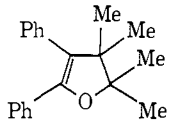
by-product in our reaction, would likely catalyze the rearrangement of **4** to **3**.[10,10a]

Treatment of dibromodesoxybenzoin (**1**) with excess zinc dust in refluxing tetramethylethylene for 2 days provides the fully substituted dihydrofuran **5**[11] in 37% yield. Analogous reactions in benzene with 1,1-diphenylethylene or diphenylacetylene produce the corresponding heterocycles **6**[12] and **7**, albeit in lower yield.



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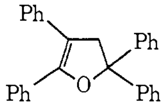

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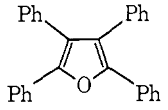

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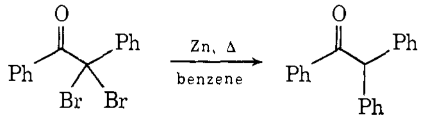
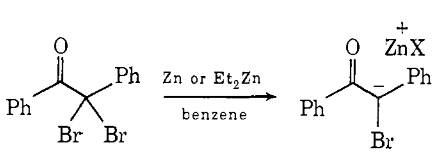
In the absence of other trapping agents, benzhydryl phenyl ketone (**8**) constitutes the major product (20–30% yield) from α debromination of **1** with zinc in refluxing benzene (eq 3). Simple insertion of the ketocarbenoid into a C–H bond of benzene satisfactorily accounts for the formation of **8**, although other mechanisms may be imagined. The possibility of Wolff rearrangement to diphenylketene followed by acylation of the solvent (zinc bromide catalyzed) was easily disproved by repetition of this reaction in benzene-d_6 which afforded **8** with all the deuterium in the benzhydryl portion of the molecule.[13] In the other trapping experiments run in benzene, ketone **8** generally appears as a by-product; desoxybenzoin and benzil have also been isolated in variable yield.



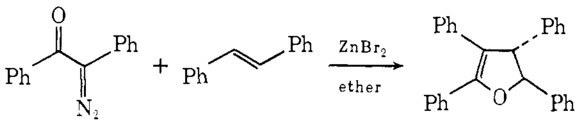
1 **8** (3)

We believe the zinc-induced α elimination of bromine from **1** involves the intermediacy of bromoenolate **9** (X = Br), formed by a process which parallels the first step of a Reformatsky reaction.[14] The related enolate **9** (X = Et) can be prepared rapidly and efficiently by the reaction of **1** with diethylzinc in benzene at 5° (eq 4); subsequent quenching with chlorotrimethylsilane, even after 24 hr at room temperature, furnishes the corresponding trimethylsilyl enol ether in high yield and attests to the stability of this α bromoenolate.[15] Complete generation of the enolate from **1**, in fact, requires only 0.5 molar equiv of diethylzinc. The α-bromoenolate formed in this manner also gives the dihydrofuran **3** with *trans*-stilbene in refluxing benzene; however, ethyl bromide, the by-product of enolate formation, interferes with olefin trapping and must first be removed by evaporation and replaced with fresh solvent.



1 **9** (4)

The classical diazo ketone route to benzoylphenylcarbene, starting from azibenzil (**10**), has been known for many decades,[16] but previous attempts to intercept this ketocarbene with olefins have failed.[17] We have found that decomposition of **10** with zinc bromide in the presence of *trans*-stilbene produces the same dihydrofuran (**3**) obtained earlier by the α-elimination route (eq 5; *cf.* eq 1). Bromoenolate **9** (X = Br), a plausible common intermediate in the production of **3** by both the diazo route and the α-elimination route, undoubtedly accounts for the monobromodesoxybenzoin isolated also from the azibenzil decomposition.



10 **2** **3** (5)

The results described herein not only provide a second example of α elimination adjacent to a ketone but also demonstrate for the first time the feasibility of trapping the resulting ketocarbenoids intermolecularly with olefins, with an acetylene, and with benzene. Efforts to develop synthetically useful α-elimination routes to carbonyl-conjugated carbenes and carbenoids for the cyclopropanation of olefins continue in our laboratories.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of California—Los Angeles Research Committee for financial support of this work.

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[10] Related rearrangements have been reported by M. I. Komendantov, T. S. Smirnova, I. N. Domnin, and L. A. Krakhmal'naya, *J. Org. Chem. USSR*, 2551 (1971).

[10a] Note Added in Proof: Cyclopropyl ketone **4**, prepared by another method, can be recovered quantitatively after treatment with zinc bromide in refluxing benzene for 3 days. Furthermore, when the reaction in eq 1 is run in the presence of independently prepared **4**, the cyclopropyl ketone is not consumed. These experiments support the dipolar addition mechanism for the formation of dihydrofuran **3**, since **4** never appears among the normal products of that reaction.

[11] Compound **5**: ir (CCl_4) 1650 (C=C) and 1250 cm^{-1} (C—O), no carbonyl; nmr (CCl_4) δ 7.30–7.05 (m, 20), 1.35 (s, 6), and 1.02 ppm (s, 6); uv max (EtOH) 285 mμ (ε 11,000); mass spectrum (70 eV) M$^+$ at *m/e* 278. *Anal.* Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.04; H, 7.82.

[12] Compound **6** had spectral properties in agreement with those reported by R. E. Lutz and D. W. Boykin, Jr., *J. Amer. Chem. Soc.*, **86**, 5046 (1964).

[13] Benzhydryl phenyl ketone (**8**) fragments in the mass spectrometer (70 eV) to give major peaks at *m/e* 167 (PhCH$^+$Ph) and 105 (PhC≡O$^+$). In the mass spectrum of **8** obtained from the benzene-d_6 trapping, only the former peak appears at higher *m/e*. The nmr signal for the two hydrogens ortho to the carbonyl group in **8** (δ 8.05–7.75 ppm) appears well separated from that of the other aromatic hydrogens (δ 7.50–7.15 ppm) and remains unchanged in the nmr spectrum of benzhydryl phenyl ketone obtained from the benzene-d_6 experiment.

[14] R. L. Shriner, *Org. React.*, **1**, 1 (1942).

[15] Other α-haloenolates show similar stability; see ref 3.

[16] G. Schroeter, *Ber. Deut. Chem. Ges.*, 42, 2336, 3356 (1909).

[17] R. Huisgen, H. König, G. Binsch, and H. J. Sturm, *Angew. Chem.*, 73, 368 (1961).

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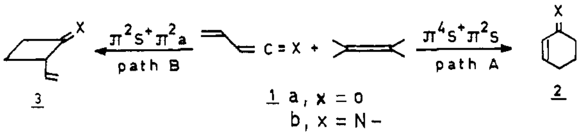
[4 + 2] Cycloadditions of a Vinylketenimine. A New Route toward Functionalized Cyclohexenone Derivatives

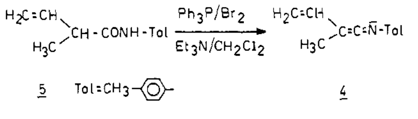
Sir:

Vinylheterocumulenes **1a** and **b** offer synthetic potentialities which have been little explored. One attractive possibility is the direct synthesis of cyclohexenones **2a** from the reaction of a vinylketene **1a** and an olefin (path A). It was found, however,[1] that,



when exposed to ethyl vinyl ether, 2-propenylketene yielded a cyclobutanone rather than a cyclohexenone. In light of more recent theoretical and experimental results,[2] the preference for path B over path A in this case is not surprising since $({}_{\pi}2_s + {}_{\pi}2_a)$ cycloadditions are initiated by an interaction of the nucleophilic π system of the olefin and the unoccupied $\pi^*_{C=O}$ orbital of the ketene. Accordingly electron-poor olefins were found quite unreactive toward ketenes;[3] however, they should be quite suitable for Diels–Alder reactions with vinylheterocumulenes like **1a** or **1b** (path A) since the dienic parts of these molecules are expected to behave as nucleophilic partners due to the effect of electron donation from the heteroatom.[4] Since alkenylketenes **1a** are not readily available and appear to be quite unstable, we decided to undertake the synthesis of a vinylketenimine **1b** and examine its behavior as a cycloaddition partner.

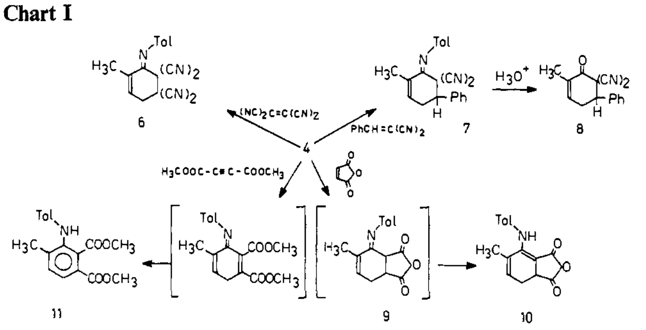
N-p-Tolylvinylmethylketenimine (**4**), the first representative of this class of vinylheterocumulenes, was obtained from the reaction of amide[5] **5** (7.06 g) with triphenylphosphine bromide (9.79 g of Ph_3P + 5.97 g of Br_2) and triethylamine (30 ml) in refluxing CH_2Cl_2 (150 ml) according to the general procedure described by Bestmann, *et al.*[6] Work-up and distillation through a short Claisen flask yielded 2.89 g (45%) of **4** as a



yellow liquid: bp 65–66° (0.2 Torr); *m/e* 171 (M^+); $\nu_{C=C=N}$ 2000 cm^{-1}; $\lambda_{max}^{cyclohexane}$ 256 nm (ϵ 37,000). The 60-MHz spectrum featured resonances at $\delta_{CDCl_3}^{TMS}$ 7.13 (s, four aromatic H's), 6.4 (d of d, $CH{=}CH_2$, J_{cis} = 10 Hz, J_{trans} = 16 Hz), 4.91 (d, one vinyl H), 4.86 (d, one vinyl H), 2.3 (s, three benzylic H's), and 1.83 (s, three allylic H's). In contrast with the related vinylketenes, **4** was *fairly stable at room temperature* and could be distilled without much loss.

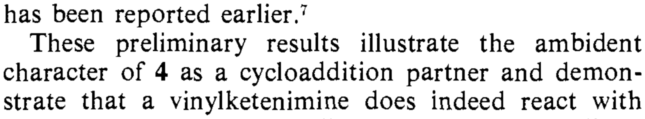
As anticipated, the dienic system of **4** *reacted readily* (*20°, acetonitrile*) *with electron-deficient dienophiles* (Chart I); with TCNE, **6** (mp 165°) was obtained in 77% yields; 1,1-dicyanostyrene cycloadded to **4** entirely regiospecifically to give **7** (100%, mp 134°) which

Chart I



was hydrolyzed to the cyclohexenone derivative **8** (95%, mp 146–147°) by treatment with water containing *p*-toluenesulfonic acid. With maleic anhydride, a crystalline product **10**, mp 173–174°, was obtained in 88% yields, which resulted from the spontaneous tautomerization of the primary adduct **9**. On the other hand, the reaction of **4** with dimethyl acetylenedicarboxylate, a less reactive dienophile, required 52 hr at 50° to give **11** as the sole isolable adduct (40%; mp 115–116°). In all cases, the structures were firmly established on the basis of spectral (mass, ir, nmr, uv) or analytical data.

Interestingly an electron-rich dienophile preferred reacting across the dienic system formed by the carbon–nitrogen double bond and one of the conjugated C=C bonds of the benzene ring; thus an equimolar mixture of **4** and *N*-diethylaminophenylacetylene in acetonitrile (4 hr, 0°) gave quantitatively the substituted quinoline derivative **12**: *m/e* 344 (M^+); $\delta_{CCl_4}^{TMS}$ 7.1–8.1



13 12

(m, eight aromatic H's), 5.3 (m, one vinylic H), 2.9 (q, 4 H, CH_2CH_3, J = 7 Hz), 2.53 (s, three benzylic H's), 1.13–1.8 (m, six allylic H's), and 0.97 (t, 6 H, CH_2CH_3). A similar reaction with triphenylketenimine and ynamines has been reported earlier.[7]

These preliminary results illustrate the ambident character of **4** as a cycloaddition partner and demonstrate that a vinylketenimine does indeed react with electron-poor olefins according to path A. The direction of these additions is such that the terminal vinylic carbon of **4** becomes attached to the electron-deficient carbon of the olefinic partner. This can be ascribed to the interaction of the dienic system of **4** with the nitrogen lone pair. In this respect, **4** differs from the related vinylallene which gives two regioisomeric adducts with methyl vinyl ketone.[8]

Finally, we wish to stress the synthetic interest of our observations. A new simple route toward polysubstituted cyclohexenone derivatives is now available (*e.g.*, **4** → **7** → **8**). Further work is now underway to enlarge the concept to other vinylheterocumulenes as well as to shed some light on the various factors (electronic, steric, conformational) responsible for their reactivity.

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(1) G. B. Payne, *J. Org. Chem.*, **31**, 718 (1966).

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971); R. Sustmann, A. Ansmann, and F. Vahrenholt, *J. Amer. Chem. Soc.*, **94**, 8099 (1972), and references cited therein.

(3) See, for instance: L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971).

(4) J. L. Reilly, G. R. Krow, and K. C. Ramey, *J. Org. Chem.*, **37**, 2364 (1972).

(5) **5** was obtained by conventional methods from the known 2-methyl-3-butenoic acid: J. F. Lane, J. D. Roberts, and W. G. Young, *J. Amer. Chem. Soc.*, **66**, 543 (1944).

(6) H. J. Bestmann, J. Lienert, and L. Mott, *Justus Liebigs Ann. Chem.*, **718**, 24 (1968).

(7) L. Ghosez and C. de Perez, *Angew. Chem., Int. Ed. Engl.*, **10**, 184 (1971).

(8) M. Bertrand, J. Grimaldi, and B. Waegell, *Chem. Commun.*, 1141 (1968); *Bull. Soc. Chim. Fr.*, 962 (1971).

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Derivative Chemistry of $HCo[P(OR)_3]_4$. I. Basic Dynamic Stereochemical Processes

Sir:

Synthesis[1] of $KCo[P(OR)_3]_4$ has provided entry to two classes of $HCo[P(OR)_3]_4$ derivatives, each of importance to an understanding of basic fluxional processes; one comprises C_{3v} XML_4 molecules and the second, trihapto allyl and benzyl derivatives of $Co[P(OCH_3)_3]_3$.

A C_{3v} HML_4 molecule cannot strictly undergo a Berry rearrangement because there is a C_{2v} constraint to the reaction path.[2] A physical process applied to quasitetrahedral HML_4 molecules is the tetrahedral jump mechanism.[2] Dnmr datafor the new $XCo[P(OR)_3]_4$[3] molecules suggest that the tetrahedral jump mechanism is a probable rearrangement path for C_{3v} or pseudo-C_{3v} XML_4 aggregates.

$CH_3Co[P(OR)_3]_4$, like the parent hydrides,[2] do not show a limiting slow exchange ^{31}P or ^{13}C spectrum to −160°. These methyl derivatives cannot have the near T_d CoP_4 microsubstructure of the hydrides[2] because of $H(CH_3)$–P repulsions (precision model analysis). Nevertheless, this structural change and the larger size of the X group does not substantially raise the rearrangement barrier. A relative measure of barrier enhancement may be inferred from a study[4] that showed $CH_3Rh[P(OCH_3)_3]_4$ to have a rearrangement barrier about 2 kcal/mol higher than the analogous hydride.[2]

The mercurial $Hg\{Co[P(OCH_3)_3]_4\}_2$ is a bi(trigonal bipyramid) with axially (mercury) shared vertices. This molecule is fluxional ($AB_3 \rightleftharpoons A_4$ ^{31}P spectra) with a barrier, $E_a^{\ddagger}$, of ~10 kcal/mol. The coordination polyhedron about cobalt should be farther removed from quasitetrahedral than the methyl derivative. $Co_2[P(OR)_3]_8$, unlike the carbonyl analog, has a symmetrical bicapped trigonal antiprismatic Co_2P_8 framework;[5] each cobalt atom has micro C_{3v} symmetry with four P and one Co ligating atoms. A precision model of the dimer indicates that the cobalt atom should be displaced out of the equatorial P_3 plane *away* from the axial phosphorus atom and that ligand–ligand interactions are so intimate as to seriously encumber any rearrangement path. The molecule is stereochemically rigid to 100° (^1H spectra).

We suggest that a low energy rearrangement path for C_{3v} XML_4 molecules is the "tetrahedral edge traverse" outlined in Figure 1 with a reaction path constrained only to C_s symmetry. Where ϕ is close to 70.5°, X will be small, there will be the identity with the tetrahedral jump mechanism, and barriers will be very low. As ϕ increases, barriers should rise to some point midway between a ϕ of 70.5 and 90°.[6] As ϕ approaches 90°, the amorphous energy surface for the five-atom family is evident because in this region[7] barriers may fall and a lower energy quasi-Berry reaction path may become available. As ϕ becomes greater than 90°, as in $Co_2[P(OR)_3]_8$, the barrier should rise rather sharply. We plan to gather X-ray and dnmr[8] data for C_{3v} XML_4 species to test the "tetrahedral edge traverse" proposal.

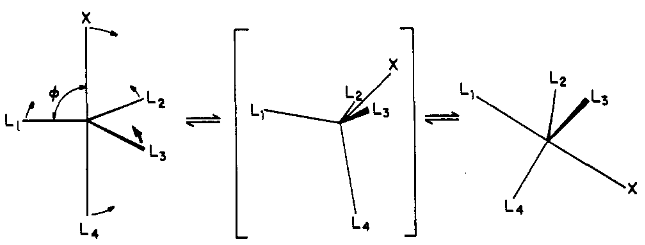

Figure 1. A representation of the tetrahedral edge traverse mechanism for C_{3v} or pseudo-C_{3v} XML_4 molecules. This simply is a more general statement of the tetrahedral jump mechanism.[2] Note that where $\phi \rightarrow 90°$ and X and L are very similar in steric and electronic character, the bracketed "transition state" is a new (labeled) trigonal bipyramid; the process then is indistinguishable from the Berry mechanism.

The ^1H spectra of h^3-$C_3H_5Co[P(OCH_3)_3]_3$ and h^3-1-$CH_3C_3H_4Co[P(OCH_3)_3]_3$ are very similar to those reported for the carbonyl analogs,[9] and there is no evidence in these spectra to 100° of a fast $\pi \rightleftharpoons \sigma$ process. A benzyl derivative is also formulated as a trihapto structure, although requisite limiting ^1H and ^{13}C spectra were not seen (*vide infra*). These molecules are fluxional with surprisingly fast ligand rotation as evidenced by the dnmr ^{31}P spectra which show A_3 (−90°) transitions to AB_2, ABC,[10] and AB_2 (−130°) for allyl, 1-methylallyl, and benzyl, respectively. The low-temperature ^{31}P spectra are best rationalized in terms of a trihapto allyl ligand either (1) above a pyramidal CoP_3 framework of C_{3v} microsymmetry or (2) as a bidentate ligand attached to two vicinal basal vertices of a square pyramid. However, these two models are so closely related by minor bending modes as to make distinctions, at least for the nmr time scale, meaningless. Conceptually, the simplest picture of the dynamic process that equilibrates P environments is a rotation[11] of the trihapto ligand in a plane normal to the Co–C_3 (centroid) axis. Alternatively, the intermediate states for such a rotation may be considered polytopal iso-

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(1) E. L. Muetterties and F. J. Hirsekorn, *J. Chem. Soc., Chem. Commun.*, in press.

(2) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

(3) R = CH_3 or C_2H_5.

(4) E. L. Muetterties, to be submitted for publication.

(5) AB_3 ^{31}P spectrum and 3:1 intensity ratio for R proton resonances.

(6) ϕ in $Hg[Co(CO)_4]_2$ is 83 ± 2°: G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc. A*, 1005 (1968). We anticipate a 10–13 kcal/mol barrier which should be determinable by ^{13}C dnmr.

(7) Especially where X and L are very similar in steric and electronic character.

(8) Mechanistic distinctions cannot be made[2] from the character of line shape changes for C_{3v} XML_4.

(9) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, **83**, 1601 (1961).

(10) The low-temperature spectrum is too simple for rigorous characterization as an ABC pattern, but this does not affect the stereochemical arguments because the allyl derivative provides the critical distinctions.

(11) For earlier discussion of ligand rotation see A. Davison and W. C. Rode, *Inorg. Chem.*, **6**, 2124 (1967); J. W. Faller and M. J. Incorvia, *J. Organometal. Chem.*, **19**, P13 (1969); J. K. Becconsall and S. O'Brien, *Chem. Commun.*, 720 (1966); J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 538 (1968).