Table I. Representative Rate Data[a]

[CNpy]/ [Me₂PhP]	10³k_{obsd} (sec⁻¹)	[Ph₃P]/ [t-Bu(py)]	10²k_{obsd} (sec⁻¹)
	P₁Co(DH)₂		
0.025	8.5 ± 0.1	0.013	2.7 ± 0.1
0.771	4.2 ± 0.1	0.981	1.6 ± 0.1
1.994	2.5 ± 0.1	2.174	0.93 ± 0.05
	CH₃Co(DH)₂		
0.013	59.0 ± 1.0	0.013	8.4 ± 0.1
1.017	25.5 ± 0.5	0.966	5.0 ± 0.1
1.675	17.1 ± 0.5	1.663	3.9 ± 0.1

[a] Errors are rounded up, so as to allow for possible errors in weighings, value measurements, etc. These values represent only part of the data used to compute the competition ratios in Table II. CNpy and Ph₃P are the leaving ligands. $T = 25°$.

Table II. Competition Data[a]

Entering ligand	———P₁Co(DH)₂———		———CH₃Co(DH)₂———	
	k_{-1}/k_2	10³k_1 (sec⁻¹)	k_{-1}/k_2	10²k_1 (sec⁻¹)
	Leaving Ligand CNpy			
(CH₃O)₃P	0.97 ± 0.1	8.3 ± 1.0	1.2 ± 0.2	6.2 ± 1.3
MeImd	1.1 ± 0.2	9.0 ± 1.0	1.3 ± 0.2	5.8 ± 1.0
t-Bu(py)	1.3 ± 0.1	9.1 ± 1.0	1.3 ± 0.2	6.1 ± 1.0
Me₂PhP	1.3 ± 0.1	8.8 ± 1.0	1.6 ± 0.2	6.4 ± 1.0
Ph₃P	1.4 ± 0.2[b]		1.8 ± 0.4[b]	
Bu₃P	5.9 ± 0.6	10.0 ± 1		
	Leaving Ligand Ph₃P			
t-Bu(py)	0.9 ± 0.1	29 ± 5	0.7 ± 0.13	7.8 ± 1.5
Bu₃P	3.5 ± 0.4	26 ± 3	3.6 ± 0.7	8.1 ± 1.5

[a] Data were analyzed using the equation $1/k_{obsd} = (1/k_1) + (k_{-1}/k_2k_1)([L]/[L'])$. The values of the limiting rate constant k_1 and the competition ratio k_{-1}/k_2 were determined from least-squares regression analyses. Errors were rounded up. The values of k_1 were not significantly different before the error limits were increased. $T = 25°$. [b] From the Ph₃P-t-Bu(py) data.

effectiveness of the highly nucleophilic Bu₃P[23] suggests that steric factors influence the competition ratios in cobaloximes. Competition ratios influenced by both steric factors and ligand nucleophilicites have been observed for carbonyl complexes.[24] Once coordinated, Bu₃P is less bulky than Ph₃P[25] but it is likely that the dangling alkyl groups interfere with the competition of Bu₃P for the five-coordinate intermediate.

The clarity of the competition data and our conclusions prompted a similar study for methylcobaloximes (Tables I and II). Our interpretation of the data for P₁Co(DH)₂ requires that the competition ratios for CH₃-Co(DH)₂ be similar. The greater reactivity in aqueous solutions of thiols than thiolate anions toward CH₃-Co(DH)₂ was explained[11] by suggesting that thiols π bond to CH₃Co(DH)₂ during formation of the product, CH₃Co(DH)₂(thiol). Our data suggest that a preferable explanation is that the thiolate anions are strongly solvated and therefore less reactive.[9,26]

More work on these systems is needed before a detailed knowledge of the degree of residual bonding in the transition state can be assessed. Insight into this problem might be gained by studying both stronger and

(23) Reference 20, p 396. The ligands in Table II cover a wide range of nucleophilicities and form cobaloximes differing in stability by at least a factor of 10³.

(24) R. J. Dennenberg and D. J. Darensbourg, Inorg. Chem., 11, 72 (1972).

(25) C. A. Tolman, J. Amer. Chem. Soc., 92, 2956 (1970).

(26) There is a trend in the data which parallels ligand basicity. Ligand solvation may be important. R. L. Courtright, R. S. Drago, J. S. Nusz and M. S. Nozari, Inorg. Chem., 12, 2809 (1973).

weaker[26] ligands. We are currently pursuing several lines of research in these areas and have evidence that dimers similar to those observed for CH₃Co(DH)₂[27] can be formed. The RR'P(O) ligands act as *pseudoalkyls* with respect to their influence on the metal center.[28]

Acknowledgment.

(27) A. W. Herlinger and T. L. Brown, J. Amer. Chem. Soc., 94, 388 (1972).

(28) In addition to the similarities between the P₁Co(DH)₂ and CH₃-Co(DH)₂ complexes reported here, we have noted that in the pmr spectra of complexes of these moieties the resonances have nearly identical chemical shifts: W. C. Trogler, R. C. Stewart, L. A. Epps, and L. G. Marzilli, Inorg. Chem., in press. These shifts were quite different from other complexes of the type XCo(DH)₂L. The affinities of different ligands for P₁Co(DH)₂ and CH₃Co(DH)₂ are quite similar and very different from that for ClCo(DH)₂. For example, CNpy is ca. five times better than Ph₃P for P₁Co(DH)₂, whereas Ph₃P is ca. 100 times better than CNpy for ClCo(DH)₂. Incidentally, pmr determination of the stability constant for the reaction P₁Co(DH)₂(CNpy) + Ph₂P ⇌ P₁Co(DH)₂(Ph₃P) + CNpy yields a values of 0.20, whereas data in Table II give $K = k_1k_2/k_{-1}k_{-2} = 0.23$. For CH₃Co(DH)₂, these values are 0.43 and 0.39, respectively. A further similarity found was that exchange reactions of neither P₁ nor CH₃ complexes are catalyzed by cobalt(II). Most other cobaloximes of the type XCo(DH)₂L undergo exchange of the neutral ligand (in CH₂Cl₂) exclusively by a cobalt(II)-catalyzed pathway: L. G. Marzilli, J. G. Salerno, and L. A. Epps, Inorg. Chem., 11, 2050 (1972).

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Anisotropic Reaction with Ammonia Gas of a Crystal of a Carboxylic Acid with Linear Hydrogen-Bonded Chains. An Example of Unitropic Attack

Sir:

Previous studies on the reaction of gaseous amines with single crystals of aromatic carboxylic acids have concentrated on cases where the acids form hydrogen-bonded dimers.[1-3] This is by far the most common packing arrangement for those carboxylic acids that are devoid of other substituents capable of taking part in hydrogen bonding.[4] In a number of crystals of benzoic acid and derivatives, fast and approximately equal rates of reaction were noted in the direction perpendicular to the plane of the carboxylic acid group (and hence of its dimer) and in the direction along the O···O vector of a particular carboxylic acid residue, while the reaction was slow along the vector defined by the C–C bond from the carboxylic acid carbon atom, i.e., the direction protected by the phenyl ring.[1,3] We propose giving the name *ditropic* (in two ways) to this type of crystal reactivity. With the aim of finding a different type of reactivity pattern, we have examined the reaction of ammonia with crystals of an optically active carboxylic

(1) R. S. Miller, D. Y. Curtin, and I. C. Paul, J. Amer. Chem. Soc., 93, 2784 (1971).

(2) J. P. Desvergne and J. M. Thomas, Chem. Phys. Lett., 23, 343 (1973).

(3) R. S. Miller, D. Y. Curtin, and I. C. Paul, manuscript in preparation.

(4) The known exceptions to this generalization are mostly compounds whose volatility, low melting point, or other properties make them undesirable or difficult candidates for such studies. Examples are formic acid, acetic acid, β-oxalic acid [see R. W. G. Wyckoff, "Crystal Structures," Vol. 5, 2nd ed, Interscience, New York, N. Y., 1966], and β-tetrolic acid [V. Benghiat and L. Leiserowitz, J. Chem. Soc., Perkin Trans. 2, 1763 (1972)].
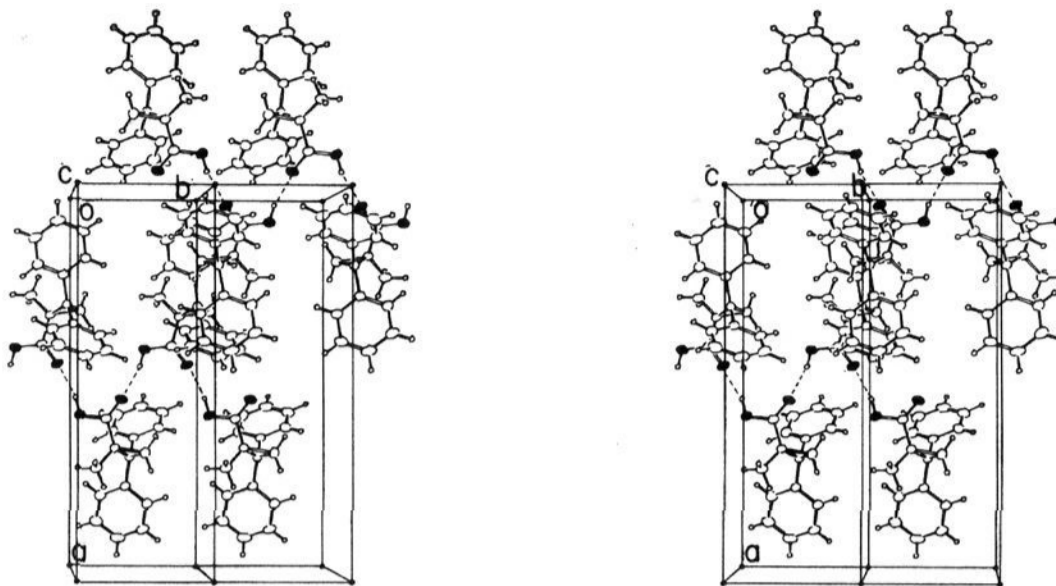
Figure 1. Stereoscopic view showing the crystal packing of **1**. Filled-in circles represent oxygen atoms. It should be noted that the well-developed face of the crystal (100), see Figure 2 and 3, corresponds to the faces of the cell at the top and bottom of this picture. H-bonded chains run along the *b* axis (from left to right).
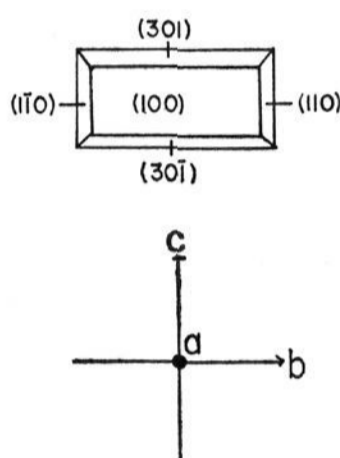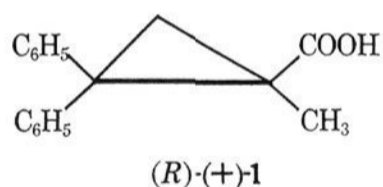

Figure 2. Crystal faces of **1** and axial orientation of the crystal.

acid that forms linear chains of hydrogen-bonded carboxyl groups.

Single crystals of (R)-(+)-2,2-diphenyl-1-methylcyclopropanecarboxylic acid (**1**) were prepared by the

(R)-(+)-**1**

method described by Walborsky and collaborators.[5–7] Crystallization of the resolved acid from acetone solution gave platelets, mp 190–191°, measuring up to 1 mm in longest dimension: $C_{17}H_{16}O_2$, mol wt = 252.3; orthorhombic; a = 18.199 (5), b = 6.309 (1), c = 11.796 (2) Å; V = 1354.3 Å^3, ρ_{measd} = 1.231, Z = 4, ρ_{calcd} = 1.238 g cm^{-3}; space group $P2_12_12_1$. The crystal structure was solved by direct methods and has been refined to an R factor of 0.038 on 1261 nonzero reflections collected on a Picker FACS-1 diffractometer (Cu Kα radiation). A stereoscopic view of the crystal packing looking along the c axis is shown in Figure 1. Clearly the linear (HO—C=O···HO—C=O) struc-

(5) H. M. Walborsky, L. Barash, A. E. Young, and F. J. Impastato, *J. Amer. Chem. Soc.*, **83**, 2517 (1961). These authors considered that on the basis of solid state ir spectra and space group determination, **1** and some related acids crystallized as linear hydrogen-bonded chains.

(6) H. M. Walborsky and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3288 (1964).

(7) We are very much indebted to Dr. Walborsky for calling these acids to our attention and for provision of some samples. We further acknowledge useful discussions with Dr. Ralph Pfeiffer of Lilly Research Laboratories regarding early X-ray measurements he made on some of these compounds.[5]
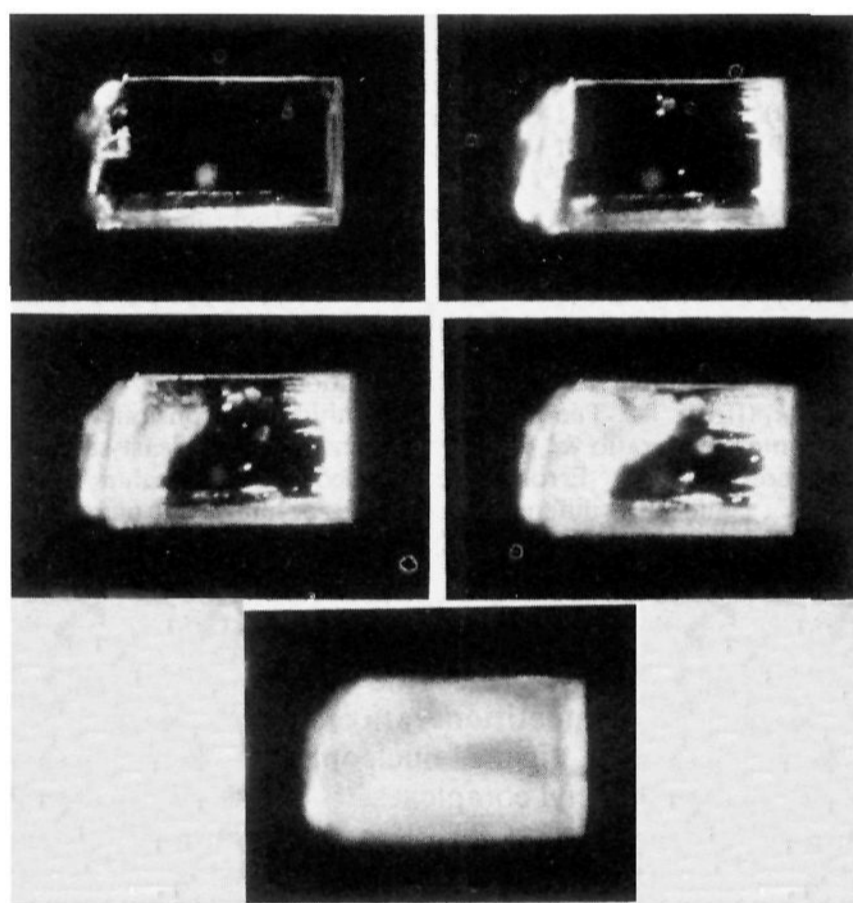
Figure 3. Crystal of (R)-(+)-2,2-diphenyl-1-methylcyclopropanecarboxylic acid undergoing reaction with ammonia vapor: upper left, t = 0; upper right, t = 1 hr; center left, t = 1.5 hr; center right, t = 2 hr; bottom, t = 24 hr. The crystal was illuminated between crossed polarizing filters and was in the extinction position initially.

ture proposed earlier[5] is confirmed with the hydrogen-bonded chains running parallel to the b axis. From the crystal data and measurement of interfacial angles for several crystals, the crystal faces indicated in Figure 2 were identified.

The crystalline acid **1** reacts readily with ammonia gas to give the 1:1 ammonium salt as shown by the results of microanalysis for carbon, hydrogen, and nitrogen. Examination on a microscope stage of single crystals of acid **1** subjected to a stream of ammonia gas showed attack to begin at those faces bounding the crystal at the ends where the b axis emerges. Reaction then proceeds almost exclusively in the directions parallel to the b axis with little observable attack at other faces until the reaction has progressed for some time. We propose to call the idealized reactivity pattern ap-

proached here unitropic, in contrast to the ditropic pattern described previously. The reaction of such a crystal is shown in Figure 3.

These results provide support for the mechanism of the reaction previously proposed.[1-3] Ammonia attack at a carboxyl group leads to disorientation of the molecules nearby and permits diffusion of additional ammonia molecules to penetrate to a further carboxyl group. The hydrogen-bonded chains provide a much-preferred reaction path through the crystal. It will be noted that tongues of reaction preceeding the general front visible in Figure 3 suggest that reaction is accelerated by crystal imperfections in certain regions. Examination of the crystal structure shows that each carboxyl–carboxyl hydrogen-bonded center is surrounded by an assembly of cyclopropyl, phenyl, and methyl groups which could be expected to slow migration of ammonia molecules in any direction except the two opposing directions parallel to the b axis. Along b the spacing of carboxyl hydrogen-bond centers is only 3.2 Å. Although this is substantially less than the closest spacing of about 3.8 Å in many acids with the cyclic hydrogen-bonded dimer structure, it may be noted that in this case only a single new carboxyl group is exposed with each 3.2 Å of travel whereas two carboxyl groups are exposed each 3.8 Å in the reaction of cyclic dimers.

It appears likely that studies of this kind can be expected to lead to knowledge of the mechanisms of solid–gas reactions which should assist in utilizing (or preventing) such reactions and also can give rapid information about the internal structure of crystals. See paragraph at end of paper regarding supplementary material.

Supplementary Material Available. A table of atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St. N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-3699.

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A New and Highly Efficient Synthesis of Rethrolones

Sir:

Allethrolone (1) and *cis*-cinerolone (2) are examples of a class of hydroxycyclopentenones commonly called rethrolones. These substances occur in nature as the alcohol moiety of the pyrethrins, a group of esters derived from either chrysanthemic or pyrethric acids.[1]

(1) L. Crombie and M. Elliott, *Fortschr. Chem. Org. Naturst.*, **19**, 120 (1961); H. J. Sanders and A. W. Toff, *Ind. Eng. Chem.*, **46**, 414 (1954).

Pyrethrins are biodegradable and exhibit high insect toxicity but low mammalian toxicity.[2] These manifold properties have led to intense interest in the synthesis of pyrethrins and preparative routes to both chrysanthemic acid and the rethrolones have been developed.[3] We wish to describe a highly efficient general construction of rethrolones *via* a one-step conjugate addition alkylation reaction which affords intermediates containing all of the carbon atoms and appropriate functionality for simple conversion into either 1 or 2.

The construction of allethrolone as well as the other rethrolones described herein was carried out in the following manner.[4] A solution of thiomethylacetone (3)[5] (1 equiv) dissolved in THF (1 M) was treated with sodium hydride (1.15 equiv) at 0°. To this solution was added the ketene thioacetal monoxide, 4[6] (1 equiv), and the resulting mixture was stirred at 0° for 5 hr. Allyl iodide (1.15 equiv) was added and the reaction mixture was then allowed to stir 16 hr at 0°. Work-up in the usual manner gave a yellow oil (99% yield) which was readily identified as compound 5 on the basis of its spectral characteristics.[7] Hydrolysis of 5 (1 equiv) in acetonitrile (1 M) using 70% perchloric acid (0.3 equiv) at 0° for 2 hr gave the keto aldehyde 6 (99% yield).[8] Conversion of 6 into allethrolone was accomplished by treatment of the keto aldehyde (1 equiv) with potassium *tert*-butoxide (1 equiv) in *tert*-butyl alcohol (1 M) at 22° for 15 min. Chromatography of the crude reaction mixture gave pure *dl*-allethrolone (80% yield, 78%

(2) M. Elliott, A. W. Farnham, N. F. Janes, P. H. Needham, and B C. Pearson, *Nature (London)*, **213**, 493 (1967); M. Elliott, N. F. Janes, and B. C. Pearson, *J. Chem. Soc. C*, 2551 (1971); Y. Katsuda, T. Chikamoto, H. Ogami, H. Hirobe, and T. Kunishige, *Arg. Biol. Chem.*, **33**, 1361 (1969).

(3) For recent preparations of chrysanthemic acid, see M. Julia and A. Guy-Rousult, *Bull. Soc. Chim. Fr.*, 1411 (1967); E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967); R. W. Milla, R. D. H. Murry, and R. A. Raphael, *J. Chem. Soc., Perkin Trans. 1*, 133 (1973). For rethrolone preparations, see M. S. Schechter, N. Green, and F. B. LaForge, *J. Amer. Chem. Soc.*, **71**, 1517, 3165 (1949); L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1152 (1950); L. Crombie, A. J. B. Edgar, S. H. Harper, M. W. Lowe, and D. Thompson, *ibid.*, 3552 (1950); L. Crombie, S. H. Harper, R. E. Stedman, and D. Thompson, *ibid.*, 2445 (1951); M. S. Schechter, N. Green, and F. B. LaForge, *J. Amer. Chem. Soc.*, **74**, 4902 (1952); R. A. LaMahiew, M. Carson, and R. W. Kierstead, *J. Org. Chem.*, **33**, 3660 (1968); L. Brombie, P. Hemseley, and G. Pattenden, *J, Chem. Soc. C*, 1016 (1969); M. Vandewalk and E. Madeleyn, *Tetrahedron*, **26**, 3551 (1970); G. Büchi, D. Minster, and J. C. F. Young, *J. Amer. Chem. Soc.*, **93**, 4319 (1971).

(4) This synthetic strategy arose from the following antithetic transformations which ultimately led to the ketone enolate i and the enolonium ion ii.
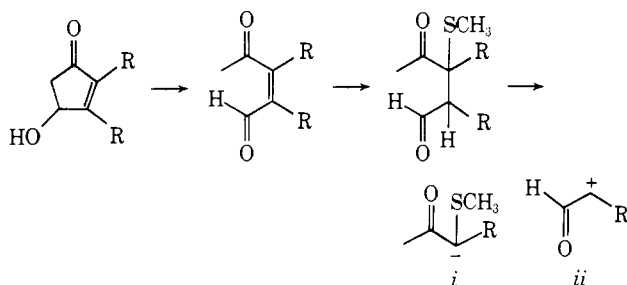
(5) C. K. Bradsher, F. C. Brown, and R. J. Grantham, *J. Amer. Chem. Soc.*, **76**, 114 (1954).

(6) J. L. Herrmann, J. E. Richman, P. J. Wepplo, and R. H. Schlessinger, *Tetrahedron Lett.*, 4707 (1973).

(7) Infrared (CHCl₃) 1687 (C=O), 1632 (C=C), 1032 cm⁻¹ (S=O). The nmr and mass spectra are also in satisfactory agreement with the structure assigned to compound 5. The reaction leading to 5 was worked-up with saturated ammonium chloride solution (pH 6).

(8) Infrared (CHCl₃) 1712, 1692, (C=O), 1637 cm⁻¹ (C=C); nmr (100 MHz, CDCl₃) δ 10.16 (s, 1 H); mass spectrum *m/e* 200.