Table I. Thermolysis Rate Data for Some Azo Compounds

Compd	Temp, °C	$10^4 k$, sec^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate
1[a]	+180.8	8.35	37.3 ± 0.3	+8.7	
	−3.5				1[c]
2[b]	−3.5	1.04[d]	17.7 ± 1.6[e]	−13[f]	2.2×10^{11}
4	+150.0	2.33	36.5 ± 0.3	+8.3	
	−3.5	4.34×10^{-11}[c]			9.2[c]
5[b]	+50.0	3.31	23.3 ± 0.4[e]	−5[f]	
	−3.5	2.46×10^{-3}[g]			5.2×10^8
6[b]	−3.5	0.90[d]	19.6 ± 0.9[e]	−6[f]	1.9×10^{11}

[a] From other reported data.[11] [b] In $CDCl_3$. [c] Estimation based on gas-phase results and extrapolation to −3.5°. [d] Taken from the Arrhenius plot of the kinetics covering the temperature range from +10 to −5°. [e] Calculated from 15–20 nmr measurements covering the range 0 to *ca.* 80% reaction. [f] Average values over the temperature range for kinetics. [g] Extrapolated to −3.5° from the data at higher temperatures.

gas phase at 150° gave **7**; no formation of quadricyclene was observed.[10]

First-order rate constants for the thermolysis of **4** in the gas phase at 121–150° were measured by following the disappearance of a uv –N=N– absorption [λ(isooctane) 338 nm].[11] The thermolyses of **5** and **6** are so much faster than that of **4** that their kinetics of decomposition were measured in the liquid phase in $CDCl_3$ at lower temperatures. Rates were determined at five temperatures between +50 and +33° for **5** and +9 and −5° for **6**. This was accomplished by periodic nmr measurement of the developing vinyl proton signals of the diene product against the vinyl protons of 2,5-dimethylfuran internal standard. Some results are summarized in Table I.

Comparison of reactivity between **1**, **4** and **2**, **5**, **6** necessitates extrapolation of the kinetic data between gas- and liquid-phase conditions. Control experiments with **1** have demonstrated that the decomposition rates of such azo compounds are not appreciably greater in the liquid phase than in the gas phase. On this basis, **4** is 10^7–10^{10} times less reactive than structurally similar **5**, **6**, and **2**. All of the criteria, enormous differences in reactivity, E_a, and $\Delta S^{\ddagger}$, suggest different decomposition mechanisms. The striking match in reactivity, E_a, and $\Delta S^{\ddagger}$ for **1** and **4** points to decomposition of **4** *via* a diradical pathway.[1,11–14] A similarity in reactivity, E_a, and $\Delta S^{\ddagger}$ for **2**, **5**, and **6** indicates that **5** and **6** decompose by concerted processes[1,15–17] involving transition states like **3**.[18]

Of the possible rationalizations for the remarkable differences in the decomposition of **4** and **5**, **6** the explanation which we prefer is that based on differences in strain in the transition states. Thus, if **4** were to follow a concerted pathway, the one-carbon bridge C_5 would cause severe strain in the transition state as C_1, C_2, C_3, and C_7 rehybridize to give diene **7**. This effect is eased substantially by the two-carbon bridge C_8C_9 in **5**. The constraint is reduced further in **6** by the three-carbon bridge $C_3C_4C_5$.[19] An additional factor which may be of relevance here is the difference in the orientation of the cyclopropyl ring. For **5** and **6** the cyclopropyl orbitals are more favorably oriented for overlap as the C–N bonds break. In both regards, molecular models show that the angle situation has become similar for **6** and **2**.

Earlier it was suggested that relief of steric interaction between C_3 and C_8 hydrogens may make a contribution to the 10^{11} rate enhancement found with **2**.[1] However, since **2** and **6** have the same reactivity such a factor contributes little, if anything, to the reactivity of **2**. The low reactivity of **4** compared to **2** indicates that relief of strain involved in opening of the cyclopropyl ring is not a major factor. The indications are that the exceptional acceleration is electronic in origin.

Acknowledgment. We express appreciation to the National Science Foundation for support of this work with Grant No. GP-9478. Special thanks are due Dr. J. C. Hinshaw for helpful discussion and for providing us with compound **2**.

---

(10) Control experiments showed that quadricyclene would have survived the experimental conditions and could have been detected if it had been formed to an appreciable extent.

(11) S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, **83**, 2895 (1961).

(12) E. L. Allred and R. L. Smith, *ibid.*, **91**, 6766 (1969).

(13) M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970); R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966), and other papers in the series.

(14) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, **702**, 1 (1967); W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967).

(15) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969).

(16) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969).

(17) M. Martin and W. R. Roth, *Chem. Ber.*, **102**, 811 (1969).

(18) The negative $\Delta S^{\ddagger}$ values are quite surprising for dissociative transition states like **3**. While we have no rationale for this observation at present, we find it most intriguing.

(19) Although the differences in strain for the dienes have not been reported, inspection of models indicates the order of decreasing strain is **7** > **8** > **9**.

Evan L. Allred,* Albert L. Johnson
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received November 9, 1970

Asymmetric Homogeneous Hydrogenation with Rhodium(I) Complexes of Chiral Phosphines

Sir:

There has been recent interest in asymmetric hydrogenations catalyzed by soluble rhodium catalysts of the Wilkinson type.[1–4] For example, asymmetric hydrogenation of α-phenylacrylic acid was accomplished

---

(1) (a) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968). Correcting for the optical purity of the phosphine (69%), the asymmetric synthesis of hydratropic acid was 22%. (b) See also *Chem. Eng. News*, **48**, 41 (July 11, 1970), where it is reported that 28% asymmetric synthesis has now been achieved.

(2) L. Horner, H. Siegel, and H. Buthe, *Angew. Chem.*, **80**, 1034 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 942 (1968).

(3) J. D. Morrison, "13th Annual Report on Research," Petroleum Research Fund, American Chemical Society, Washington, D. C., 1968, p 223.

(4) J. D. Morrison and R. E. Burnett, Abstracts of Papers, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, No. ORGN 85.

with a rhodium complex of (*R*)-methylpropylphenylphosphine in an ethanol–benzene solution containing triethylamine. (*S*)-Hydratropic acid (15% enantiomeric excess, ee) was obtained.[1] Similarly α-ethylstyrene was reduced to 2-phenylbutane (about 8% enantiomeric excess).[2] Instead of using tertiary phosphines which are asymmetric at phosphorus,[5] we have prepared a number of catalytically active, chiral rhodium complexes from phosphine ligands which are asymmetric at carbon and much more accessible.[3,4] This paper describes one of these complexes that has proven to be very effective as an asymmetric homogeneous hydrogenation catalyst.

The reaction of lithium diphenylphosphide[6] with menthyl chloride or bromide produces a tertiary phosphine which, on the basis of nmr studies at 220 MHz, is neomenthyldiphenylphosphine (NMDPP).[7] When allowed to react with Rh(I) μ complexes of ethylene or dienes in ethanol–benzene,[8] NMDPP forms a catalytically active species in solution, presumably of the type L_3RhCl where L is the chiral ligand. Oxidative addition of hydrogen and dissociation of one of the ligands leads to a coordinatively unsaturated (or solvent saturated) Rh(III) intermediate which transfers hydrogen to an alkene.[9]

Reduction of (*E*)-β-methylcinnamic acid in a 1:1 benzene–ethanol solution of prereduced tris(neomenthyldiphenylphosphine)rhodium(I) chloride was carried out in the presence of 6 equiv of triethylamine under 300 psi of hydrogen pressure, at 60° over a period of 24 hr. The solvent was removed under reduced pressure and the product extracted into a 10% NaOH solution which was successively filtered through Celite, acidified, and extracted with ether. The ether extracts were dried ($MgSO_4$) and fractionated to obtain 3-phenylbutanoic acid (80% isolated yield after fractional distillation),[10] $\alpha^{25}\mathrm{D}$ +34.5° (neat), 61% enantiomeric excess of the *S* isomer.[11] Similarly, reduction of (*E*)-α-methylcinnamic and atropic acids gave (*R*)-2-methyl-3-phenylpropanoic (52% ee)[12] and (*S*)-hydratropic acid (28% ee).[13]

To our knowledge the 61% asymmetric synthesis (80.5% *S*-(+) enantiomer and 19.5% *R*-(−) enantiomer) of 3-phenylbutanoic acid represents the highest degree of asymmetric bias ever accomplished with a chiral hydrogenation catalyst, homogeneous or heterogeneous.[14]

These observations are significant for several reasons. First, the initial studies[1,2] of asymmetric homogeneous hydrogenation concentrated upon tertiary phosphines which were chiral at phosphorus. This was most reasonable, since there is an intuitive tendency to want to design a system with the asymmetry as close to the metal as possible in the hope of increasing the asymmetric bias. However, it follows from general symmetry principles that the only necessary condition for asymmetric synthesis is that the hydrido complex be chiral, and complexes of ligands that are dissymmetric remote from phosphorus also fulfill this requirement. Our results show that at least one such ligand is remarkably effective.

A second important consideration follows from the first; from a practical point of view, some attention should be focused upon catalytically active complexes prepared from readily available chiral compounds. The NMDPP ligand was prepared from an inexpensive, readily available, chiral precursor ((−)-menthol *via* menthyl chloride[17]) and no classical resolution step was necessary. Many other similar possibilities can be envisaged. It may be that similar ligands can be used to induce high degrees of asymmetry not only in hydrogenations *via* soluble complex catalysts but also in other reactions catalyzed by metal complexes.

Finally, it should be noted that α,β-unsaturated carboxylates appear to be especially interesting substrates. We have observed uniformly higher asymmetric synthesis with them than with olefins. This is in agreement with the recent observations of others[1b] and may suggest a different mechanism, possibly involving coordination through the carboxylate anion. Nevertheless, we have also found NMDPP to be comparable to a ligand asymmetric at phosphorus in its ability to induce asymmetry during the hydrogenation of α-ethylstyrene, where bifunctional interaction with the rhodium is not possible. A 7% enantiomeric excess of (*R*)-2-phenylbutane was obtained using NMDPP, compared to an 8% enantiomeric excess of (*S*)-2-

---

(5) (a) Prepared by deoxygenation of chiral phosphine oxides which are, in turn, prepared from diastereomerically enriched menthyl phosphinates: O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4842 (1968). (b) A significant extension of the Mislow method of chiral phosphine oxide synthesis has been reported recently: W. B. Farnham, R. K. Murray, Jr., and K. Mislow, *ibid.*, **92**, 5810 (1970).

(6) A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, **27**, 1001 (1962). In the present work the reaction of diphenylphosphinous chloride with lithium in THF was used to prepare the phosphide: A. M. Aguiar and T. G. Archibald, *Tetrahedron Lett.*, 5541 (1966).

(7) N. S. Bhacca, A. M. Aguiar, C. Morrow, R. Turkel, R. E. Burnett, and J. D. Morrison, manuscript in preparation. The reaction of lithium diphenylphosphine with menthyl chloride is very sluggish compared to its reaction with, for example, cyclohexyl chloride. We have found it convenient to use a large excess of halide and reaction times of about 12 hr. The phosphine distils at 165–170° (0.2 mm) and should be carefully purified by repeated crystallizations from petroleum ether (30–60°) to remove Ph_2PH and phosphine oxide impurities. Samples of phosphine that were not purified gave lower stereoselectivity; the stereoselectivity observed with purified phosphine was reproducible within 1 or 2%.

(8) C. Djerassi and J. Gutzwiller, *J. Amer. Chem. Soc.*, **88**, 4537 (1966).

(9) For recent accounts of mechanistic studies in this area see (a) A. S. Hussey and Y. Takeuchi, *ibid.*, **91**, 672 (1969); (b) C. H. Heathcock and S. R. Poulter, *Tetrahedron Lett.*, 2755 (1969); (c) G. V. Smith and R. J. Shuford, *ibid.*, 525 (1970); (d) R. L. Augustine and J. F. Van Peppen, *Chem. Commun.*, 495, 497 (1970); (e) A. S. Hussey and Y. Takeuchi, *J. Org. Chem.*, **35**, 643 (1970), and references therein. For a general review see J. E. Lyons, L. E. Rennick ,and J. L. Burmeister, *Ind. Eng. Chem., Prod. Res. Develop.*, **9**, 2 (1970).

(10) The hydrogenation is essentially quantitative and crude yields are 95–100%. The undistilled acid has a slightly lower rotation (about 2% lower apparent per cent enantiomeric excess). This is most likely due to traces of impurities. The slightly higher rotation observed after distillation is most probably due to the separation from impurities rather than to separation of the enantiomer in excess from racemate, since when a sample of (+)-3-phenylbutanoic acid (65% ee) was carried through the hydrogenation sequence the crude recovered acid had an apparent 63% ee, but the distilled acid had a 65% ee of the *S*-(+) enantiomer, the same as that of the starting acid.

(11) D. J. Cram, *J. Amer. Chem. Soc.*, **74**, 2137 (1952).

(12) (a) R. H. Pickard and J. Yates, *J. Chem. Soc.*, **95**, 1011 (1909); (b) M. B. Watson and G. W. Youngson, *ibid.*, *C*, 258 (1968).

(13) J. P. Bakshi and E. E. Turner, *ibid.*, 171 (1961).

(14) Hydrogenation of methyl β-methylcinnamate, catalyzed by a rhodium borohydride complex of chiral α-methylbenzylformamide and pyridine, with 54% asymmetric synthesis[15] is, as far as we are aware, the only other asymmetric hydrogenation to give better than 50% asymmetric bias. Heterogeneous systems in which an insoluble catalyst is modified with an optically active additive typically give only a few per cent asymmetric synthesis.[16]

(15) P. Abley and F. J. McQuillin, *Chem. Commun.*, 477 (1969).

(16) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, Sections 6-7.3, 7-1.1, and 7-1.2.

(17) J. G. Smith and G. F. Wright, *J. Org. Chem.*, **17**, 1116 (1952).

phenylbutane when (*S*)-methylpropylphenylphosphine was the ligand.[2]

Experiments with other readily prepared ligands having multiple chiral centers are in progress.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, for support of this research at the University of New Hampshire (No. PRF 3182-ACl, 3), and the National Science Foundation (No. NSF GP 10739) for support at Tulane University.

(18) NSF Undergraduate Summer Research Participant, 1969.

James D. Morrison,* Robert E. Burnett
Department of Chemistry, University of New Hampshire
Durham, New Hampshire 03824

Adam M. Aguiar, Cary J. Morrow, Carol Phillips[18]
Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

Received November 16, 1970

3,4-Pyridyne and Its Dimer

Sir:

We report a study of gaseous 3,4-didehydropyridine[1] or 3,4-pyridyne (I), and its unimolecular decomposition and dimerization to 2,6- (or 2,7-) diazabiphenylene (II).

Solid pyridine-3-diazonium-4-carboxylate[2] was photolyzed neat. The reaction was monitored by time-of-flight (TF) mass spectroscopy and kinetic ultraviolet spectroscopy. Gaseous products were separated by low-temperature sublimation and analyzed by mass spectroscopy. Solids were separated by glc.

Pyridine-3-diazonium-4-carboxylate upon photolysis decomposes to CO_2, N_2, and I (by inference from the formation of II). We observe that I may undergo any of three related unimolecular reactions as well as dimerization to II. These are: (a) rearrangement to a stable product of mass 77 with a prominent fragment at 50 (77 is presumably β-ethynylacrylonitrile,[3] or one of its stable isomers, one bond having broken in the pyridine ring); (b) decomposition to HCN (27) and $HC{\equiv}CC{\equiv}CH$ (50) (two bonds broken); and (c) decomposition and rearrangement to C_2H_2 (26) and $HC{\equiv}CCN$ (51) (two bonds broken).

Kinetics were followed by TF mass spectroscopy. Initial products and intermediates appeared at about 100–150 μsec after initiation. The first mass spectral sweep showing products contains masses 28 and 44, N_2 and CO_2. Mass 77 appears, as a parent peak, together with 51, 50, 27, 26, and others in the first or second product spectrum. At ionizing energies of 25 and 50 eV, masses 51, 50, 27, and 26 all appear prominently. Thus mass 77 at early times may correspond to I, β-ethynylacrylonitrile, or a combination of the two. Likewise, 51, 50, 27, and 26 may be parents, fragments, or both. Mass 154 (II) appears at the same time as mass 77, increases in intensity for approximately 100 μsec, and then levels off. In the same time interval, 77 is approximately constant. Quantitative measurements of the dimerization rate constant are now in progress.

The differences between gaseous benzyne chemistry and 3,4-pyridyne chemistry are striking. Benzyne, under similar conditions, dimerizes to biphenylene in good yield[4] ($\sim$35%) and shows no unimolecular decomposition.[5] I dimerizes in poor yield ($\sim$5%) and shows three channels of unimolecular decay. Energetics seem to explain the differences: the resonance energy of pyridine is about 15 kcal/mol less than that of benzene; the C–N bond is about 10 kcal/mol weaker than the C—C bond; and the $C{\equiv}N$ bond is about 13 kcal/mol stronger than the $C{\equiv}C$ bond. The net difference of $\sim$38 kcal/mol opens many bond-breaking channels in I which are energetically impossible in benzyne.

To test the unimolecular reaction hypothesis, products were studied as a function of pressure of inert gas (N_2). One expects that, with increasing pressure of N_2, I would be stabilized, unimolecular reactions would be quenched, and the yield of II would increase.

II was produced in 5% yield with no added gas, 12% with one-third atmosphere of N_2, and 11% with two-thirds atmosphere. All absolute concentrations of gaseous products decreased with added N_2. The ratio of C_2H_2:$HC{\equiv}CCN$ (uncorrected for sensitivity) remained approximately constant: 1.2 with no added N_2 and 1.6 with two-thirds atmosphere—compatible with I decomposing to $C_2H_2 + HC{\equiv}CCN$. The ratio of C_4H_2:$HC{\equiv}CCN$ (uncorrected for sensitivity or fragmentation of 77) was approximately 2 at all pressures. Thus the two decomposition modes are about equally likely and are affected similarly by pressure. The ratio of diacetylene to β-ethynylacrylonitrile was approximately 6.5 at all pressures. The ratio of HCN:$HC{\equiv}CC{\equiv}CH$ was 2.2 with no added N_2 and 5.6 at two-thirds atmosphere of N_2. This change was due to the larger decrease in the yield of C_4H_2 with added N_2. Since the C_4H_2:$HC{\equiv}CCN$ ratio remained approximately constant it was concluded that HCN was produced in another reaction.

Two other possible sources of HCN are another primary reaction or unimolecular decay of II. No product compatible with an additional primary reaction was observed. At 10 atmospheres of N_2 or CH_4, excess HCN was still present and there was no increase in II with 10 atmospheres of N_2. II initially contains approximately 135 kcal/mol (estimated from bond energies). This suggests an immediate loss of HCN in some dimerizations.

II is a white solid, mp 169–169.5°. A high-resolution mass spectrum shows a parent (100% base peak) at 154.0544 ($C_{10}H_6N_2$ = 154.0531) with metastables at 104.8, 78.8, and 54.8 corresponding to $154^+ \rightarrow 127^+ + 27$, $127^+ \rightarrow 100^+ + 27$, and $100^+ \rightarrow 74^+ + 26$, respectively. Fragments at 127.0429 (C_9H_5N = 127.0422), 100.0301 (C_8H_4 = 100.0313), and 74.0134 (C_6H_2 = 74.0156) correspond to the loss of two molecules of HCN and one of C_2H_2. The strongest band in the ir spectrum (KBr pellet) is at 838 cm^{-1} characteristic of a 1:2:4 trisubstituted benzene.[6] No $C{\equiv}N$ stretching vibrations were present. The uv spectrum (in methanol) contains maxima at 338 (log

---

(1) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, Chapter 6.

(2) T. Kauffmann and F. P. Boettcher, *Chem. Ber.*, **95**, 949 (1962).

(3) M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Lett.*, **26**, 2947 (1966).

(4) R. S. Berry, G. N. Spokes, and R. M. Stiles, *J. Amer. Chem. Soc.*, **82**, 5240 (1960).

(5) Reference 1, p 257.

(6) W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 2666 (1958).