)



5a **5b**
(3)

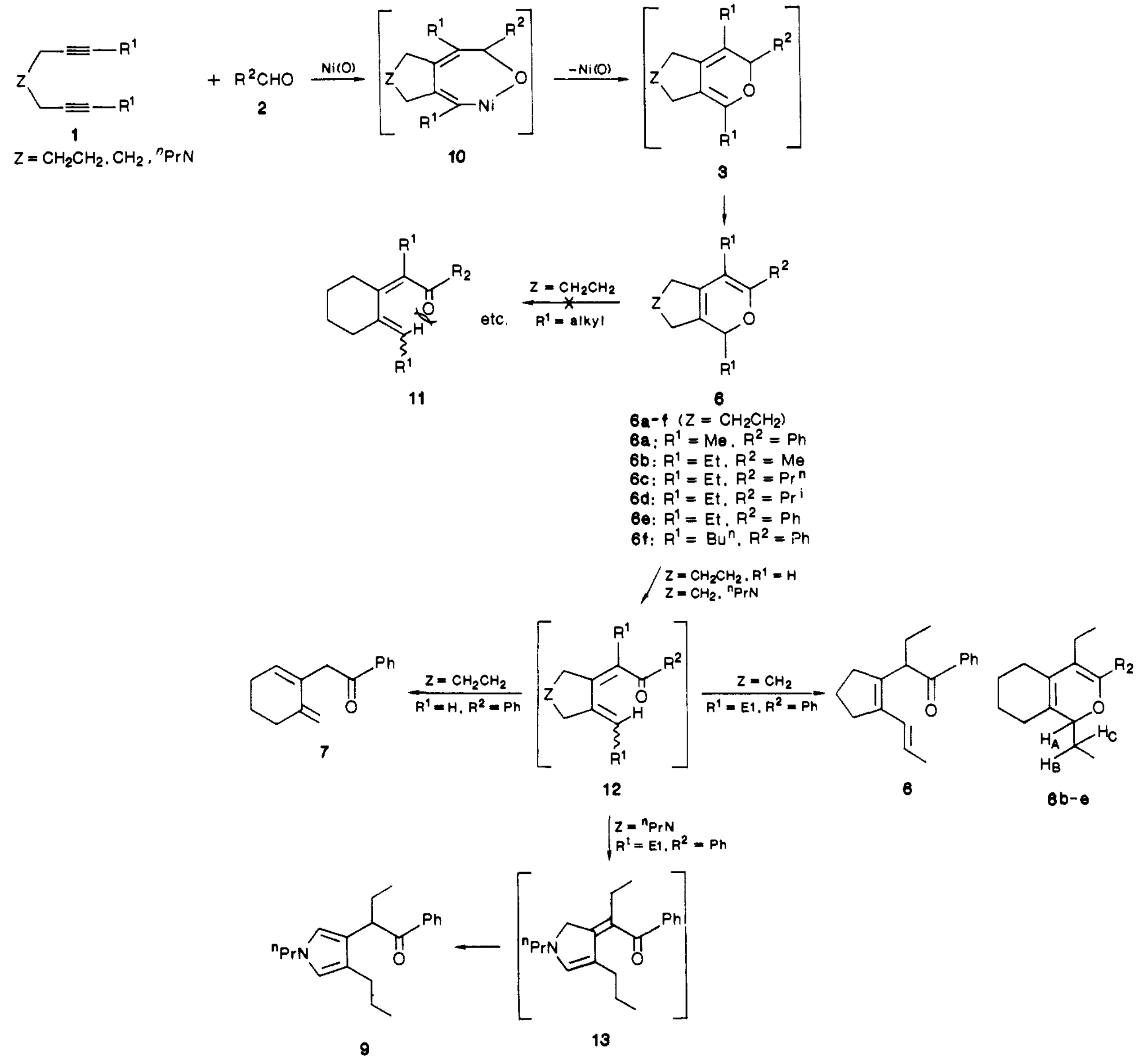
Table I. Reaction of Diynes and Aldehydes Catalyzed by the Ni(O)–PR$_3$ Complexes[a]

diyne (**1**)	aldehyde (**2**)	PR$_3$	product	isolated yield	%[d]
 **1a**[b]	PhCHO **2d**	PBu$_3^t$ PCy$_3$		**7**	15 1.2
 **1b**[c]	**2d**	PBu$_3^t$ PCy$_3$		**6a**	52 39
 **1c**	MeCHO **2a** ^{n}PrCHO **2b** ^{i}PrCHO **2c** **2d**	PCy$_3$		**6b** (R^2=Me) **6c** (R^2=Pr^n) **6d** (R^2=Pr^i) **6e** (R^2=Ph)	28 90 69 79
		PBu$_3^n$ PPh$_3$			77 78
 **1d**	**2d**	PCy$_3$		**6f**	78
 **1e**	**2d**	PCy$_3$		**8**	71
 **1f**	**2d**	PCy$_3$		**9**	97

[a] Diyne **1**, 1.00 mmol; **2**/**1** = 1.5; Ni(COD)$_2$/**1** = 0.05; PR$_3$/Ni(COD)$_2$ = 2; solvent, THF (10 mL); temperature, 120 °C; time, 5 h. [b] Temperature, 100 °C; time, 20 h. [c] Temperature, 135 °C; time, 5 h. [d] The product has the spectroscopic data and the elemental composition (HRMS) in accord with its structure.

0002-7863/88/1510-8570$01.50/0

Scheme I



temperature as the isomeric dienal **4b**.[7] On the other hand, the substituted 2,3-cyclohexano-α-pyran **5a**,[8] which is prepared by irradiation of trans-β-ionone, is stable at room temperature. The Ni(0)-catalyzed cycloaddition of **1** with **2** therefore is interesting in relation to the almost unexplored chemistry of the bicyclic α-pyran.

The Ni(0) catalyst generated from Ni(COD)$_2$ and 2 equiv of trialkyl- or triphenylphosphine (PR$_3$) effected the cycloaddition of terminally dialkyl-substituted 1,7-octadiynes **1b–d** with aldehydes **2a–d** to afford new bicyclic α-pyrans **6a–f** with a fused cyclohexane ring. The results are summarized in Table I. The formation of **6e** was not dependent upon the structure of the phosphine ligand used: PBu$_3^n$, tricyclohexylphosphine (PCy$_3$), and PPh$_3$ ligands were similarly effective. This finding exhibits a contrast to the Ni(0)-catalyzed cycloaddition of **1** with carbon dioxide to the bicyclic α-pyrone where the structure of the phosphine ligand plays an important role.[2]

The structure of the diyne, i.e., the terminal alkyl substituent and the length of the chain connecting the two carbon–carbon triple bonds, exerted a great influence on the bicyclic α-pyran formation reaction (Table I). The reaction of the terminally unsubstituted diyne **1a** with **2d** gave an oxoalkyl-substituted cyclohexene derivative **7**.[9] 3,8-Undecadiyne (**1e**) reacted with **2d** to produce the oxoalkyl-substituted cyclopentene **8**. A pyrrole derivative **9** was obtained in excellent yield by the reaction of **2d** and the terminally diethyl-substituted 1,6-heptadiyne **1f** containing a nitrogen heteroatom in the methylene chain. No corresponding bicyclic α-pyran was detected in these three reactions.

Thus, depending upon the structure of the diyne employed, the present Ni(0)-catalyzed reaction of diynes with aldehydes affords a variety of carbo- and heterocycles: bicyclic α-pyrans with a fused

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(1) See, for example: (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (c) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788.

(2) (a) Tsuda, T.; Morikawa, S.; Sumiya, R.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 3140. See, also: Tsuda, T.; Sumiya, R.; Saegusa, T. *Synth. Commun.* **1987**, *17*, 147.

(3) Hepworth, J. D. *Comprehensive Heterocyclic Chemistry*; Boulton, A. J., Mckillop, A., Eds.; Pergamon: New York, 1984; Vol. 3, p 769.

(4) See, for example: (a) Danishefsky, S. J. *Aldrich. Acta* **1986**, *19*, 59. (b) Schmidt, R. R. *Acc. Chem. Res.* **1986**, *19*, 250.

(5) Hepworth, J. D. *Comprehensive Heterocyclic Chemistry*; Boulton, A. J., Mckillop, A., Eds.; Pergamon: New York, 1984; Vol. 3, p 737.

(6) Kluge, A. F.; Lillya, C. P. *J. Org. Chem.* **1971**, *36*, 1977.

(7) Schiess, P.; Chia, H. L. *Helv. Chim. Acta* **1970**, *53*, 485.

(8) (a) Büchi, G.; Yang, N. C. *J. Am. Chem. Soc.* **1957**, *79*, 2318. (b) Marvel, E. N.; Chadwick, T.; Caple, G.; Gosink, T.; Zimmer, G. *J. Org. Chem.* **1972**, *37*, 2992. (c) Kurata, S.; Kusumi, T.; Inouye, Y.; Kakisawa, H. *J. Chem. Soc., Perkin Trans. 1* **1976**, 532.

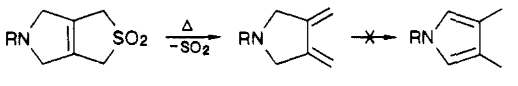
(9) An unidentified higher molecular weight product having a carbonyl group was produced together with **7**.

cyclohexane ring and oxoalkyl-substituted cyclopentene, cyclohexene, and pyrrole derivatives.

Clarification of the reaction mechanism is an interesting subject of a further study. One possible reaction path[2,10] is depicted in Scheme I. The strained 1,2-bis(alkylidene)cycloalkane intermediates **3** and **12** are transformed into various cyclic products **6**–**9** via different hydrogen transfer isomerizations.

The 400 MHz ^{1}H NMR spectra of the bicyclic α-pyrans **6b**–**e** show that they are sterically congested molecules, in which the free rotation of the ethyl group on the 2-C atom is restricted. Thus the methylene hydrogen atoms H_B and H_C (Scheme I) of **6b**–**e** are not equivalent (J_{BC} = 14–15 Hz) and exhibit the different coupling constants (J = 9 and 3 Hz) to the methine hydrogen H_A, which appears as a broad doublet (J = 9 Hz). Furthermore, the methylene hydrogens of the ethyl group on the 5-C atom of **6e** are not equivalent. The free rotation of the butyl group on the 5-C atom of **6f** is also restricted. However, it may be inferred that, in comparison with the dienone **11** which is a highly strained molecule owing to the steric repulsion arising from H vs O, H vs R^2, R^1 vs O, or R^1 vs R^2, the bicyclic α-pyrans **6b**–**f** are relatively stable and can exist without undergoing the ring-opening isomerization to **11**.

The formation of **7** from the unsubstituted diyne **1a** indicates that an alkyl substituent is necessary at least on the 5-C atom for the existence of the bicyclic α-pyran **6** ($Z = CH_2CH_2$). The transformation of **6** ($Z = CH_2$ and ^{n}PrN) to **8** and **9** via the dienone key intermediate **12**[11] ($Z = CH_2$ and ^{n}PrN) suggests that the α-pyran ring fused with a five-membered ring is unstable and undergoes the electrocyclic ring cleavage to the dienone. The conjugated δ-amino-$\alpha,\beta,\gamma,\delta$-dienone intermediate **13** may play an important role in the formation of **9** because it is known that 3,4-dimethylenepyrrolidine (**14**) does not isomerize to 3,4-dimethylpyrrole (**15**)[12] (eq 4).



14 **15** (4)

Supplementary Material Available: Typical experimental procedures and characterization (IR, ^{1}H NMR, ^{13}C NMR, MS, and HRMS) data for the products **6a**–**f** and **7**–**9** listed in Table I (5 pages). Ordering information is given on any current masthead page.

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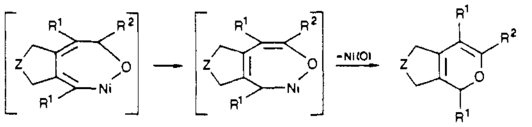
(10) Another possible reaction path may be the one involving the hydrogen transfer isomerization via a metallacycle containing the nickel atom: for example



10 6

(11) Equilibration of **12** ($Z = CH_2$ and ^{n}PrN) $\rightleftharpoons$ **6** ($Z = CH_2$ and ^{n}PrN) may be possible.[8b]

(12) Ottenbrite, R. M.; Alston, P. V. *J. Org. Chem.* **1974**, *39*, 1115.

Additions and Corrections

pH Dependence of the Mechanism of Hydrolysis of Benzo[*a*]pyrene-*cis*-7,8-diol 9,10-Epoxide Catalyzed by DNA, Poly(G), and Poly(A) [*J. Am. Chem. Soc.* **1987**, *109*, 2108–2111]. NAFISA B. ISLAM, DALE L. WHALEN,* H. YAGI, and DONALD M. JERINA

Page 2109, Table I: The values of $k^{\mathrm{H}}_{\mathrm{cat}}$ (M^{-1} s^{-1}) and k^{0}_{cat} (s^{-1}) for the reaction of **DE-1** in solutions of Poly(G) should be $>6.3 \times 10^5$ and >0.20, respectively, and not $<6.3 \times 10^5$ and <0.20 as reported.

Reaction of Dinitrogen Pentoxide with Fluoranthene [*J. Am. Chem. Soc.* **1986**, *108*, 4126–4132]. BARBARA ZIELINSKA,* JANET AREY, ROGER ATKINSON, THOMAS RAMDAHL, ARTHUR M. WINER, and JAMES N. PITTS, JR.

The ^{1}H NMR spectrum reported for 1,2,5-trinitrofluoranthene was actually that of 2,3,5-trinitrofluoranthene. The correct ^{1}H NMR spectrum of 1,2,5-trinitrofluoranthene is as follows ($CDCl_3$): δ 8.95 (d, 1, $J_{(4,6)}$ = 1.6 Hz, C_6H), 8.85 (s, 1, C_3H), 8.83 (d, 1, C_4H), 8.02 (d, 1, $J_{(7,8)}$ = 6.4 Hz, C_7H), 7.86 (d, 1, $J_{(9,10)}$ = 7.6 Hz, $C_{10}H$), 7.63 (t, 1, C_8H), 7.55 (t, 1, C_9H). Both trinitrofluoranthenes are formed in the reaction of 2-nitrofluoranthene with N_2O_5 in CCl_4 solution, with 1,2,5-trinitrofluoranthene being the major trinitro isomer formed.

Computer Software Reviews

Number Cruncher Statistical System. Version 5.01. Dr. Jerry L. Hintze: 865 East 400 North, Kaysville, UT 84037. List price $99.00. Optional NCSS 5.1 Graphics ($59.00) and NCSS 5.3 Power Pack ($49.00) require NCSS 5.0.

Number Cruncher Statistical system (NCSS) is an advanced statistical analysis software package. The program requires an IBM-PC, XT, AT, or close compatible machine. NCSS 5.1 Graphics is an integrated statistical analysis and graphics accessory for NCSS and requires a CGA, EGA, VGA, and Hercules compatible graphics board and was designed to output to an HP-compatible plotter. Other plotters require special drivers, not supplied by NCSS. NCSS Power Pack is an accessory designed to perform advanced statistical procedures. This review was conducted on a Leading Edge Model D (8088, 4.7 MHz) and an Acer 1100 (80386, 16 MHz) equipped with an HP Color Pro Plotter.

The basic NCSS package comes on three 360 Kb floppy disks and is designed to run on either a floppy-disk or hard-disk system with at least 450 Kb of memory. NCSS Graphics needs 512 Kb of memory, two floppy disk drives or a hard-disk, and graphics equipment. NCSS is not copy protected.

NCSS offers a surprising repertoire of statistical techniques, probably well in excess of the needs of the average chemist. At first glance, the organization of the package seems lacking. However, the sheer volume of features presented in NCSS is probably to blame, and closer examination reveals a simply organized system centered around a transfer menu packed with options. A statement of the organizational scheme of the program early in the manual would alleviate this confusion, although this is not a serious flaw. The documentation is otherwise straightforward and able to be followed even by the computer novice. The statistical options of NCSS are thoroughly described, with tutorials for the major features appended. Installation is accomplished easily and quickly by