Figure 1. Minimum energy path for the H^- + CH_2O reaction (in the xz plane). The points A, B, C, D, and E correspond respectively to an $H^- \cdots C$ distance of 3.0, 2.5, 2.0, 1.5, and 1.12 Å (see Table I). Energy curves for deviations of 0.6 (----) and 6.0 (.....) kcal/mol from the minimum energy path are also shown. Insert top right: Energy profiles for lateral angular displacements (in degrees) out of the xz plane, at values of the x coordinate corresponding to points A, B, C, and D respectively. These profiles illustrate the more and more stringent "orientation" constraint of the H^- approach as the reaction proceeds. Energies are given in kcal/mol with respect to the energy of the most stable species (i.e., point E, methanolate) taken as zero.

Figure 2. Plot of the deviation Δ of the C atom out of the H_1, H_2, and O plane vs. the distance d between H^- and C of H_2CO (bottom curve) and between N and C of a carbonyl group as obtained experimentally from crystal structure data[1a] (top curve). The point ▲ is that calculated for NH_3 + H_2CO at 2.0 Å N...C separation and corrected to make it comparable to the structural data.[9]

planar,[8] and correspondingly the gradual deviation from planarity of the formaldehyde molecule as the reaction proceeds can be attributed partly to the mixing of π^* with $1s(H^-)$, in agreement with the electron distribution calculated for the HOMO.

When Δ (out-of-plane deformation) is plotted against $d(H^- \cdots C)$, the resulting curve is strikingly similar to that obtained from the crystal structure data for the approach of an amino group to carbonyl. The points at 1.12, 1.5, and 2 Å follow a logarithmic relationship (Figure 2)

$$d(H^- \cdots C) = -1.805 \log + 0.415 \text{ Å}$$

similar to the one found from structural data[1a]

$$d(N \cdots C) = -1.701 \log + 0.867 \text{ Å}$$

The difference in the constant term largely reflects the difference between the C–H and C–N bond lengths.

In order to compare the results derived from crystal structure data and model calculations, the energy of the species formaldehyde ammonia was minimized at a fixed $N \cdots C$ distance of 2.0 Å. Calculated data are $\Delta_{corr} = 0.14$ Å,[9] $\alpha(N \cdots C-O) = 105°$, and $r(C-O) = 1.23$ Å. The experimental values at $d(N \cdots C) = 1.993$ Å are $\Delta = 0.21$ Å, $\alpha(N \cdots CO-) = 107 \pm 5°$, and $r(C-O) = 1.258$ Å.[1a]

Thus, although the angles of approach agree, the distortion of the carbonyl group observed in the crystal is larger than that calculated. This discrepancy could result from the differing microenvironments: polar in the crystal and therefore stabilizing the species $H_3N^{\delta+} \cdots H_2CO^{\delta-}$ showing partial separation of charge, but nonpolar for isolated reactants considered in the calculation. Also, steric interactions—between alkyl sub-

stituents on the amino and carbonyl group of the real molecule[1a]—are reduced in the model system bearing hydrogen substituents only.

The qualitative agreement between the results calculated for isolated reactants and those derived from solid-state data encourages us to believe that the two descriptions complement and mutually confirm each other. Theoretical and experimental studies on other systems now in progress will provide further tests of our present results.

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Facile Carbon → Nitrogen and Nitrogen → Carbon Acyl Migrations in Acyl Derivatives of 2-Mercaptobenzimidazole. A Model of Biotin

Sir:

We wish to report a new type of acyl migration that should provide information useful in mechanistic studies of bioorganic or enzymic reactions. Migrations of acyl groups constitute an important class of reactions in biochemistry. Detailed studies, however, have been reported only for acyl migrations from one heteroatom to another, such as solvolyses of esters or amides. Yet, acyl migrations between carbon atoms and heteroatoms are also important in bioorganic reactions, e.g., syntheses and degradations of fatty acids. These summarized in Scheme I are the first examples of acyl migrations between formally neutral carbon and formally neutral nitrogen under mild conditions.

When 2-benzimidazolyl disulfide (1) was treated at room temperature with benzoylacetone in the presence of sodium hydride,[1] 1-phenyl-2-(2'-mercaptobenzimid-

(8) V. A. Job, V. Sethuraman and K. K. Innes, J. Mol. Spectrosc., 30, 365 (1969); V. T. Jones and J. B. Coon, ibid., 31, 137 (1969).
(9) In order to compare the value of Δ calculated in this study (0.11 Å) with the experimental result, a correction has to be made for the difference between the C–C bond length in a ketone (1.53 Å from the experimental data[1a]) and the C–H bond length in formaldehyde (1.12 Å in this model calculation), yielding $\Delta_{corr} = 0.14$ Å.
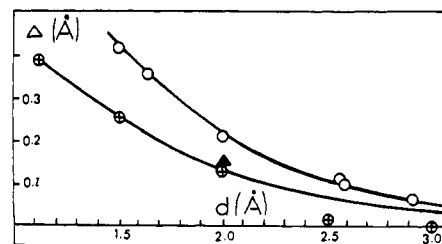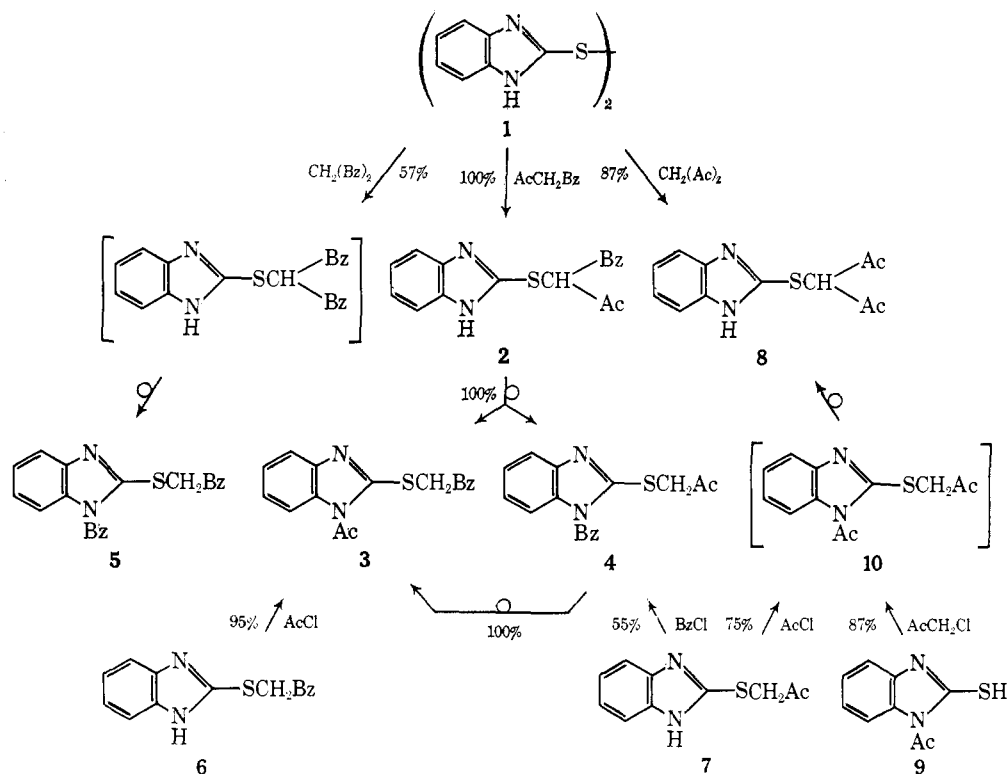
(1) T. Fujisawa, K. Hata, and T. Kojima, Chem. Lett., 287 (1973).

Scheme I

azolyl)butane-1,3-dione (2)[2] was obtained in 90% yield: mp 118–119°; ir (KBr) 3400 (ν_{OH}) and 1590–1540 cm^{-1} (broad, ν_{CO}); mass spectrum (m/e) 310 (M$^+$) and 105 (base); nmr ($\delta_{CDCl_3}^{TMS}$) 2.20 (broad s), 2.48 (s) (total 3 H), 7.08–8.05 (m, 9 H), and 17.6 (broad s).[3]

In chloroform or benzene at room temperature for 2 days, 2 was almost quantitatively transformed into S-phenacyl-N-acetyl-2-mercaptobenzimidazole (3)[4] and S-acetonyl-N-benzoyl-2-mercaptobenzimidazole (4).[2,5] This transformation also takes place even with crystalline 2 in a refrigerator, although slowly. However, the reaction is retarded by the addition of a base and prevented completely by an acid.

From the reaction of 1 with dibenzoylmethane a compound analogous to 2 could not be isolated; instead the sole product obtained was 5,[2,6] in which a benzoyl group had already been rearranged.

Products 3 and 4 can be prepared from S-phenacyl-2-mercaptobenzimidazole (6)[7] and S-acetonyl-2-mercaptobenzimidazole (7),[8] respectively. On the other hand, the reaction of 7 with acetyl chloride in the presence of pyridine at room temperature provided the rearranged product 8,[8] which was alternatively prepared from 1 by the reaction with acetylacetone. That 8 was not formed by direct C attack of acetyl chloride was proved by the fact that the acetonylation of 9[2] also afforded 8.

(2) Elemental analyses gave satisfactory results.

(3) This signal appears only when the spectrum is recorded below −30° and disappears on addition of a few drops of methanol-d_4, an observation suggesting that the methyne proton of 2 is rapidly exchanging with the proton on a ring nitrogen. The N-carboethoxy derivative of 2 displays an nmr signal at δ 18.3 at room temperature.

(4) A. N. Krasovskii, P. M. Kochergin, and T. E. Kozlovskaya, *Khim. Geterotsikl. Soedin.*, 7, 393 (1971); *Chem. Abstr.*, 76, 14433z (1972).

(5) Mp 105–107°; ir (KBr) 1733 and 1695 cm^{-1} (ν_{CO}); nmr ($\delta_{CDCl_3}^{TMS}$) 2.40 (s, 3 H), 4.16 (s, 2 H), and 6.50–7.85 (m, 9 H).

(6) Mp 136–137°; ir (KBr) 1698 and 1678 cm^{-1} (ν_{CO}); nmr ($\delta_{CDCl_3}^{TMS}$) 4.90 (s, 2 H) and 6.50–8.23 (m, 14 H).

(7) S. Nakajima, I. Tanaka, T. Seki, and T. Anmo, *Yakugaku Zasshi*, 78, 1378 (1958).

(8) A. E. Alper and A. Taurins, *Can. J. Chem.*, 45, 2904 (1967).

It was found that this rearrangement is facilitated by the presence of pyridine; i.e., the reaction of 7 with acetic anhydride without pyridine gave 10,[8] which rearranged into 8 on standing with pyridine at 50°, whereas 10 was stable at this temperature without pyridine.[9] An attempt to synthesize the authentic sample of 5 was unsuccessful because the reaction of 6 with benzoyl chloride gave 11a[2] quantitatively.

Significantly, quantitative rearrangement of 4 into 3 was observed when a solution of 4 in chloroform or benzene was kept at room temperature for 4 days. Intermediacy of 2 for this rearrangement has been unequivocally determined by nmr spectroscopy and isolation of this compound from a chloroform solution of 4.

Although the detailed mechanism of the reaction, including the direction of migrations, is yet to be clarified, there is no doubt that a cyclic carbinolamine (12) is
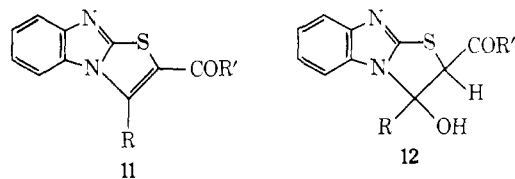
a, R = Ph; R' = Ph
b, R = Ph; R' = Me
c, R = Me; R' = Ph

involved as a common intermediate of C → N and N → C acyl migrations,[8,10] which was confirmed by isolating small amounts of 11b and 11c from a chloroform solution of 2. The facts that 2 exhibits two nmr

(9) Occurrence of this migration at an elevated temperature in pyridine has been reported in ref 8. Also cf. J. J. D'Amico, R. N. Campbell, and E. C. Guinn, *J. Org. Chem.*, 29, 865 (1964).

(10) (a) H. Singh and S. Singh, *Indian J. Chem.*, 11, 311 (1973); (b) *ibid.*, 9, 918 (1971).

signals for methyl protons and that **12**-type structure is predominant for **8**[8] also support the idea.

The function of biotin in enzymic carboxylation has long been associated with activation of carbon dioxide through bonding to a ring nitrogen.[11] Recently, however, Bruice and coworkers proposed that the "activated CO_2" is that which is bonded to the carbonyl oxygen.[12] The argument by the latter author is based mainly on the low reactivity of a ring nitrogen toward carbon dioxide.[13] Thus, the facile transfer of an acyl group which we have described above may well be related to the reactivities of a ring nitrogen in biotin and the nitrogen-bonded carbon dioxide in question.

Acknowledgment. We wish to thank Mr. E. Kodama for technical assistance.

(11) F. Lynen, *Biochem. J.*, **102**, 381 (1967).
(12) (a) R. F. Pratt and T. C. Bruice, *J. Amer. Chem. Soc.*, **94**, 2823 (1972); (b) T. C. Bruice and A. F. Hegaty, *Proc. Nat. Acad. Sci. U. S.*, **65**, 805 (1970).
(13) (a) M. Caplow, *J. Amer. Chem. Soc.*, **90**, 6795 (1968); (b) M. Caplow and M. Yager, *ibid.*, **89**, 4513 (1967); (c) M. Caplow, *ibid.*, **87**, 774 (1965).

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Synthesis and Luminescence of the Tris(2,2'-bipyridine)iridium(III) Ion

Sir:

Previous attempts to synthesize $[Ir(bipy)_3]^{3+}$ (bipy = 2,2'-bipyridine) using halogen–iridium species (*e.g.*, $K_3IrCl_6 \cdot 3H_2O$, $IrCl_3 \cdot xH_2O$) yielded only chloro complexes.[1] We speculated that an iridium (a "soft" metal) compound containing only "hard" ligands would react more readily with "softer" 2,2'-bipyridine to give $[Ir(bipy)_3]^{3+}$ than do chloride (a "soft" ligand) containing species. Proceeding accordingly, we have obtained the long-sought $[Ir(bipy)_3]^{3+}$. Luminescence results add to our knowledge of the lowest lying excited states of platinum metal–diimine complexes.

The best procedure started with boiling a mixture of 1.0 g (1.7 mmol) of $K_3IrCl_6 \cdot 3H_2O$, 0.3 g of $K_2S_2O_8$, and 48 g of $KHSO_4$ in 17 ml of water to dryness, followed by fusion in air for up to 0.5 hr at 220–300°. The clear deep green melt[2] thus obtained was cooled to room temperature, treated with 3.1 g of 2,2'-bipyridine and 17 ml of water, and boiled to dryness (little color change). This mixture was fused in a CO_2 atmosphere; with agitation it became brown-yellow in 0.2 hr (two liquid phases). The mixture was kept at 220–240° for 6 hr (CO_2 atmosphere, occasional agitation). Then it was cooled, and further work was carried out in air. The solid was dissolved in 170 ml of water (heat) and neutralized with $KHCO_3$. Removal of K_2SO_4 was completed by adding 340 ml of methanol, cooling to 5–10° for 1–2 hr, and filtering. The filtrate was evaporated to about 35 ml, cooled (bipy precipitated), checked for neutrality, and treated with diethyl ether to extract the excess bipy. The solution was diluted with 500 ml of

(1) R. E. DeSimone and R. S. Drago, *Inorg. Chem.*, **8**, 2517 (1969).
(2) Similar reactions involving sulfuric acid produce apparently halogen-free sulfate complexes; see D. B. Brown, M. B. Robin, J. D. E. McIntyre, and W. F. Peck, *Inorg. Chem.*, **9**, 2315 (1970).
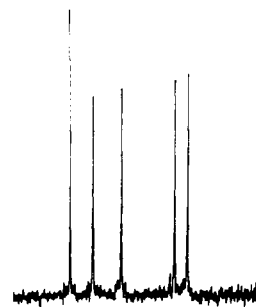
Figure 1. ^{13}C nmr spectrum of $[Ir(bipy)_3](NO_3)_3$ in H_2O–D_2O. The chemical shifts starting at the left are -89.46, -83.77, -80.14, -76.69, and -60.04 ppm relative to internal dioxane standard. There were no additional peaks above the noise level from *ca.* -110 to $+90$ ppm. Areas or peak heights cannot be used to compare relative abundances.

0.2 F HNO_3 and evaporated at 90–100° to 10–20 ml, then carefully at 40–60° to dryness. The solid was dissolved in 10–20 ml of water, and the solution was neutralized with a little $KHCO_3$. It was chromatographed on Cellex-P cation resin (H^+ form) with 0.05 F and then 0.1 F HNO_3. The highly luminescent 0.1 F HNO_3 fraction was evaporated to dryness and chromatographed (methanol) repeatedly on Sephadex LH-20. The weakly green-luminescing zone eluted from the column[3] gave crystals of $Ir(bipy)_3(NO_3)_3$ on addition of 2-propanol and evaporation. These were recrystallized from methanol–2-propanol, giving pale yellow needles in nearly 50% yield based on the potassium hexachloroiridate. A light yellow perchlorate salt, obtained by metathesis with aqueous $LiClO_4$, was recrystallized from water. *Anal.* Calcd for $[Ir(C_{10}H_8N_2)_3](ClO_4)_3 \cdot 3H_2O$: C, 35.57; H, 2.98; N, 8.30; Cl, 10.50. Found: C, 35.52; H, 3.01; N, 8.33; Cl, 10.35. Both salts were pure as shown by tlc (aqueous $NaClO_4$ on polyamide).

The ^{13}C nmr spectrum (Figure 1) coupled with the elemental analysis proved the product to be $[Ir(bipy)_3]^{3+}$. The five lines correspond to the five distinct carbon atoms of a D_3-symmetry tris complex. The simplest *cis*-$[Ir(bipy)_2X_2]^{n+}$ contains ten kinds of carbon atoms. The complex ^1H nmr spectrum in D_2O strongly resembles the spectra[1,4] of $[Os(bipy)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$, while it is distinctly different from the characteristic spectra[1,5] of *cis*-$[Ir(bipy)_2Cl_2]^+$ and *cis*-$[Si(bipy)_2(OCH_3)_2]^{2+}$. A *trans*-$[Ir(bipy)_2XY]^{n+}$ structure is rejected on the basis of the elemental analyses, the ^1H nmr spectrum and the failure to observe such species in many systems, although *cis*-bis(2,2'-bipyridine) complexes are common.[6,7]

The absorption ($\sim$22°) and luminescence spectra (77°K) of $[Ir(bipy)_3]^{3+}$ are given in Figure 2. The 77°K mean lifetime (τ) of $\sim$80 μsec establishes the emission as a phosphorescence.

The emission spectra of $[Ir(bipy)_3]^{3+}$ and [Rh-

(3) This zone was preceded and followed by brightly yellow or green-yellow luminescent products which are under investigation.
(4) S. Castellano, H. Gunther, and S. Ebersole, *J. Phys. Chem.*, **69**, 4166 (1965).
(5) D. Kummer and K. Köster, *Z. Anorg. Allg. Chem.*, **398**, 279 (1973).
(6) L. H. Berka, R. R. Gagne, G. E. Philippon, and C. E. Wheeler, *Inorg. Chem.*, **9**, 2705 (1970).
(7) P. Andersen and J. Josephsen, *Acta Chem. Scand.*, **25**, 3255 (1971).