Synthetic Reactions by Complex Catalysts. XXXVII. A Novel and Versatile Method of Carbodiimide Synthesis. Oxidation of Carbene Palladium(II) Complex with Silver Oxide

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For several years, there has been much interest in metalcarbene complexes.¹ However, most studies are concerned with the isolation and characterization of stable metal-carbene complexes¹ and with the mechanism of reactions involving transient metal-carbene intermediates.² Studies of the synthetic applications of metal-carbene complexes are scanty. In preceding papers, we have reported that Cu(I), Ag(I), and Au(III) salts catalyze the insertion reactions of isonitriles with amines,³ alcohols,⁴ and thiols,⁵ and that Ag(I),⁶ Cu(I),⁶ and Pd(II)⁷ salts catalyze the cyclization reaction of isonitriles with diamines, amino alcohols, and amino thiols. It has been established⁸ that all these reactions involved the heteratom-substituted carbene-metal complexes as the key intermediates.

Herein we wish to report a versatile synthetic method for symmetrical and unsymmetrical carbodiimides (2), in which the N,N'-disubstituted diaminocarbene Pd(II) complex (1)⁹ prepared from primary amine and Pd(II)Cl₂(RNC)₂ is oxidized with Ag₂O (Table I). The isolation of carbene Pd(II) complex 1 is not necessarily required for the carbodiimide synthesis. In practice, the synthesis of carbodiimides is accomplished just by stirring a heterogeneous mixture of primary amine, isonitrile, Ag₂O, and a catalytic amount of $Pd(II)Cl_2$ at room temperature or an elevated temperature (Table II). Thus, the present reaction presents a general convenient preparative method of carbodiimide.



In the stoichiometric reaction of diaminocarbene Pd(II) complex (1) with Ag₂O, the desired carbodiimide (2) was obtained as a sole product (76–96% yields) (Table I). In the $Pd(II)Cl_2$ -catalyzed reaction of amine and isonitrile with Ag₂O, on the other hand, product of carbodiimide (2) was always accompanied by the corresponding urea (RNHCONHR'), which is derived from the carbodiimide (2) and water produced. The use of molecular sieve or anhydrous Na₂SO₄ in the reaction helped to exclude the formation of the urea.

The products of carbodiimides were identified by elemental analysis, ir (an absorption at 2110 cm⁻¹ characteristic of -N=C=N-), NMR, and a chemical conversion to the corresponding ureas which were compared with the authentic samples.

The previous carbodiimide synthesis¹⁰ from isocyanate requires phosgene in the preparation of precursor of isocyanate. This new method has the advantages of the higher yields of carbodiimides and the simplicity of manipulation. Further studies are in progress to extend the potential of

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Carbene Pd(II) complex 1 ^a	Reaction ^b time, hr	Product, (%) c, d
$PdCL_{(t-C_{t}H_{y}NC)}\left(:C \underbrace{NHC_{t}H_{y}, t}_{NHC_{t}H_{y}, \eta}\right)$	3	$t-C_4H_9-N=C=N-C_4H_9-n (82)$
$PdCL(t - C_{1}H_{9}NC) \left(C < \frac{NHC_{1}H_{9} + t}{NHC_{6}H_{5}} \right)$	4	$t-C_4H_9$ —N=C=N-C ₆ H ₅ (93)
$PdCl_{2}(t \cdot C_{i}H_{u}NC) \left(:C \leq \frac{NHC_{i}H_{u} \cdot t}{NHCH_{i}CH = CH_{u}}\right)$	2	$t-C_4H_9$ —N=C=N-CH ₂ CH=CH ₂ (76)
$\operatorname{PdCl}_{2}(t - C_{4}H_{0}\operatorname{NC}) \left(:C \underbrace{\operatorname{NHC}_{H_{0}} \cdot t}_{\operatorname{NHCH}(CH_{4})\operatorname{CO}_{2}C_{2}H_{5}}\right)$	4	$t-C_4H_3$ N=C=N-CH(CH_3)CO_2C_2H_5 (96)

 Table I

 Reaction of N.N'-Disubstituted Diaminocarbene Pd(II) Complex 1 with Ag2O

^a Registry numbers are, respectively, 56195-59-6, 56195-63-2, 56195-64-3, and 56195-58-5. ^b 20°. ^c Yields were determined by GLC. ^a Registry numbers are, respectively, 56195-54-1, 2219-34-3, 56195-55-2, and 56195-56-3.

 Table II

 Synthesis of Carbodiimides

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 Pd(IDCL)

RNH_2	+	R'NC	+	Ag_2O	-H ₂ O	RN = C = NR'	+	RNHCONHR'	
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		Reaction b				
Amine ^a (RNH ₂)	Isonitrile (R'NC)	Temp, ^o C	Time, hr	$RN = C = NR', \%^{\circ}$	RNHCONHR', %	
$n-C_4H_9NH_2$	$t - C_4 H_9 NC^d$	20	3	93 (85) ^e	< 3	
$c - C_6 H_{11} N H_2$	$t-C_5H_9NC$	20	4	94	0	
$c - C_6 H_{11} N H_2$	$c - C_6 H_{11} N C^f$	67	0.5	77 (68) ^e	0	
$C_6H_5NH_2$	$t - C_4 H_9 NC$	80	4	72	0	
$C_6H_5NH_2$	$t - C_4 H_9 NC$	80	3 ^{<i>s</i>}	77	<3	
CH2=CHCH2NH2	$t-C_4H_9NC$	20	3	77	<3	
CH ₃ CH(NH ₂)CO ₂ C ₂ H ₅	t-C ₄ H ₉ NC	20	7	80	8	

^a Registry numbers are, respectively, 109-73-9, 108-91-8, 62-53-3, 107-11-9, 56195-57-4, 630-18-2, and 766-05-2. ^b No attempts have been made to optimize the reaction conditions. Molecular sieves were added as a dehydrating agent. ^c Yields were determined by GLC. ^d Registry number, 1202-53-5. ^e Isolated yields. ^f Registry number, 538-75-0. ^g Anhydrous sodium sulfate was added in place of molecular sieves.

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_2O . A heterogeneous mixture of complex 19 (1 mmol) and Ag₂O (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)Cl₂-Catalyzed Reaction of Amine and Isonitrile with Ag₂O. A heterogeneous mixture of primary amine (5 mmol), isonitrile (6 mmol), and Ag₂O (5 mmol) in benzene (10 ml) was stirred in the presence of Pd(II)Cl₂ (0.5 mmol) and molecular sieve (1.5 g) or anhydrous Na₂SO₄ (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.—Ag₂O, 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, and K. Hirota, Tetrahedron Lett., 521
- T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, Tetrahedron Lett., 521 (4)
- (1967). (1907).
 T. Saegusa, S. Kobayashi, K. Hirota, Y. Okumura, and Y. Ito, *Bull. Chem. Soc. Jpn.*, **41**, 1638 (1968).
 Y. Ito, Y. INUBUSHI= M. Zenbayashi, S. Tomita, and T. Saegusa, *J. Am. Chem. Soc.*, **95**, 4447 (1973).
 Y. Ito, I. Ito, T. Hirao, and T. Saegusa, *Synth. Commun.*, **4**, 97 (1974). (5)
- (6)

 Y. Ito, I. Ito, I. Hirao, and I. Saegusa, Synth. Commun., 4, 97 (1974).
 (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).
 (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. 20, 2080 (1067) Chem., 32, 2895 (1967).

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

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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.



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.



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 $(\mathbf{R} = \mathbf{b} \text{ and } \mathbf{c}).^4$ 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 model⁵ 6. A noticeable difference was observed in the shift of the low-field H_x doublet of AMX spin system of 6 in compari-



son 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**.

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-NH₂ bridge in structure 5a.

To distinguish between these two possibilities the structure elucidation was continued with the help of ¹³C NMR spectroscopy. Should the first explanation be correct, a