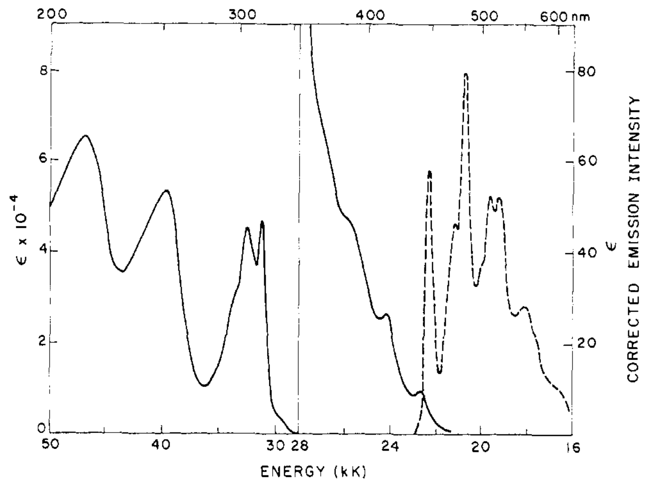

Figure 2. Absorption (22° in methanol or water) and luminescence (77°K in methanol–ethanol glass) spectra of $[Ir(bipy)_3]^{3+}$. The emission spectrum is corrected by use of the published spectrum of $[Ir(bipy)_2Cl_2]^+$.[8b]

$(bipy)_3]^{3+}$[8] are virtually identical in band shapes and energies. The highest energy emission band of $[Ir(bipy)_3]^{3+}$ is at 22.3 kK while that of $[Rh(bipy)_3]^{3+}$ is at 22.4 kK. The $[Rh(bipy)_3]^{3+}$ emission (τ = 2.2 msec) is a ligand π–π^* phosphorescence.[8] In striking contrast, the charge transfer (CT) emission of $[Ir(bipy)_2Cl_2]^+$ falls at 21.5 kK (τ = 11.4 μsec).[9] τ's for "pure" CT emissions of Ir(III)–diimine type complexes are ~10–20 μsec.[9] Thus, we assign the emission of $[Ir(bipy)_3]^{3+}$ to a predominantly π–π^* ligand phosphorescence. It seems unlikely that the emitting state contains a *large* component (>20–30%) of CT parentage on the basis of decay time and the failure to observe low-lying CT-excited singlet states in absorption, but a definitive answer on state parentage awaits determination of the absolute quantum yield.

Of particular interest is the weak absorption progression in the 22–26 kK range which is the mirror image of the emission (~1.3–1.5 kK vibrational progression). The luminescence (~22°) is the same for excitation at 23.0, 24.5, or 27.4 kK and also mirror images the absorption. Thus, we assign these weak absorption bands to an $S_0 \rightarrow {}^3\pi$–π^* transition, the inverse of the luminescence. The unusually high intensity of these transitions for a $S_0 \rightarrow T_1$ process probably arises from a large internal heavy-atom effect (Z = 77 for Ir) and possibly to some admixing of T_1 with upper CT states. The apparent absence of $S_0 \rightarrow T$ absorptions in $[Rh(bipy)_3]^{3+}$ is probably due to the lower Z of Rh and the very high energy of the CT states.

Our current work indicates that the previously unknown tris(1,10-phenanthroline)iridium(III) and possibly the bis(2,2′2′′-terpyridine)iridium(III) cations can be prepared by analogous procedures. The highly luminescent species are being tested as photosensitizers.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation with a Cottrell Research Grant, to the National Institutes of Health for a Biomedical Support Grant administered through the University of Virginia, and to the Department of Chemistry for partial support of this work. The National Science Foundation (GP-32799) provided partial funding for purchase of the JEOL nmr spectrometer. We also thank Mr. W. C. Hutton for running the nmr spectra and for his invaluable comments and suggestions and to L. D. Iroff for running the emission and τ measurements.

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[8] (a) D. H. W. Carstens and G. A. Crosby, *J. Mol. Spectrosc.*, **34**, 113 (1970). (b) D. H. W. Carstens, Ph.D. Dissertation, University of New Mexico, 1969.

[9] R. J. Watts, G. A. Crosby, and J. L. Sansregret, *Inorg. Chem.*, **11**, 1474 (1972).

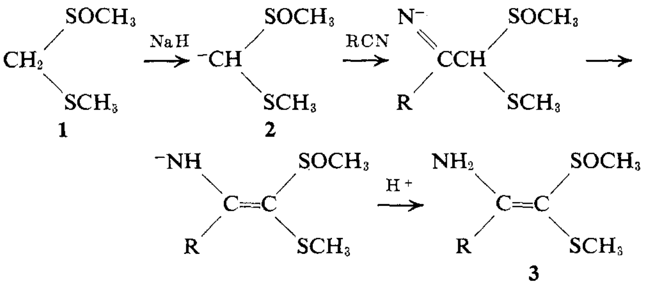
New Synthesis of α-Amino Acids from Nitriles

Sir:

We would like to describe an entirely new route to α-amino acids from nitriles[1] and its application to the synthesis of 5-hydroxytryptophan, a biologically important compound in the metabolic cycle of the tryptophan–serotonin system.[2]

We have found that the carbanion (**2**) derived from methyl methylthiomethyl sulfoxide (**1**)[3] adds to nitriles to form a new type of enamine, *i.e.*, an enaminosulfoxide (**3**).[4] The formation of an enaminosulfoxide may be rationalized by assuming addition of the carbanion (**2**) to the C–N triple bond, followed by proton migration (Scheme I).[5]

Scheme I



The synthesis of methyl esters of N-acetyl-α-amino acids was accomplished by sequential treatment of **3** with acetic anhydride to give the unusual rearrangement product **4**,[6] base-catalyzed ester exchange to **5**, and reductive desulfurization with Raney nickel[7] (Scheme II).

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[1] For the general synthesis of nitriles, see K. Friedrich and K. Wallenfels in "The Chemistry of the Cyano Group," Z. Rappoport Ed., Interscience, New York, N. Y., 1970, Chapter 2.

[2] V. Erspamer, *Progr. Drug Res.*, **3**, 151 (1961).

[3] We have reported new synthetic methods for labile aldehydes, α-hydroxyaldehydes, and phenylacetic acid derivatives by using this reagent. See K. Ogura and G. Tsuchihashi, *Tetrahedron Lett.*, 3151 (1971); 1383, 2681 (1972).

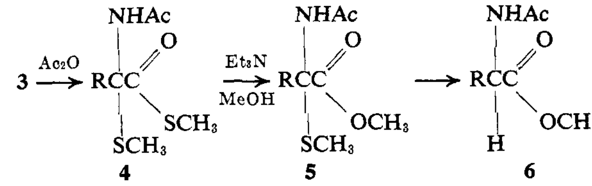
[4] The enaminosulfoxide **3** is a mixture of geometric isomers (Z- and E-forms; the ratio being *ca.* 9:1). See ref 11.

[5] A similar mechanism is proposed for the Thorpe–Ziegler cyclization of dicyanides to form enaminonitriles by E. C. Taylor and A. McKillop, *Advan. Org. Chem.*, **7**, 1 (1969).

[6] The transformation of **3** to **4** may be accounted for by a mechanism involving acetylation of the amino group and the Pummerer-type rearrangement of the sulfinyl group, with the concomitant migration of the methylthio group. Details of the mechanism are now being studied.

[7] Reduction of **4** with deactivated Raney nickel in acetone afforded methanethiol esters of N-acetyl-α-amino acids in 75–82% yields [Raney nickel (W-II activity) was deactivated prior to use by refluxing in acetone for several minutes].

Scheme II



A representative procedure is as follows. Benzonitrile (1.520 g, 14.8 mmol) was added to the THF solution of **2**, generated from **1** (1.830 g, 14.8 mmol) by the action of sodium hydride (1.24 equiv)[8] at room temperature, and the resulting solution was stirred at 50° for 16 hr. After the addition of water (2 ml) together with CH_2Cl_2 (70 ml), the mixture was dried over anhydrous sodium sulfate (without separation of the aqueous layer) and the solid phase was filtered off. Evaporation of the filtrate under reduced pressure and subsequent crystallization from CH_2Cl_2–CCl_4–cyclohexane (1:1:1) afforded a crystalline material (2.391 g, 10.5 mmol):[9] mp 162–163° dec;[10] nmr ($CDCl_3$) δ 2.38 (s, 3 H), 2.57 (s, 3 H), 5.43 (broad, 2 H), 7.38 (s, 5 H). The structure was assigned to be 1-methylsulfinyl-1-methylthio-2-amino-2-phenylethylene (**3**, R = Ph) by the physical data[11] and its chemical reactivity[12] (*vide infra*).

A mixture containing **3** (R = Ph; 2.439 g, 10.7 mmol), acetic anhydride (1.5 ml, 15.9 mmol), and pyridine (1.0 ml, 12.4 mmol) in CH_2Cl_2 (10 ml) was stirred for 4 hr at room temperature. After evaporation of CH_2Cl_2, the residue was washed with water to give the methanethiol ester of *N*-acetyl-α-methylthiophenylglycine (**4**, R = Ph; 2.593 g, 9.64 mmol), mp 174–175.5°.[13]

A solution of **4** (R = Ph; 215 mg, 0.799 mmol) in methanol (10 ml) was refluxed for 13 hr in the presence of two drops of triethylamine. After column-chromatographic separation (silica gel, CH_2Cl_2), crude methyl ester (**5**, R = Ph; 192 mg, 0.759 mmol) was obtained, mp 166–167° (recrystallization from CH_2Cl_2–CCl_4–*n*-hexane and water–methanol). Crude **5** (R = Ph) thus obtained was treated with deactivated Raney nickel (1.2 g) in acetone at room temperature for 5.5 hr to afford the methyl ester of *N*-acetylphenylglycine (**6**, R = Ph; 144 mg, 0.696 mmol).

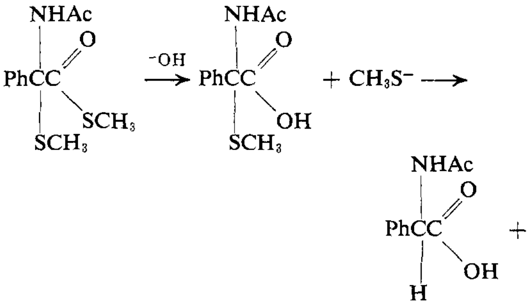
In a similar way, methyl esters of *N*-acetylalanine and *N*-acetylvaline were obtained from acetonitrile and isobutyronitrile, respectively. Yields of **3** (from **1**), **4** (from **3**), and **6** (from **4**) are listed in Table I.[14]

Table I. Yields of the Products

R	Yield (%)		
	$1 \rightarrow 3$	$3 \rightarrow 4$	$4 \rightarrow (5) \rightarrow 6$
Ph	75	88	87
CH_3	76	87	85
i-Pr	72	87	94

N-Acetylphenylglycine was directly obtained in 91% yield, when a solution of **4** (R = Ph) in methanol–water (9:1) was refluxed for 3 hr in the presence of potassium carbonate (2 mol equiv). This direct transformation can be explained in terms of self-reductive desulfurization, whereby methylthiolate anion, produced by the hydrolysis of **4** (R = Ph), attacks the α-methylthio group in the starting compound to form dimethyl disulfide and the α-carbanion of *N*-acetylphenylglycine (Scheme III).[15] In this way, *N*-acetylphenylglycine can be achieved by a three-step procedure from benzonitrile (over-all yield of 60%).

Scheme III



Versatility of this new method was demonstrated by the synthesis of DL-5-hydroxytryptophan. According to the method described above, 1-methylsulfinyl-1-methylthio-2-amino-5,5-dimethoxy-1-pentene (**8**), obtained from 4,4-dimethoxybutyronitrile (**7**)[16] in 77% yield, was converted into 2-acetylamino-2-methylthio-5,5-dimethoxyvaleric acid methanethiol ester (**9**) in 73% yield. The Fischer reaction[17] of **9** with *p*-benzyloxyphenylhydrazine hydrochloride (**10**) afforded DL-*N*-acetyl-5-benzyloxy-α-methylthiotryptophan methanethiol ester (**11**); when a suspension containing **9** and **10** (1 mol equiv to **9**) in acetic acid–water (1:3) was stirred at 80° for 4 hr, **11** was obtained in 88% yield. The ester-exchange reaction afforded the corresponding methyl ester (**12**, 82% yield).[18] The reductive desulfurization of **12** with Raney nickel (W-II activity, in ethanol at room temperature) produced the methyl ester of DL-*N*-acetyl-5-hydroxytryptophan (**13**, 90% yield), with the concomitant cleavage of benzyl group (Scheme IV).

Further synthetic applications of these new reactions are the subject of an on-going study.

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(8) Methyl methylthiomethyl sulfoxide is hygroscopic and needs be dried over molecular sieves (Linde type 3A or 4A) before use.

(9) After evaporation of the mother liquor, the residue was separated by column chromatography (silica gel) to give 105 mg of **3** (R = Ph) and 240 mg of **1**. The yield of **3** amounted to 75%.

(10) *Anal.* Calcd for $C_{10}H_{13}NOS_2$: C, 52.83; H, 5.76; S, 28.21. Found: C, 52.57; H, 5.62; S, 28.38.

(11) Existence of a geometric isomer (about 10%) was observed in the nmr spectrum of **3** (R = Ph): δ 2.03 (CH_3S–) and 2.83 (CH_3SO–). We assign tentatively that the major isomer is *Z*-form, since S–O stretching (ir) appearing at 995 cm^{-1} suggests hydrogen bonding between SO and NH_2.

(12) The enamines **3** can be converted into the corresponding carbonyl compounds. Thus, the reaction of **3** with 1 mol equiv of $CuCl_2 \cdot 2H_2O$ in CH_2Cl_2 or ethanol afforded $RCOCOSCH_3$ or $RCOCOOEt$, respectively, in high yields. *Details of this new synthesis of α-keto-carboxylic acids will be published elsewhere.*

(13) Ir (KBr) 3230, 1690 (sh), 1680 (sh), 1655, and 1520 cm^{-1}; nmr ($CDCl_3$) δ 2.05 (s, 3 H), 2.08 (s, 3 H), 2.25 (s, 3 H), and 7.2–7.7 (5 H + NH); mass spectrum, *m/e* 222 ($M^+ - SCH_3$, 14%), 192 (27), 180 (24), 174 (23), 152 (41), 146 (23), 104 (88), 77 (30), 48 (27), 47 (37), and 43 (base peak). *Anal.* Calcd for $C_{12}H_{15}NO_2S_2$: C, 53.50; H, 5.61; S, 23.81. Found: C, 53.44; H, 5.44; S, 23.88.

(14) Satisfactory elemental analyses and spectral data were obtained for all new compounds.

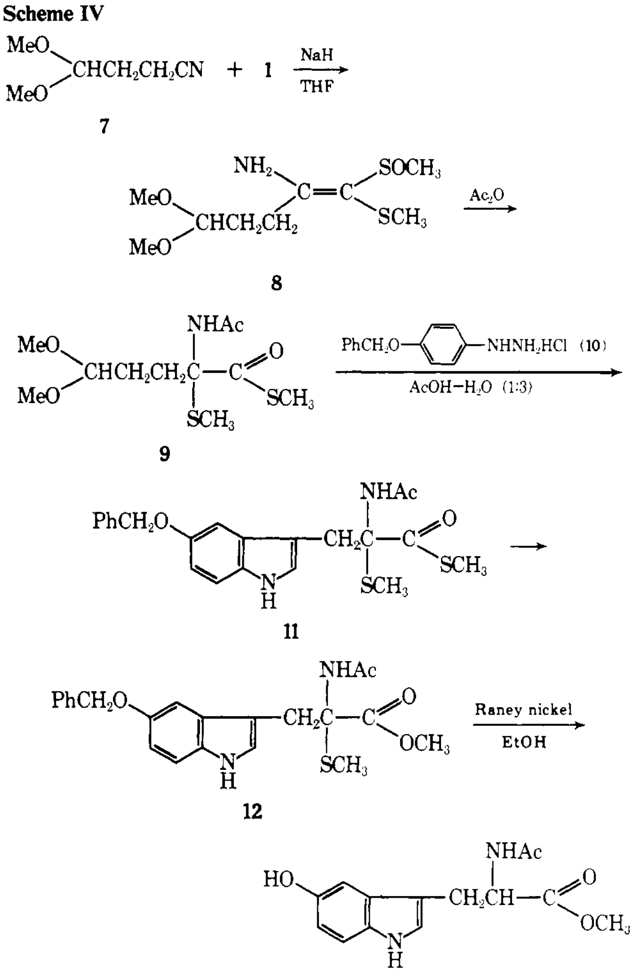
(15) Desulfurization of α-alkylthio carbonyl compounds with thiolate anions was reported by M. Ōki, W. Funakoshi, and A. Nakamura, *Bull. Chem. Soc. Jap.*, **44**, 828 (1971).

(16) This compound can be synthesized by the acetalization of the oxo product of acrylonitrile.

(17) B. Robinson, *Chem. Rev.*, **63**, 373 (1963); **69**, 227 (1969).

(18) A mixture of 449 mg of **11**, 1 ml of triethylamine, and 10 ml of methanol was refluxed for 17 hr.

Scheme IV



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Sigmatropic Rearrangements of 1,1-Diarylindenes. Migratory Aptitudes in Ground and Excited States

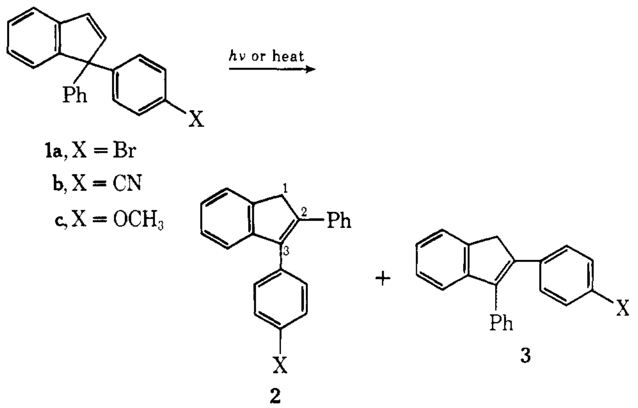
Sir:

Migratory aptitudes of substituted aryl groups in reactive intermediates have been used to determine the transition state structure for the migration.[1–6] 1,2-Phenyl shifts in 1,1-diphenylindene can be induced by heating[7,8] or by ultraviolet irradiation,[6b,9] and this structure therefore provided an attractive opportunity to compare aryl group migratory aptitudes in the ground and excited states. We report here the results of such a study.

The 1,1-diarylindenes used were 1-(*p*-bromophenyl)-1-phenylindene (**1a**), 1-(*p*-cyanophenyl)-1-phenylindene (**1b**), and 1-(*p*-methoxyphenyl)-1-phenylindene (**1c**). The bromo compound **1a** was synthesized from 3-(*p*-bromophenyl)-3,3-diphenylpopionic acid, as described for 1,1-diphenylindene.[9,10] The *p*-cyano and *p*-methoxy compounds were prepared from the bromo derivative by copper-catalyzed displacements.[11,12]

The reactions are shown in Scheme I. The thermal reactions[8] were conducted by heating 50–100 mg of the indene in diphenyl ether (2–3 ml) at reflux (258°) under nitrogen for 18–24 hr. Two products were found in each case—the 2,3-diphenylindene derivatives, **2** and **3**.

Scheme I



The photorearrangements were performed as described previously,[9] using 50–200 mg of the indene in 300–400 ml of solution. Aliquots were withdrawn and analyzed by vpc and nmr. Since two 1,2- and two 2,3-diarylindene products are formed,[9] the aliquots were treated with diethylamine in pyridine.[13] This converted the 1,2- into the 2,3-isomers,[9] and the ratio of the latter two products[14] was measured.[15] Products were isolated by crystallization and chromatography and identified by comparison with authentic materials.

The results are given in Table I. The striking feature is that the excited-state process is more selective

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[1] Accounts may be found in (a) G. W. Wheland, "Advanced Organic Chemistry," Wiley, New York, N. Y., 3rd ed, 1960, p 573–597; (b) Y. Pocker in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 22.

[2] C. Ruckardt and R. Hecht, *Ber.*, **98**, 2471 (1965).

[3] H. E. Zimmerman and J. H. Munch, *J. Amer. Chem. Soc.*, **90**, 187 (1968).

[4] (a) H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *J. Amer. Chem. Soc.*, **87**, 1138 (1965); (b) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967); (c) H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969).

[5] S. S. Hixson, *J. Amer. Chem. Soc.*, **94**, 2307 (1972).

[6] (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, **87**, 1410 (1965); (b) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

[7] C. F. Koelsch and P. R. Johnson, *J. Amer. Chem. Soc.*, **65**, 567 (1943).

[8] L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Amer. Chem. Soc.*, **91**, 1578 (1969); L. L. Miller and R. F. Boyer, *ibid.*, **93**, 650 (1971).

[9] J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1968).

[10] R. F. Brown and L. M. Jackman, *J. Chem. Soc.*, 3147 (1960).

[11] (a) M. S. Newman and H. Boden, *J. Org. Chem.*, **26**, 2525 (1961); (b) R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1097 (1964); (c) R. G. R. Bacon and S. C. Rennison, *ibid.*, 312 (1969).

[12] All new compounds gave satisfactory analytical figures, gave infrared and nmr spectra consistent with the assigned structures, and gave sharp-melting crystals: **1a** mp 118–119°; **1b** mp 152–154°; and **1c** mp 78–79°.

[13] G. Bergson, *Acta Chem. Scand.*, **17**, 2691 (1963).

[14] The structures of **2** and **3** were established by unambiguous synthesis, using the general route described for 2,3-diphenylindene.[9] **3a**, **b**, and **c** had melting points of 184–186, 214–216, and 124–126° and **2a**, **b**, and **c** had melting points of 163–165, 139–141, and 115–116°, respectively. These products were stable under the reaction conditions.

[15] Analysis by vpc was conducted on 5 ft × 1/8 in. of 5% QF-1 on Chromosorb W at 200°. Nmr analysis was performed on the HA-100, and the singlet resonances of the methylene groups (which were in the range 3.5–4.0 ppm) were used to determine ratios. Both vpc and nmr figures were checked against standard mixtures of synthetic materials, and results from the two methods were in good agreement.