should be magnetic field dependent with an extremum near the comparatively low (<1 KG) field corresponding to the hyperfine coupling between the nucleus and the unpaired electron in the radical. It should be emphasized that this magnetic field effect involves a direct correlation between the magnitude of the hyperfine splitting and the field dependence. It is qualitatively different from the comparison of isotope enrichments in very low and very high fields which has so far been offered as evidence for a nuclear spin isotope effect.[2a,c] The connection between nuclear spins and the (often intriguing) chemical effects of high magnetic fields does not yet appear to be well established.[8] For example, recent calculations[7] show that, at least for a symmetrical triplet-born radical pair with a single $I = \frac{1}{2}$ nucleus, the isotope effect should be the same in very low and very high fields but still pass through the extremum described above.

III. The theory of isotope effects has progressed to the point where it is feasible to design experiments in which *the spin and mass isotope effects anticipated on chemical grounds should be in opposite directions.* This does not appear to be the case for recently reported photoinduced carbon-13 enrichments in dibenzyl ketone[2a,c,e] and phenylbenzoate.[2b] In both cases the heavier isotope appears preferentially where it would be expected if a mass isotope effect simply retarded photofragmentation. The mass effect could be discounted only by postulating the fragmentation step(s) to be kinetically unimportant or appealing to the unexpectedly large magnitude of the isotope effect.[9] A reasonable way (equivalent to criterion I above) to document the nuclear spin effect in this particular case would be to measure the $^{13}C/^{14}C$ isotope effect since the lighter isotope has the spin in that case. Alternatively, where chemistry permits, the initial multiplicity of the radical pair might be changed, thereby inverting the effect of the nuclear spin on radical pair reactivity.

In view of recent reports of unusually large isotope enrichments observed during free-radical reactions, it becomes important to apply as many of the above criteria as possible to the evaluation of these effects. The extent to which these criteria will be met, and nuclear spin isotope effects fully documented, depends to a large extent on the largely unknown accuracy with which one can extrapolate from the properties of radical pairs, as revealed by CIDNP, to the actual yields of stable products.

Acknowledgment. The ideas presented here are an outgrowth of research supported by the National Science Foundation.

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(3) Maugh, T. H., II *Science* **1979**, *206*, 317.

(4) These exclude the recent ingenious suggestion[2d] that nuclear spin isotope effects might be observed using *isomeric* nuclei with different magnetic moments but the same masses and atomic numbers.

(5) For a summary of examples supporting this idea for carbon isotopes see: Bigeleisen, J.; Wolfsberg, M. *Adv. Chem. Phys.* **1958**, *1*, 15.

(6) In the case of heavy elements, such as Sn, which possess several stable isotopes distributed widely in mass, the potential exists for a large mass isotope effect if two of the isotopes are at the extremes of the mass range. It is therefore essential that the analytical method employed distinguish individual isotopes and not simply average together into two groups those with and without magnetic moments. For example, the NMR satellite method recently used[2d] to measure Sn isotope enrichment does not distinguish among the seven stable isotopes of Sn which span a total range of 12 mass units, i.e., a fractional mass change comparable with that between ^{12}C and ^{13}C.

(7) (a) Sagdeev, R. Z.; Salikhov, K. M.; Molin, Yu. M. *Russ. Chem. Rev.* **1977**, *46*, 297. (b) Zientara, G. P.; Freed, J. H. *J. Chem. Phys.* **1979**, *70*, 2587.

(8) Indeed, at least two reports have appeared in which magnetic field effects have *not* been observable for radical pair reactions of the type which give CIDNP: (a) Sakuragi, H.; Sakuragi, M.; Mishima; T.; Watanabe, S.; Hasegawa, M.; Tokumaru, K. *Chem. Lett.*, **1975**, 231. (b) Broomhead, E. J.; McLaughlan, K. A. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 775.

(9) A referee has pointed out that in delocalized radicals the nuclear spin effect should overwhelm secondary mass isotope effects at positions with appreciable spin density which are far removed from the reaction site. Isotope enrichment of *any* detectable magnitude at such positions, regardless of direction, might then serve as evidence for a nuclear spin isotope effect. Furthermore, the magnitudes of the enrichments at different positions in the same radical should depend in some systemic way on the magnitude of the hyperfine splittings at those positions. These two effects, where applicable, are philosophically similar to criteria III and I, respectively.

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A Copper(I)-Bicarbonato Complex. A Water-Stable Reversible CO$_2$ Carrier

Sir:

The preparation of CO$_2$-related transition-metal complexes is important in connection with recent research activities in CO$_2$ coordination chemistry[1] and in organic synthesis using CO$_2$.[2] Transition-metal-bicarbonato complexes are attracting a considerable interest.[3] Until recently, however, few studies on transition-metal bicarbonato complexes have been reported in spite of their relevance to carbonic anhydrase[4] and to transition-metal-catalyzed organic reactions of CO$_2$ in aqueous media.[5] Here we report the preparation of a Cu(I)-bicarbonato complex by three routes: (i) hydrolysis of a Cu(I)-alkylcarbonato complex, (ii) hydrolytic carboxylation of a Cu(I)-carbonato complex, and (iii) carboxylation of a Cu(I)-hydroxo complex. The relationship of interconversions among the above various Cu(I) complexes is also shown. The Cu(I)-bicarbonato complex which reversibly decarboxylates in both organic solvents and water acts as a CO$_2$ carrier to carboxylate cyclohexanone and propylene oxide.

All operations described below were carried out under nitrogen. A reaction mixture of t-BuOCO$_2$Cu(PEt$_3$)$_3$ (**1a**)[6] and 1.2 equiv of water in n-pentane was stirred for 6 h at 0 °C. t-BuOH was formed in 98% yield.[17] Evaporation of the solvent in vacuo produced a viscous oil. Crystallization of the oil from n-pentane at −78 °C gave a white microcrystalline solid. The solid melted at ambient temperature to produce a colorless viscous oil which was identified as HOCO$_2$Cu(PEt$_3$)$_3$ (**2a**): Cu content 13.1% (calcd 13.3%); CO$_2$ evolution by acidolysis 98%; IR (neat) 2621 (ν_{OH}), 1612 cm^{-1} ($\nu_{C=O}$); ^{1}H NMR (C$_6$D$_6$) δ 8.75 ppm (HOCO$_2$−). The deuterated complex, DOCO$_2$-Cu(PEt$_3$)$_3$(**2a**-d_1), prepared by the reaction using D$_2$O did not show the IR and NMR absorptions due to the proton of bicarbonate group of **2a**. **2a**-d_1 showed its ν_{OD} band at 2143 cm^{-1}. It is reasonably assumed that **2a** is a coordinatively saturated complex and the bicarbonate group coordinates as a monodentate ligand. The molecular weight of **2a** determined by cryoscopy in benzene was 866 (calcd for dimeric **2a**, 958). The value of molecular weight together with the low IR ν_{OH} absorption suggests that **2a** has a dimeric structure involving a hydrogen bond between the two bicarbonate groups, which may be similar to that of Pd(Me)(OCO$_2$H)(PEt$_3$)$_2$.[3b] Hydrolysis of t-BuOCO$_2$Cu(t-BuNC)$_3$ (**1b**)[6] in tetrahydrofuran (THF) at 0 °C quantitatively produced a white precipitate of HOCO$_2$Cu(t-BuNC)$_3$ (**2b**), which was recrystallized from CH$_2$Cl$_2$-n-pentane.[7] **2b** reacted with an equimolar amount of EtI in dimethylformamide (DMF) at room temperature to give EtOH in 57% yield and diethyl carbonate in 16% yield with 80% CO$_2$ evolution. When the amount of water was decreased to 0.5 equiv in the reaction of **1b** with water, a Cu(I)-carbonato

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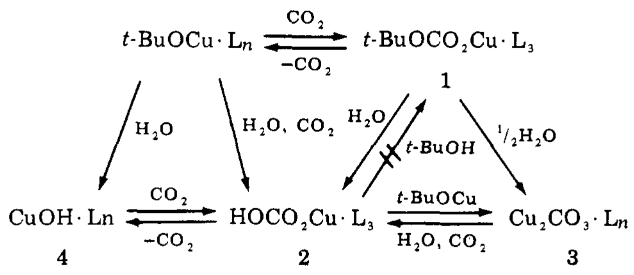
Scheme I



L = PEt$_3$ (a), *t*-BuNC (b)

Scheme II

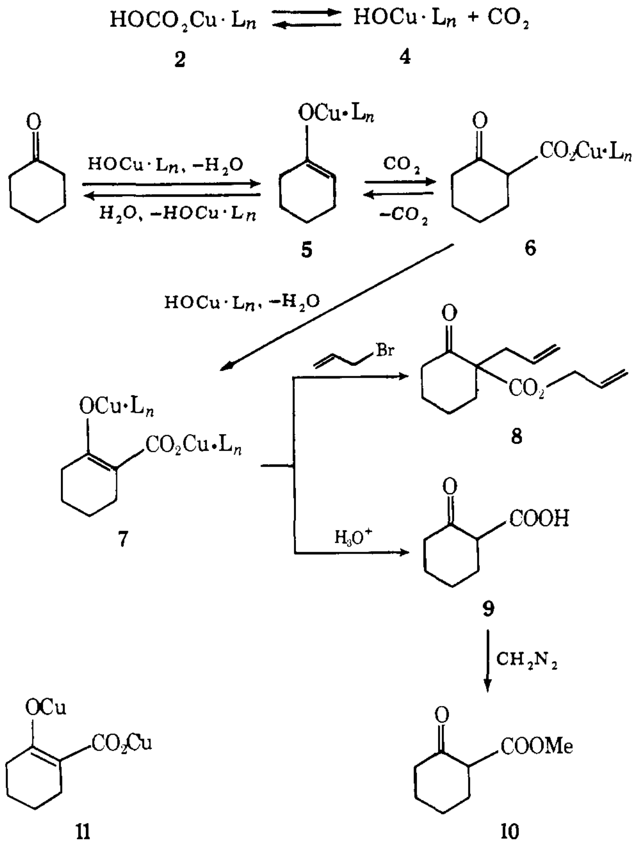
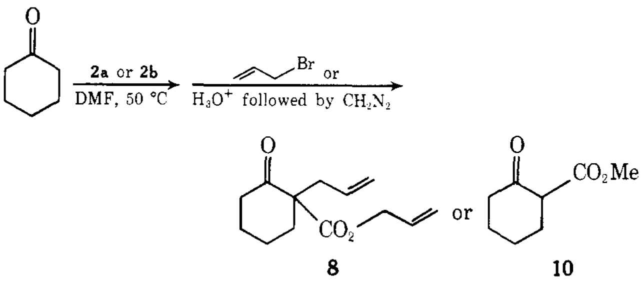


Table I. Transcarboxylation to Cyclohexanone by **2**[a]



run	complex	additional H_2O, H_2O/Cu	carboxylated product, %[b] **8**	carboxylated product, %[b] **10**
1	**2a**	0	46	
2	**2a**	0		69
3	**2a**	1		51
4	**2b**	0	45[c]	
5	**2b**	0		62
6	**2b**	1		57
7	$NaHCO_3$	0		0
8	$NaHCO_3$	1		0

[a] **2**, 0.5 mmol; c-$C_6H_{10}O$/**2** = 3; DMF solvent, 3 mL. [b] Yields were determined by GLC based on **2**. [c] H_2O was detected in 85% yield.

complex, Cu_2CO_3(*t*-BuNC)$_n$ (**3b**), was produced as a white precipitate with simultaneous formation of 94% *t*-BuOH.[8] **3b** reacted with 2 equiv of EtI in DMF at ambient temperature to give diethyl carbonate in 67% yield and EtOH in 5% yield with 12% CO_2 evolution, which made a sharp contrast to the behavior of **2b** with EtI. Hydrolytic carboxylation of **3b** with 1.2 equiv of water and 1.5 equiv of CO_2 in THF including additional 3 equiv of *t*-BuNC at ambient temperature produced **2b**. Hydrolysis of *t*-BuOCu[9] in THF at ambient temperature produced a brown precipitate of HOCu[10] with 92% *t*-BuOH formation. HOCu absorbed an equimolar amount of CO_2 under ordinary pressure in DMF at 0 °C in the presence of 3 equiv of PEt_3 or *t*-BuNC to give **2a** or **2b**, respectively. Abstraction of the proton of the bicarbonate group of **2b** was examined using *t*-BuOCu or *n*-BuLi. Treatment of **2b** with *n*-BuLi in THF at 0 °C evolved *n*-butane in 98% yield. The deuterated complex **2b**-d_1 generated butane-d_1. The equimolar reaction of **2b** and *t*-BuOCu in THF at 0 °C in the presence of 3 equiv of *t*-BuNC converted **2b** into **3b** with concomitant formation of 98% *t*-BuOH.

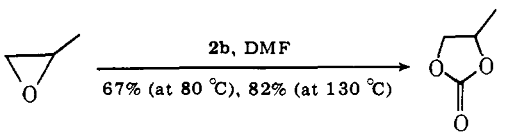
The preparative methods of **2** and its related reactions are summarized in Scheme I, in which the routes of **1** → **2** and **3** → **2** are novel for the preparation of a transition-metal-bicarbonato complex. **2a**, **2b**, and **3b** are new Cu(I) complexes. The relationship of interconversions of **2** and its related complexes is useful information for the chemistry of transition-metal-bicarbonato complexes.

It is very interesting to note that **2a** and **2b** are highly soluble in both organic solvents and water. **2a** is soluble in common organic solvents including benzene and *n*-pentane. **2b** is soluble in CH_2Cl_2, DMF, and HMPA. **2a** and **2b** also are soluble in water without any decomposition. Both of them can be extracted unchanged from their aqueous solutions with CH_2Cl_2. **2a** underwent reversible decarboxylation under mild conditions both in DMF and in water:

$$\mathrm{HOCO_2Cu(PEt_3)_3 \rightleftharpoons HOCu(PEt_3)_3{}^{10} + CO_2}$$

Nearly the same state of equilibrium was attained from either direction of the above equation and a cycle of carboxylation-decarboxylation caused by changing the reaction temperature was repeatable.[11] This is the first example of an isolable transition-metal-bicarbonato complex which undergoes reversible decarboxylation both in an organic solvent and in water.[3c] On the other hand, **2b** decarboxylated with the simultaneous evolution of CO, which was produced from the copper-induced deoxygenation of CO_2 by the *t*-BuNC ligand.[12] At the higher temperature of 120 °C in mesitylene, the CO_2 moiety in **2b** was quantitatively converted into CO.

Recently we have reported that the Cu(I)-cyanoacetatophosphine complex transferred its CO_2 unit to cyclohexanone.[13] **2** effected this type of carboxylation in the presence of a nearly stoichiometric amount of water to act as a water-stable reversible CO_2 carrier (Table I). The transcarboxylation may be reasonably assumed to proceed via a dicopper(I) complex of enol of cyclohexanone-2-carboxylic acid (**7**) as a key intermediate which is stable toward decarboxylation (Scheme II). Formation of **7** requires simultaneous liberation of two molecules of water. Actually the transcarboxylation took place in the presence of an additional 1 equiv of water. **7**[14] produced only trace amounts of **9** (analyzed as **10**) in the reaction with 2 equiv of water and an isolated complex **11** was recovered unchanged from the DMF solvent containing 2 equiv of water.[15] Thus, the feature of Scheme II, that is, the Cu(I)-induced carboxylation of cyclohexanone in the presence of a nearly stoichiometric amount of water, may be considered to have been brought about by the following factors: (i) stability of both **2** and **4** toward water, (ii) some tolerance of **5** to the stoichiometric amount of water and regeneration of **4** and cyclohexanone by the hydrolysis of **5**, (iii) stability of **7** to the stoichiometric amount of water. **2b** also transcarboxylated its CO_2 moiety to propylene oxide to produce propylene carbonate[16] (eq 1). These are the first examples of the transcarboxylation reaction by means of a transition-metal-bicarbonato complex.



(1)

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(2) See, for example, (a) Y. Inoue, Y. Sasaki, and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **51,** 2375 (1978); (b) T. Tsuda, Y. Chujo, and T. Saegusa, *Synth. Commun.*, **9,** 427 (1979).

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(6) T. Tsuda, S. Sanada, K. Ueda, and T. Saegusa, *Inorg. Chem.*, **15,** 2329 (1976).

(7) Identification data of **2b**: Cu content 17.0% (calcd 17.0%); CO_2 evolution by acidolysis 99.1%; IR (Nujol) 2602 (ν_{OH}), 2162 ($\nu_{N\equiv C}$), 1618 cm^{-1} ($\nu_{C=O}$).

(8) Owing to the high sensitivity of **3b** to moisture, recrystallization of **3b** was not successful and the exact number of the coordinated *t*-BuNC ligand was not determined. Identification data: CO_2/Cu ratio, 0.51, which was determined from Cu content by iodometry (4.23 mmol/g) and CO_2 gas evolution by acidolysis (2.14 mmol/g); IR (Nujol) 1511 ($\nu_{C=O}$), 2164 and 2189 cm^{-1} ($\nu_{N\equiv C}$).

(9) T. Tsuda, T. Hashimoto, and T. Saegusa, *J. Am. Chem. Soc.*, **94,** 658 (1972).

(10) Identification data: Cu content 79.7% (calcd 78.9%); H_2O formation by acetolysis 91%; allyl alcohol formation by the reaction with allyl bromide 24%. HOCu was solubilized in organic solvents by the addition of a ligand (L) such as PEt_3 or *t*-BuNC. The resulting solution of the Cu(I)–hydroxo complex (**4**) showed the IR ν_{OH} band at 3300 cm^{-1}. However, the isolation of the $HOCu\cdot L_n$ complex was unsuccessful. For the preparation of CuOH, see also P. Bevillard, *Bull. Soc. Chim. Fr.*, 561 (1956).

(11) For example, the equilibrium values of evolved CO_2 gas in the decarboxylation of **2a** were 27 (in DMF at 70 °C) and 15% (in water at 50 °C).

(12) T. Tsuda, S. Sanada, and T. Saegusa, *J. Organomet. Chem.*, **116,** C12 (1976).

(13) T. Tsuda, Y. Chujo, and T. Saegusa, *J. Am. Chem. Soc.*, **100,** 630 (1978).

(14) **7** was prepared in situ in DMF by adding 3 equiv of PEt_3 to the isolated complex **11.**[13]

(15) **7** and **11,** however, were hydrolyzed at 0 °C in DMF by an excess of water (H_2O/Cu, $\simeq 100$) to produce **9** in $\sim$20% yield.

(16) T. Tsuda, Y. Chujo, and T. Saegusa, *J. Chem. Soc., Chem. Commun.*, 415 (1976).

(17) Throughout this study, the yields of conversions in percentages were determined by GLC analyses. Estimated error in their percentages is within 5%.

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Book Reviews

Neutron Diffraction (Topics in Current Physics. 6). Edited by H. DACHS (Hahn-Meitner-Institut für Kernforschung, Berlin). Springer-Verlag, Berlin. 1978. 357 pp. ~$29.

On encountering a book entitled "Neutron Diffraction", the alert reader will immediately want to know how it compares with the classic volume by G. E. Bacon, the Third Edition of which was released by the Oxford University Press in 1975. The answer is that Bacon's book starts from first principles and may be used as an introductory text, while the volume under review consists of chapters on specialized topics by prominent workers in the field (although the first chapter, written by Dachs, is a useful introduction).

The chapter of most interest to chemists is the one by Coppens, describing the combined use of X-ray and neutron crystallographic data to map charge-density distributions. The technique thus gives direct information about chemical bonds—differences between single, double, and triple bonds are apparent, lone-pair electrons may be visualized, and theoretical results may be tested. G. Zaccaï has contributed a chapter on the application of neutron diffraction to biological problems. Much of his emphasis is on the technique of small-angle scattering, which is discussed at greater length in the chapter on disordered systems, written by W. Schmatz. P.-A. Lindgård reviews the contributions of neutron diffraction to the study of phase transitions and critical phenomena. Other chapters deal with polarized neutrons (J. B. Hayter), the investigation of magnetic structures (W. Prandl), and liquid structures (P. Chieux), and with applications (including neutron interferometers) of the theory of dynamical neutron diffraction (H. Rauch and D. Petrascheck).

Reproduced directly from typescript, this book is comparatively inexpensive and may well be purchased by some readers with a strong interest in one or more of the topics covered.

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Comprehensive Chemical Kinetics. Volume 20: Complex Catalytic Processes. Edited by C. H. BAMFORD and C. F. H. TIPPER (University of Liverpool). Elsevier Scientific Publishing Co., Amsterdam. 1978. xii + 414 pp. $98.00 (subscription price $85.00).

This series of volumes on chemical kinetics has been appearing over the past ten years, and is providing a valuable compendium of facts and theories, written by experts. Section 8 of the series, comprising four volumes, is concerned with heterogeneous reactions, and Vol. 20 is the second in this section; the first, dealing with simple surface processes, has not yet appeared—possibly because such processes are hard to find.

The volumes in this series have consistently maintained a high standard, and this volume is no exception. As usual, the editors have chosen authors who are knowledgeable and diligent, and who are skillful in presenting their material in simple and clear language.

The volume contains only three rather lengthy chapters, with 79 illustrations, 109 tables of data, and copious references. Chapter 1, by Geoffrey Webb, deals with "Catalytic Hydrogenation", and appropriately begins with an account of the nature of the metal catalysts and a helpful summary of theories of heterogeneous catalysis, including applications of activated-complex theory. The hydrogenations of olefins, alkynes, dienes, and cyclic molecules are dealt with in detail, and the chapter concludes with a thoughtful discussion of the influence of geometrical and electronic factors.

The second chapter, by K. van der Wiele and P. J. van den Berg, on "Heterogeneous Oxidation Processes", deals mainly with work done since 1970, previous work having been reviewed elsewhere. There is a thorough discussion of the oxidations of ethylene and propene, followed by accounts of the higher olefins, aromatic hydrocarbons, methanol, ammonia, and sulfur dioxide. Again, there are many helpful comments on the role of the catalysts and other theoretical aspects.