Table I. Self-Induced Chemical Shift Nonequivalence ($\Delta\delta$) of the Amide NH Proton of **1** in (0.1 M) CCl_4 Solution[a]

	C^b							
		0.9^c			0.7^c			
temp, °C	1.0	$\delta_L{}^d$	$\delta_D{}^d$	$\Delta\delta^e$	$\delta_L{}^d$	$\delta_D{}^d$	$\Delta\delta^e$	0.5^f
20	6.127 (0)	0.011	0.097	0.086	0.028	0.071	0.043	0.051
0	6.389 (0)	0.010	0.143	0.133	0.032	0.098	0.066	0.073
−20	6.729 (0)	0.004	0.163	0.159	0.021	0.100	0.079	0.084

[a] NMR spectra were recorded at 200 MHz with Me_4Si (δ 0.00) as the internal standard. Chemical shifts of the amide NH doublets were determined by a homodecoupling technique, with irradiation of $^\alpha$H of the solute **1**. [b] Relative content of the L enantiomer in the mixtures. [c] Identical spectra were obtained in the reverse enantiomeric ratio (C of 0.1 for 0.9, C of 0.3 for 0.7), but assignment of the two lines has been reversed. [d] δ_D and δ_L values exhibit upfield deviation for the D and L enantiomers in enriched mixtures, respectively, from the homo shift of the pure L enantiomer (C 1.0). [e] $\Delta\delta = \delta_D - \delta_L$. [f] The sense of nonequivalence has vanished.

functioning to produce the latter bond showed a difference in the local magnetic environment, as was evident by a comparison of the racemic and pure enantiomeric solutions. This NH--O═C ester bond is thus a primary driving force for diastereomeric associations. We expect the observed sense of nonequivalence to be induced through formation of diastereomeric dimers in which associative interactions are the bidentate NH--O═C ester hydrogen bonds. Figure 2 illustrates a structure of the homochiral dimer (S_lS_l) as one of the diastereomeric dimers.

The magnitude of self-induced nonequivalence ($\Delta\delta$) was enhanced dramatically with a decrease in sample temperature. This means that lower temperatures cause an increase in the fractional population of diastereomeric species in self-association equilibria. The chemical shift deviation from the homo shift (δ_L) in the NH resonance assigned to the L enantiomer in enriched mixtures increased linearly while that of the D enantiomer (δ_D) decreased linearly with a decrease in C values at 20 °C, as evident from Table I. This linear δ–C relationship indicates the proportion of homochiral or heterochiral dimers to certainly be under statistical control.[6] An increase in $\Delta\delta$ while lowering the temperature was accompanied, however, by deviation from this linearity and the δ–C relationship gave a concave line approaching the homo shift at each temperature. This behavior reflects the existence of additional stability imparted to the homochiral dimer in diastereomeric associations and, by virtue of the difference in their stabilities, an enhancement of differences in the fractional populations of these species at lower temperatures. The linear δ–C relationships obtained at 20 °C thus suggest that the association stereoselectivity explicitly observed at lower temperatures is still dormant at this temperature. IR spectra confirmed this stability difference in diastereomeric dimers. L-Enantiomeric solutions provide stronger intensities of the hydrogen-bonded NH stretching band (3360 cm^{-1})[7] in their amide groups than those in the racemic mixtures at concentrations greater than 0.01 M in CCl_4 (ca. 23 °C).[8]

The NMR spectra of unequal mixtures of the congener *N*-acetylvaline ethyl ester (**2**) in CCl_4 revealed no chemical shift nonequivalence at 20 °C. Lower sample temperatures had little effect on the shift difference between the D and L enantiomers of **2** in the enriched mixtures, which was as high as 0.078 ppm even for an enantiomeric ratio of 1:9 (0.1 M) at −20 °C. The marked reduction in the magnitude of $\Delta\delta$ by substitution of the *tert*-butyl with an ethyl group demonstrates that the chemical shift nonequivalence observed for the chiral solute **1** depends strongly on the steric bulkiness of *tert*-butyl substituent. It appears likely that steric bulkiness contributes to preponderant dimer formation in self-association equilibrium as well as imparts greater intrinsic magnetic nonequivalence between the nuclei of diastereomeric dimers.

Acknowledgment. We gratefully acknowledge the capable assistance of Dr. Kinzou Watanabe in carrying out this research and also thank Toshikazu Ohkuma for his many instructive comments.

Registry No. L-**1**, 75552-82-8; D-**1**, 75552-81-7; L-**2**, 2382-78-7; D-**2**, 92998-92-0.

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(8) Optically active and racemic **1** samples showed stretching vibration of hydrogen-bonded NH as well as that of nonhydrogen-bonded NH (3460 cm^{-1}) in their amide groups at concentrations greater than 0.01 M: Abs(bonded NH)/Abs(nonbonded NH) = 2.5/7.2 for the L enantiomer and 2.0/7.15 for the racemate in (0.1 M) CCl_4 solution.

(9) *N*-Acetyl-L-valine ethyl ester, $[\alpha]^{30.5}{}_D$ −30.8° (*c* 1.00, ethanol) and its D enantiomer $[\alpha]^{30.5}{}_D$ +30.2° (*c* 1.00, ethanol).

A Novel Photocatalytic Process of Amine N-Alkylation by Platinized Semiconductor Particles Suspended in Alcohols

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Received July 17, 1985

Among many reactions being photocatalyzed by suspended semiconductor particles, several processes are applicapable to synthesis in organic solvents.[1-7] Our recent report has demonstrated the preparation of symmetrical secondary amines from primary amines using photocatalysis by platinized titanium dioxide (TiO_2/Pt) suspension in water.[8] The present paper describes photocatalytic preparation of unsymmetrical secondary and tertiary amines by TiO_2/Pt suspended in a variety of alcohols as solvents. The alcohols were potent N-alkylation reagents, in contrast to the aqueous system in which the substrate amines acted as N-alkylation reagents. This N-alkylation proceeds efficiently at room temperature, providing an advantage over the thermal catalytic processes by nickel,[9] rhodium,[10] and ruthenium.[11-13]

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Table I. Photocatalytic N-Alkylation of Amines by TiO_2/Pt Suspended in Alcohols under Ar at Room Temperature[a]

			yield/%[b]		
substrate	solvent	irradn/h	sec amine	tert amine	efficiency[c]/%
$C_6H_5CH_2NH_2$	CH_3OH	10	15.8	27.8	63.8
$C_6H_5CH_2NH_2$	CH_3CH_2OH	5[d]	84.4	2.4	87.3
$C_6H_5CH_2NH_2$	CH_3CH_2OH	10	6.8	74.1	62.2
$C_6H_5CH_2NH_2$	CH_3CH_2OH	48[e]	77.9	16.2	41.4
$C_6H_5CH_2NH_2$	CH_3CH_2OH	10[f]	19.3	3.2	37.2
$C_6H_5CH_2NH_2$	CH_3CH_2OH	10[g]	9.5	77.8	55.8
$C_6H_5CH_2NH_2$	$CH_3(CH_2)_3OH$	20	72.0	≃0	70.6
$C_6H_5CH_2NH_2$	$(CH_3)_2CHOH$	10	36.3	≃0	52.6
$C_6H_5NH_2$	CH_3OH	20	0.6	≃0	0.6
$C_6H_5NH_2$	CH_3CH_2OH	20	8.1	≃0	13.9
$CH_3(CH_2)_3NH_2$	CH_3OH	5	9.4	≃0	25.3
$CH_3(CH_2)_3NH_2$	$CH_3(CH_2)_3OH$	20	68.5	≃0	70.7
$(CH_3)_2CHNH_2$	$(CH_3)_2CHOH$	20	13.5	≃0	8.8
$(CH_3)_2CHNH_2$	$C_6H_5CH_2OH$	20	4.9	≃0	4.5
$C_6H_5CH_2NHCH_3$	CH_3OH	5		84.7	72.9
piperidine	CH_3OH	20		93.4	73.8
piperidine	CH_3CH_2OH	20		75.8	49.9

[a] Amine (100 μmol), alcohol (5.0 cm^3), and catalyst (52.5 mg) were placed in a test tube and irradiated under Ar by 400-W high-pressure mercury arc. [b] Based on the starting amine. [c] Molar ratio of H_2 used for N-alkylation (reactions 3 and 4). [d] Quantum efficiency was evaluated as ca. 2% by using a Blak-Ray J-221 Ultraviolet Meter on the assumption that the incident light consists of photons at 365 nm. [e] A 5.0-mg portion of TiO_2/Pt catalyst was used. [f] CdS with 5 wt % of Pt black (52.5 mg) was used as a catalyst. [g] Rutile TiO_2 with 5 wt % Pt black (52.5 mg) was used as a catalyst.

The preparation of TiO_2/Pt from anatase TiO_2 (Merck) and Pt (5 wt %) black and the photoreaction procedure are described previously.[8] Alcohols and amines used were of the highest available purity.

Irradiation ($\lambda_{ex} > 300$ nm) of TiO_2/Pt suspended in alcohols containing primary amines under Ar at room temperature led to N-alkylation and N,N-dialkylation of amines together with formation of small amount of H_2 and dehydrogenated products of the alcohols, aldehydes, or ketones. The other products derived from amines were negligible. The incorporated alkyl chains clearly originated from the solvent alcohols rather than from the substrate amines; e.g., *N*-ethyl and *N*-isopropyl derivatives were produced in ethanol and 2-propanol, respectively. On the other hand, tertiary alcohol such as 2-methyl-2-propanol did not give appreciable amount of N-alkylated products.

Among the primary amines used in the present study, benzylamine was N-alkylated most readily and aniline most slowly. The quantum efficiency of the N-alkylation of benzylamine, which is defined as the molar ratio of *N*-ethylbenzylamine to photon just incident upon the reaction vessel, was roughly estimated as 2%. Secondary amines, *N*-methylbenzylamine and piperidine, were comparably or more reactive than primary amines with similar structure and converted into tertiary amines almost quantitatively in methanol or ethanol. This suggests that the N,N-dialkylation of benzylamine in ethanol was due to the successive N-alkylation of *N*-ethylbenzylamine.

Neither the N-alkylation of amines nor the dehydrogenation of alcohols could be observed by irradiation with Pt-free TiO_2 or by thermal reaction with TiO_2/Pt. Furthermore, "catalytic" fashion of TiO_2/Pt was clearly demonstrated by the fact that a molar excess amount of *N*-ethyl and *N*,*N*-diethyl derivatives (total amount of 94.1 μmol) were obtained in the system containing 5 mg of TiO_2/Pt (TiO_2, 60 μmol; Pt, 1.3 μmol) (see Table I). The present N-alkylation is therefore accounted for by the well-documented photoelectrochemical process involving the creation of electron (e^-)-positive hole (h^+) pairs.[14-16] Alcohols, which are

$$TiO_2 + h\nu \rightarrow e^- + h^+ \tag{1}$$

in large excess compared with the substrate amines, are predominantly dehydrogenated via reduction of H^+ to H_2 at a Pt site[17,18] and hydrogen abstraction by $\cdot OH$.[19,20] Substrate amines are

$$R^1R^2CHOH \rightarrow R^1R^2C{=}O + H_2 \tag{2}$$

N-alkylated by way of extensively studied processes: condensation of photoproduct carbonyl with amine[21-24] and reduction of the resulting intermediate by H_2[22-25] liberated in situ. Pt-catalyzed

$$R^3NH_2 + R^1R^2C{=}O \rightarrow$$
$$(R^3NHC(OH)R^1R^2 \underset{-H_2O}{\rightarrow} R^3N{=}CR^1R^2) \xrightarrow{H_2/Pt} R^3NHCHR^1R^2 \tag{3}$$

$$R^3NHCHR^1R^2 + R^1R^2C{=}O \rightarrow$$
$$(R^3N(CHR^1R^2)C(OH)R^1R^2 \underset{-OH^-}{\rightarrow} R^3\overset{+}{N}(CHR^1R^2){=}CR^1R^2)$$
$$\xrightarrow{H_2/Pt} R^3N(CHR^1R^2)_2 \tag{4}$$

hydrogenation of a mixture of benzylamine (100 μmol) and acetaldehyde (200 μmol) proceeded to yield *N*-ethylbenzylamine and *N*,*N*-diethylbenzylamine under H_2 atmosphere (ca. 1000 μmol) at room temperature, indicating that reactions 3 and 4 occur in the dark without TiO_2.

The efficiency of these in situ hydrogenations, which was defined as the molar ratio of consumed H_2 (via reactions 3 and 4) to produced H_2 (via reaction 2), could be evaluated from the observed product yields (Table I); i.e.,

$$\text{efficiency}/\% = 100[1 - Y_{H_2}/(Y_{H_2} + Y_{sec} + 2Y_{tert})] \tag{5}$$

where, Y_{H_2}, Y_{sec}, and Y_{tert} denote the molar amounts of products H_2, secondary amine, and tertiary amine, respectively. The ef-

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ficiency exceeded 50% in most systems except the cases of aniline and isopropylamine.[26] The highest efficiency of 87.3% was obtained in the initial stage (5 h) of N-ethylation of benzylamine; prolonged irradiation (10 h) to yield *N,N*-diethylbenzylamine in this system decreased the efficiency to some extent (62.2%). Thus, only small amount of the byproducts, H_2 and carbonyl derivatives, remained because of the incorporation to the N-alkylated products.

Similar to platinized anatase TiO_2, CdS, and rutile TiO_2 (prepared by hydrolysis of titanium(IV) tetra-2-propoxide followed by calcination at 1000 °C in air) with 5 wt % of platinum black also exhibited the photocatalytic activity for the N-alkylation of amines (Table I); benzylamine was converted into *N*-ethylbenzylamine in ethanol solution. Consistent with the proposed reaction scheme the photocatalytic activity of several semiconductor powders was parallel to that for the dehydrogenation of alcohols. On the basis of this relationship, semiconductor materials with higher activities are now being explored.

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(26) The lower efficiency of N-alkylation of aniline may be attributed to the fact that *N*-ethylideneaniline in ethanol solution was little reduced in the dark under H_2 at room temperature even in the presence of Pt.

Reactions of Substituted Carbonyltungsten Carbyne Complexes with Dithiocarbamate Salts. Carbonyl Carbyne Coupling and Formation of Coordinated Thioaldehydes

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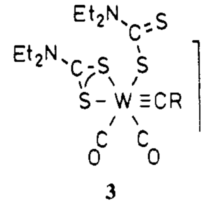
Received June 11, 1985

Group 6[19] transition-metal carbyne complexes stabilized by nitrogen donor ligands, $X(CO)_2(L)_2M{\equiv}CR^1$ (X = halide; L = nitrogeneous ligand; M = Cr, Mo, W), combine thermal stability, coordinative lability, and high reactivity of the carbyne ligand. We have recently developed efficient and simple methods for their preparation[2] and have begun to investigate their chemistry. We made use of the coordinative lability of $Cl(CO)_2(py)_2W{\equiv}CR$ (**1**) (py = pyridine; **1a**, R = C_6H_5; **1b**, R = CH_3) in the synthesis of stable (alkene)tungsten carbyne complexes.[3] Here we wish to report about reactions of **1** with diethyldithiocarbamate salts, $Kat^+Et_2NCS_2^-$ (Kat = Na, H_2NEt_2). These reactions involve not only facile ligand substitution reactions but also transformations of the carbyne ligands which depend strongly on the nature of the counterion.

Reaction of $Cl(CO)_2(py)_2W{\equiv}CPh$ (**1a**) with 2 equiv of sodium diethyldithiocarbamate, NaS_2CNEt_2, in THF results in the formation of a green anionic product which was isolated as its tetraethylammonium salt **2** (eq 1).[4] Complex **2** contains two dithiocarbamate ligands, a carbonyl ligand, and a phenylketenyl ligand.[4] The compound evidently was formed by substitution of the two pyridine ligands and the chloro ligand in **1a** by two dithiocarbamate ligands and a coupling step between one carbonyl and the carbyne ligand.[5] The immediate precursor of **2** is presumably an anionic intermediate **3** containing one chelating and one monodentate dithiocarbamate ligand. Coupling is then induced by chelation of the second dithiocarbamate ligand.[6]

$$\underset{\mathbf{1a}}{\mathrm{Cl(CO)_2(py)_2W{\equiv}CPh}} \xrightarrow[\substack{\text{2. NEt}_4\text{Cl,} \\ \text{CH}_2\text{Cl}_2}]{\substack{\text{1. 2NaS}_2\text{CNet}_2\text{,} \\ \text{THF}}} \underset{\mathbf{2},\ 96\%}{\mathrm{NEt_4[(Et_2NCS_2)_2(CO)W(PhCCO)]}} \quad (1)$$



3

In case the diethylammonium salt of the dithiocarbamate ligand is used in the reaction with **1**, the products formed are very different (eq 2). Again, 2 equiv of the ligand react with the metal complex, but the deep green products[7] **4** are neutral compounds

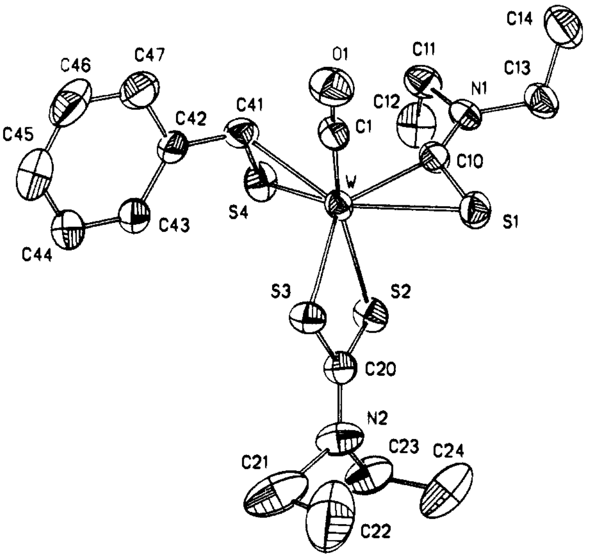


Figure 1. Molecular structure and labeling diagram for **4a**. W–C(1), 1.958 (6); W–C(10), 2.040 (6); W–C(41), 2.251 (6); W–S(1), 2.542 (2); W–S(2), 2.547 (2); W–S(3), 2.417 (2); W–S(4), 2.296 (2) Å. S(1)–W–C(10), 41.9 (2)°; C(1)–W–C(10), 87.0 (3)°; C(1)–W–S(1), 81.0 (2)°; S(2)–W–S(3), 70.6 (1)°; C(1)–W–S(2), 159.3 (2)°; C(1)–W–S(3), 95.7 (2)°; S(1)–W–S(3), 91.8 (1)°; C(1)–W–S(4), 113.5 (2)°; C(1)–W–C(41), 69.5 (2)°; S(1)–W–S(4), 148.0 (1)°; S(3)–W–S(4), 113.7 (1)°; W–S(4)–C(41), 66.1 (2)°.

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(4) **2**: mp 84 °C dec. Anal. Calcd for $C_{27}H_{45}N_3O_2S_4W$: C, 42.91; H, 6.00; N, 5.56. Found: C, 42.34; H, 6.07; N, 5.95. IR (cm^{-1}, CH_2Cl_2) ν_{CO} 1833 (vs), ν_{CCO} 1673 (m); ^{13}C NMR (ppm, $CDCl_3$) 234.9 (CO), 212.1, 210.3 ($Et_2N\mathit{C}S_2$), 201.7 (PhC*C*O), 187.9 (Ph*C*CO).

(5) Carbonyl–carbyne coupling reactions have been observed previously, for example: (a) Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Angew. Chem.* **1976**, *88*, 649–650; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632–633. (b) Kreissl, F. R.; Sieber, W. J.; Alt, H. G. *Chem. Ber.* **1984**, *117*, 2527–2530. (c) Fischer, E. O.; Filippou, A. C.; Alt, H. G. *J. Organomet. Chem.* **1984**, *276*, 377–385. (d) Churchill, M. R.; Wassermann, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766–768. (e) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474–4483. (f) Reference 15d.

(6) Dithiocarbamate-induced carbonyl–carbyne coupling has been observed in $Et_2NCS_2(CO)_2(Ph_2PCH_2CH_2PPh_2)WCCH_2Ph$.[5c]

(7) **4a**: mp 138–144 °C dec. Anal. Calcd for $C_{18}H_{26}N_2OS_4W$: C, 36.12; H, 4.38; N, 4.68; S, 21.43. Found: C, 36.05; H, 4.48; N, 4.99; S, 20.73. IR (cm^{-1}, CH_2Cl_2) ν_{CO} 1925 (s), ν_{Et_2NCS} 1526 (s), $\nu_{Et_2NCS_2}$ 1509 (s); ^1H NMR (ppm, $CDCl_3$) 5.42 (*H*CSPh); ^{13}C NMR (ppm, $CDCl_3$) 256.9 (J_{CW} = 111 Hz, $Et_2N\mathit{C}S$), 217.5 (J_{CW} = 151 Hz, CO), 214.6 ($Et_2N\mathit{C}S_2$), 57.0 (J_{CH} = 173 Hz, H*C*SPh). **4b**: mp 82–86 °C. Anal. Calcd for $C_{13}H_{24}N_2OS_4W$: C, 29.11; H, 4.48; N, 5.23; Found: C, 29.88; H, 4.83; N, 4.98. IR (cm^{-1} CH_2Cl_2); ν_{CO} 1913 (s), ν_{Et_2NCS} 1525 (s), $\nu_{Et_2NCS_2}$ 1509 (s); ^1H NMR (ppm, $CDCl_3$) 4.58 (9, *H*CSMe), 2.16 (d, J_{HH} = 5.76 Hz, $HCSC\mathit{H}_3$); ^{13}C NMR (ppm, $CDCl_3$) 256.6 (J_{CW} = 108 Hz, $Et_2N\mathit{C}S$), 217.9 (J_{CW} = 147 Hz, CO), 54.8 (d, J_{CH} = 175 Hz, H*C*SMe), 30.6 (q, J_{CH} = 128 Hz, $HCS\mathit{C}H_3$).

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