this synthetic method and to investigate the reaction mechanism.

Experimental Section

The general experimental procedure is as follows.

A. A Stoichiometric Reaction of Diaminocarbene Pd(II) Complex (1) with Ag$_2$O. A heterogeneous mixture of complex 1[9] (1 mmol) and Ag$_2$O (1 mmol) in benzene (10 ml) was stirred at room temperature for 2–4 hr. The reaction mixture was worked up by filtration to remove insoluble inorganic materials and solvent distillation in vacuo, leaving the desired carbodiimide as a sole product (76–96% yields) (Table I).

B. A Pd(II)Cl$_2$-Catalyzed Reaction of Amine and Isonitrile with Ag$_2$O. A heterogeneous mixture of primary amine (5 mmol), isonitrile (6 mmol), and Ag$_2$O (5 mmol) in benzene (10 ml) was stirred in the presence of Pd(II)Cl$_2$ (0.5 mmol) and molecular sieve (1.5 g) or anhydrous Na$_2$SO$_4$ (1.5 mmol) at room temperature or an elevated temperature. The reaction mixture was filtered to remove inorganic materials, and then distilled in vacuo to give the corresponding carbodiimide in good yield (Table II).

Registry No.—Ag$_2$O, 20667-12-3.

References and Notes

(1) (a) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972); (b) E. O. Fischer and A. Maasböl, *Chem. Ber.*, **100**, 2445 (1967); (c) R. Aumann and E. O. Fischer, *Angew. Chem.*, **79**, 900 (1967).

(2) (a) M. Sakai, H. H. Westburg, H. Yamaguchi, and S. Masamune, *J. Am. Chem. Soc.*, **93**, 4611 (1971); (b) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971); (c) R. Noyori, H. Kawauchi, and H. Takaya, *Tetrahedron Lett.*, 1749 (1974); (d) W. R. Moser, *J. Am. Chem. Soc.*, **91**, 1135, 1141 (1969); (e) D. J. Cardin, M. J. Doyle, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, **927** (1972); (f) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).

(3) T. Saegusa, Y. Ito, and S. Kobayashi, *Tetrahedron Lett.*, 6121 (1966).

(4) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *Tetrahedron Lett.*, 521 (1967).

(5) T. Saegusa, S. Kobayashi, K. Hirota, Y. Okumura, and Y. Ito, *Bull. Chem. Soc. Jpn.*, **41**, 1638 (1968).

(6) Y. Ito, Y. INUBUSHI= M. Zenbayashi, S. Tomita, and T. Saegusa, *J. Am. Chem. Soc.*, **95**, 4447 (1973).

(7) Y. Ito, I. Ito, T. Hirao, and T. Saegusa, *Synth. Commun.*, **4**, 97 (1974).

(8) (a) J. E. Parks and A. L. Balch, *J. Organomet. Chem.*, **71**, 453 (1974); (b) Y. Ito, T. Hirao, and T. Saegusa, *ibid.*, **82**, C47 (1974).

(9) B. Crociani, T. Boschi, and U. Belluco, *Inorg. Chem.*, **9**, 2021 (1970).

(10) (a) J. J. Monagle, T. W. Campbell, and H. F. McShane, Jr., *J. Am. Chem. Soc.*, **84**, 4288 (1962); (b) W. Neumann and P. Fischer, *Angew. Chem.*, **74**, 801 (1962); (c) C. L. Stevens, G. H. Singhal, and A. B. Ash, *J. Org. Chem.*, **32**, 2895 (1967).

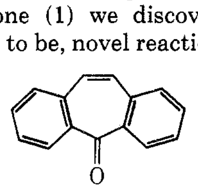
A Novel Reaction of 5*H*-Dibenzo[*a,d*]cyclohepten-5-one with Hydrazine

Sandor Barcza, Gary M. Coppola,
Goetz E. Hardtmann,* and Ruth I. Mansukhani

Chemistry Research Department, Sandoz, Inc.,
East Hanover, New Jersey 07936

Received May 15, 1975

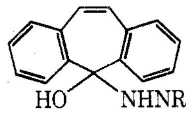
Recently, various transannular reactions producing a variety of bridged dibenzsuberans have been reported.[1-3] During the course of our investigation into the reactions of dibenzocycloheptenone (1) we discovered an interesting and, what we believe to be, novel reaction.



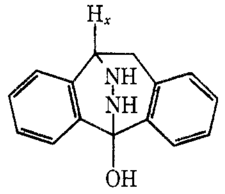
1

When 1 was treated with anhydrous hydrazine at elevated temperature, a stable product was isolated whose infrared spectrum lacked a carbonyl absorption and elemental composition indicated an addition of hydrazine without concomitant loss of water.

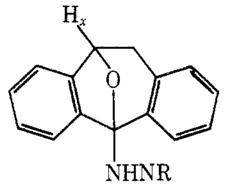
Four possible structures can be postulated for such a product (**2a–5a**). Structure **2** can be ruled out because of the unlikelihood of its stability and the distinct absence of the olefinic proton signal in the NMR.



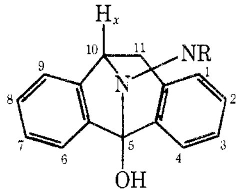
2



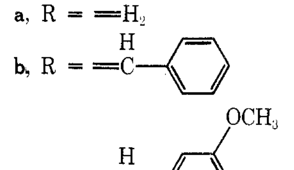
3



4

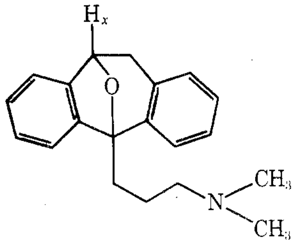


5



We attempted to elucidate the structure of the adduct by further functionalizing the compound on the hydrazino group. It was found that treatment of the adduct with various aldehydes produced corresponding hydrazones in good yields (R = **b** and **c**).[4] Disappointingly, no firm structure proof was obtained as not even the use of shift reagents in proton NMR led to a clear conclusion.

Therefore, it was then necessary to compare the NMR spectra of all the compounds to that of a known model[5] **6**. A noticeable difference was observed in the shift of the low-field H$_x$ doublet of AMX spin system of **6** in comparison to our adduct. Upon conversion of the adduct to the benzylidene derivatives, H$_x$ is drastically shifted, appearing close to that of the model compound **6**. The respective chemical shift values of H$_x$ are 5.55 ppm for compound **6**, 5.36 ppm for **b**, 5.26 ppm for **c**, and 4.38 ppm for **a**.



6

The large shift difference noticed when the benzylidene derivative (R = **b, c**) and model compound **6** are compared to the adduct where R = H$_2$ can be rationalized by two possible explanations: (1) introduction of the benzylidene function into the substrate causes a rearrangement from the N-bridged structure **3** or **5** to the O-bridged structure **4**, or (2) the benzylidene function is directly added to the N-NH$_2$ bridge in structure **5a**.

To distinguish between these two possibilities the structure elucidation was continued with the help of ^{13}C NMR spectroscopy. Should the first explanation be correct, a downfield shift of the bridgehead carbon atom at position 10 would be expected because of the replacement of the nitrogen (bonded to this carbon) with the more strongly deshielding oxygen. If the second explanation is correct, carbon atom 10 would receive an additional γ carbon and therefore experience an upfield shift owing to the γ effect. It was found that introduction of the benzylidene function caused an upfield shift of the C-10 doublet from 63 to 59 ppm, indicating that **5a** is the most probable structure.

It was also observed that the proton and carbon spectra of **5a** were broadened at room temperature. Quantitative work on temperature dependence was not performed, but sharp spectra were obtained at 80–120°. The origin of broadening may be either slow flipping of the seven-membered carbocyclic ring[6] or a slow pyramidal inversion of the bridge nitrogen. Formation of the benzalhydrazone derivative would be expected to flatten the nitrogen by conjugation, but encumber ring flipping somewhat. The fact that sharp spectra on the hydrazones were obtained at room temperature suggests that in their precursors slow pyrimidal inversion rather than slow ring flipping was responsible for broadening.

Experimental Section[7]

Melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected. The infrared spectra were recorded on Perkin-Elmer Model 237 and 457 spectrophotometers. All pure materials were run as Nujol or halocarbon mulls. Nuclear magnetic resonance spectra were determined on Varian A-60 and T-60 spectrophotometers using tetramethylsilane as an internal reference. ^{13}C NMR spectra were determined on a Varian XL-100 spectrophotometer. Mass spectra were recorded on an LKB 9000 spectrometer.

Interpretation of NMR data: δ, chemical shift in parts per million (multiplicity, number of protons, coupling constant, proton assignment); s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

12-Amino-10,11-dihydro-5,10-imino-5*H*-dibenzo[*a,d*]cyclohepten-5-ol (5a). A suspension of 30.0 g of 1 in 150 ml of anhydrous hydrazine was refluxed for 4 hr. The excess hydrazine was removed under reduced pressure and methylene chloride was added to the residue. The resulting solid was filtered, washed twice with ethanol and then with ether to yield 26.8 g (77%) of **5a**, mp 191–194°. An analytical sample was recrystallized from methanol: mp 192–194°; NMR (Me_2SO) δ 7.8–6.5 (m, 8), 4.4 (d, 1, J = 5 Hz, NCH), 3.4 (q, 1, J = 5 Hz, 17, CHH′), 3.5 (s, broad, 3, OH, NH_2), 2.4 (d, 1, J = 17 Hz, CHH′); ^{13}C NMR (Me_2SO) δ 62.8 (CH), 28.1 (CH_2).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.6; H, 5.9; N, 11.8. Found: C, 75.2; H, 6.3; N, 12.0.

12-Benzylideneamino-10,11-dihydro-5,10-imino-5*H*-dibenzo[*a,d*]cyclohepten-5-ol (5b). To a hot solution of 0.5 g of **5a** in 30 ml of methanol was added 1.0 ml of benzaldehyde. The solution was refluxed for 5 min. Upon cooling, a crystalline precipitate formed and was filtered and washed twice with ethanol and then with ether to yield 0.55 g (81%) of **5b:** mp 158–161°; NMR (Me_2SO) δ 8.3 (s, 1, N=CH), 7.9–6.7 (m, 13), 5.4 (d, 1, J = 4 Hz, NCH), 3.5 (m, 1, J = 4, 17 Hz, CHH′), 3.4 (s, 1, OH), 2.5 (d, 1, J = 17 Hz, CHH′); ^{13}C NMR (Me_2SO) δ 59.8 (CH), 27.9 (CH_2).

Anal. Calcd for $C_{22}H_{18}N_2O$: C, 81.0; H, 5.6; N, 8.6. Found: C, 81.1; H, 5.7; N, 8.4.

12-(3,4-Dimethoxybenzylidene)amino-10,11-dihydro-5,10-imino-5*H*-dibenzo[*a,d*] cyclohepten-5-ol (5c). To a hot solution of 10.0 g of **5a** in 400 ml of methanol was added 5.0 g of 3,4-dimethoxybenzaldehyde. The solution was refluxed for 6 hr (after 1 hr a precipitate forms). Upon cooling, the solid was filtered and washed twice with methanol and then with ether to yield 9.0 g (56%) of **5c:** mp 152–155°; NMR (Me_2SO) δ 8.2 (s, 1, N=CH), 7.9–6.8 (m, 11), 5.3 (d, 1, J = 4 Hz, NCH), 3.7 (s, 6, OCH_3), 3.4 (s, 1, OH), 3.35 (q, 1, J = 4, 17 Hz, CHH′), 2.4 (d, 1, J = 17 Hz, CHH′).

Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.6; H, 5.7; N, 7.3. Found: C, 75.0; H, 5.9; N, 7.3.

Acknowledgments. The authors wish to thank Mrs. Alicia Kahle and Mrs. Susan DiCataldo for running all NMR spectra and Mr. William Bonkoski and associates for performing the microanalyses. The authors also wish to express their gratitude to Dr. Byron H. Arison (Merck Institute) for supplying spectral data for compound 6.

Registry No.—**1**, 2222-33-5; **5a**, 55991-62-3; **5b**, 55991-63-4; **5c**, 55991-64-5; hydrazine, 302-01-2; benzaldehyde, 100-52-7; 3,4-dimethoxybenzaldehyde, 120-14-9.

References and Notes

(1) T. A. Dobson, M. A. Davis, A. M. Hartung, and J. M. Manson, *Can. J. Chem.*, **46**, 2843 (1968).

(2) G. N. Walker, D. Alkalay, A. R. Engle, and R. J. Kempton, *J. Org. Chem.*, **36**, 466 (1971).

(3) G. N. Walker and A. R. Engle, *J. Org. Chem.*, **37**, 4294 (1972).

(4) Compound **3** would not be expected to react with a carbonyl compound per se. A rearrangement during the hydrazone formation cannot be ruled out.

(5) M. E. Christy, Belgian Patent 649,168 (1964); *Chem. Abstr.*, **64**, 8148*f* (1966).

(6) M. S. Puar, H. L. Yale, and A. I. Cohen, *Org. Magn. Reson.*, **6**, 106 (1974).

(7) No attempts were made to optimize yields of the reactions.

Changing the Reaction Paths of a Metathesis Catalyst

Henry R. Menapace,* N. A. Maly, J. L. Wang, and L. G. Wideman

Contribution No. 523 from Research Division,
The Goodyear Tire & Rubber Company, Akron, Ohio 44316

Received May 9, 1975

Numerous papers and several reviews have been published on the metathesis of olefins.[1–7] This reaction has also been called olefin "dismutation" or "disproportionation", and involves breaking carbon double bonds and rejoining the fragments: $2RCH{=}CHR' \rightleftharpoons RCH{=}CHR + R'CH{=}CHR'$. We have observed a new phenomenon in catalysis of this kind: the transformation of a metathesizing system into a dimerizing system simply by increasing the amount of aluminum component in the catalyst. Ligands also play an important role in such processes, completely changing the course of the reaction.

Table I shows the importance of the order in which reagents are combined in this metathesizing system.

Table I
Metathesis of Mixed 2-Pentenes
(0.2 m*M* WCl_6, 10 m*M* olefin, 0.3 m*M* $PhNH_2$, 0.3 m*M* $Et_3Al_2Cl_3$)

Injection order[a]	1	2	3	4
Conversion, %	55	51	50	61
Selectivity to 3-hexene, mol %	46	50	53	41
Selectivity to 2-butene, mol %	36	40	44	28
Total selectivity, %	82	90	97	69
2-Pentene, *trans-/cis*[b]	4.9	5.6	5.2	6.1
2-Butene, *trans-/cis-*	2.5	2.0	2.0	2.6

[a] Injection order: 1, W + 2-pentenes (2-P) + aniline ($PhNH_2$) + Al; 2, W + $PhNH_2$ + 2-P + Al; 3, W + $PhNH_2$ + Al + 2-P; 4, W + Al + $PhNH_2$ + 2-P. [b] Initial trans/cis ratio of 2-pentene was 0.59.

Most critical is the interaction of WCl_6 and the aniline ligand: nearest approach to theoretical equilibration was attained when this interaction was most direct, as in injection orders 2 and 3. The poorest selectivity was observed in order 4, where $Et_3Al_2Cl_3$ had reacted with WCl_6 before ani-