to yield III which, by reaction with a second chloromethyl site, can produce IV.

In order to limit the formation of doubly bound species, the formation of III has to be prevented through control of both the number of dithiolate units present in the medium and the proton exchange reaction. It was thought that such control could be achieved through the use of a three-phase system[10] in which most of the reactive species would be kept from the polymer to limit the proton exchange reaction. Our system consists of a polymer phase swollen in benzene with an aqueous solution of NaOH to which 1,4-butanedithiol is added. The reactive thiolate and dithiolate species are present in the aqueous phase and can be carried to the polymer through the use of a phase transfer catalyst. Using this approach, only a small amount of thiolate can ever be present in the organic phases, and, in addition, since it is known that dianions are transported less easily than monoanions[11] under phase transfer conditions, the influence of the dithiolate on the reaction should be reduced. Our results seem to confirm this expectation as illustrated by the data for expt 2 and 5, in which a drastic reduction of the amount of double coupling is observed with the three-phase system (39 vs. 94%). Double coupling can be reduced to $\simeq$5% by a modest increase[12] in the ratio of dithiol:base which produces an increase in the relative concentration of the monoanion vs. dianion in the aqueous phase (expt 7 and 8). Similarly, double coupling can be increased to $\simeq$87% by ensuring that all dithiol is converted into the dianion (expt 4).

We are presently exploring the application of phase transfer catalysis to the control of site-site interactions in other reactions involving polyfunctional molecules.

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(6) Chloromethylated resin prepared from Bio-Beads SX-1 (Bio-Rad Laboratories), capacity 2.10 mequiv of Cl/g, or degree of functionalization = 0.244.
(7) The percent double coupling can be calculated as follows. Polymer (1000 g) contains T styrene units, of which X are unsubstituted (mol wt 104), Y are singly bound (mol wt 238), and Z are doubly bound (mol wt 177)

$$1000 = X(104) + Y(238) + Z(177) \quad (1)$$

and $X + Y + Z = T$. Since the degree of functionalization is 0.244, $Y + Z = 0.244\ T$ and $X = 0.756\ T$. From the sulfur analysis (S expressed in milliequivalents/gram, one gets $S = 2Y + Z$; thus $T = (S - Y)/0.244$. Substituting for X, Z, and T in eq 1, $1000 = 499\ S - 438\ Y$, or $Y = (1000 - 499S)/438$ and percent double coupling = $100\ Z/(Y + Z)$.
(8) Our experience with the reaction has shown that the ratios of Cl:base or Cl:dithiol have little bearing on the end result of the reaction provided that the nucleophile is always present in excess.
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(10) A typical three-phase reaction was carried out as follows. To a suspension of 1.40 g of chloromethylated polymer (2.1 mequiv/g) in 15 mL of benzene were added 0.8 g of NaOH in 6 mL of H_2O, 0.13 g of a 40% aqueous solution of tetrabutylammonium hydroxide, and 6 mL of 1,4-butanedithiol. The mixture was stirred vigorously under nitrogen at room temperature for 22 h and filtered, and the polymer was washed with THF–HCl–H_2O (2:1:1), H_2O, THF, acetone, dichloromethane, and methanol. After drying in vacuo, the polymer weighed 1.57 g and contained a trace of chlorine and 11.21% (3.50 mequiv/g) sulfur.
(11) For an excellent review, see E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.*, **16**, 493 (1977).
(12) Phase-transfer reactions are best carried out with fairly concentrated aqueous ionic solutions. For this reason it was not practical to test the reaction under conditions in which the dithiol:base ratio would approach the 12:1 value of expt 3. Under such conditions essentially no double coupling would be observed. Unfortunately, when the amount of base is reduced drastically, the phase transfer reaction becomes very slow and after 24 h the polymer still contains appreciable amounts of chlorine.

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Complete Syn Selectivity in the Alkylation of Lithiated Ketimines

Sir:

The pioneering work of Stork[1] and Wittig[2] on the metalation of ketimines and their subsequent reaction with a variety of electrophiles has proven extremely useful for controlled aldol condensation and also for regioselective functionalization of ketones.[3] Recently reactions of chiral lithiated ketimines[4,5] and aldimines[6] have been established as an important method of asymmetric synthesis, producing chiral ketones in optical yields as high as 95%.[5a] Work in many laboratories on the lithiation and alkylation of other cyclohexanone derivatives, including dimethylhydrazones,[7] oximes and substituted oximes,[8] and also on the structurally related nitrosamines,[9] and *N,N*-dimethylbenzamides[10] has, in every case, revealed a surprisingly large stereoselectivity with the syn product being formed almost exclusively. Alkylation of conformationally fixed lithiated derivatives with methyl iodide gave in each series a single product (>99%) whose methyl group was shown to possess the syn and axial orientation.[8c,9a] In view of the current conflict as to the origin of this stereoselectivity[11] in these synthetically useful reactions, we have undertaken an investigation of the stereochemistry of lithiation and alkylation of a number of ketimines by direct examination of the products of ^{13}C NMR. We report that this sequence of reactions on ketimines also gives *only* syn and *only* axial (in cyclohexanones) alkylation products, a result of major theoretical and practical significance.

Our initial experiments to test for any difference in syn-anti anion stabilities involved a study of the base-catalyzed H–D exchange of acetone-*N*-benzylketimine[13] (**1**). Only in Me_2SO-d_6 (*tert*-butyl alcohol-*O*-*d*, 0.03 M in potassium *tert*-butoxide) was the basicity of the medium sufficiently strong to effect an isotopic exchange. The relative rates of syn vs. anti exchange at the two methyl groups[14] was determined to be 50:1 at 20 °C. Since exchange of the anti protons may occur by syn deuteration and then base-catalyzed inversion, the 50:1 rate ratio represents a lower limit for this selectivity.

Lacking other solvent systems sufficiently basic to promote isotopic exchange, we turned our attention to the determination of the stereochemistry of the products of lithiation and alkylation of ketimines. Using standard aprotic conditions, i.e., addition of 1 equiv of ketimine to 1.05 equiv of lithium diisopropylamide (LDA) in THF at −20 °C, then at 0 °C for 1 h, and then cooling to −78 °C, followed by addition of 1.1 equiv of methyl iodide and reaction for 1 h at −78 °C, rapid concentration at <0 °C, and dissolution in $CDCl_3$, gave a sample whose ^{13}C NMR was immediately recorded at −2 °C. The results of alkylation of a number of ketimines **2a**, summarized in Table I, demonstrate the reaction to be totally stereoselective, yielding syn product only.[15,16] Subsequent isomerization to the thermodynamically more stable anti configuration could be followed by ^{13}C NMR and the position of this equilibrium is also given in Table I.

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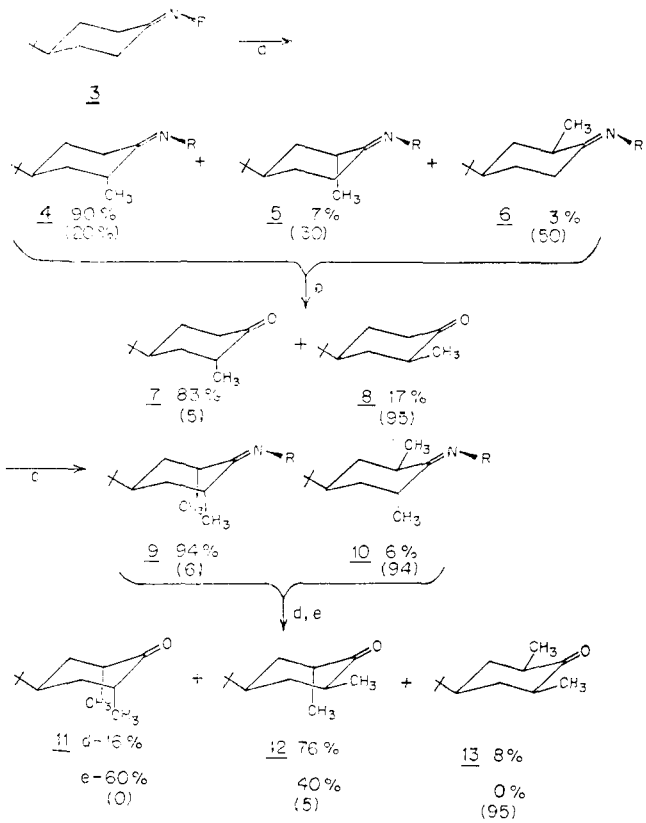
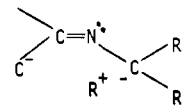
Scheme I[a] (R = $CH(CH_3)_2$)



[a] (a) LDA, THF (0 °C), 1 h; MeI (−78 °C), 1 h. (b) Saturated NH_4Cl-$NaHCO_3$, THF, 1 h. (c) LDA, THF (0 °C), MeI (−78 °C), 1 h; inverse addition to LDA, THF (25 °C) 2 h; MeI (−78 °C) 1 h. (d) Saturated NH_4Cl-$NaHCO_3$, THF (25 °C), 1 h. (e) pH 7, KH_2PO_4-NaOH buffer (25 °C) 16 h. All yields in parentheses refer to distribution of isomers at equilibrium.

Additional stereochemical results are provided in Scheme I. The conformationally fixed ketimine **3** undergoes syn-axial alkylation only (if we accept the interpretation that the anti alkylation products are formed by isomerization of the *syn*-methyl derivative, as the data in Table I suggests). This axial attack predominates even in formation of the diaxial derivative of 2,6-dimethyl-4-*tert*-butylcyclohexanone (**9**). Hydrolysis can be achieved with partial epimerization to give a mixture dominant in *r*-2-methyl-*t*-4-*tert*-butyl-*c*-6-methylcyclohexanone (**11**).[17] This exclusive axial attack, as was rationalized previously,[8,9a] results from the fact that equatorial attack of the syn anionic intermediate is strongly retarded by both the steric effect of the nitrogen substituent and by an unfavorable stereoelectronic factor.[18]

Thus every reaction of lithiated ketimines yielded the less stable syn methylation product with extremely high stereoselectivity. In fact, for cases in which some anti product was observable, inversion which was occurring during spectral accumulations appeared responsible for all of the anti isomers present. The unusual stereochemical result is indicative of a large preferential stability of the syn lithiated imine. The energy difference, assuming that product ratios reflect the position of the syn and anti lithiated imines at equilibrium,[21] is a minimum of 1.8 kcal/mol (from the >99:1 ratio at −78 °C). The reason for this energy difference is not readily apparent. Arguments to account for the syn selectivity of lithiated oxime derivatives, hydrazones, and nitrosamines appear inapplicable to the case of a lithiated ketimine. Certainly, chelation cannot stabilize the syn form, nor would orbital symmetry[12] be expected to play as significant a role, since the 4-atom, 6π-electron framework must involve a hyperconjugative donation of a C-H or C-C bond to attain the butadiene dianion-like system, e.g.,

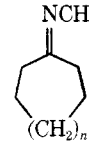


Another possible source of preferential syn stability might be differences in torsional interactions in the two anions. However, the data in Table I shows that the variation in the size of the cyclic ketone which would be expected to cause variation in torsional effects has no detectable influence on the selectivity of the reaction. One other effect perhaps deserves consideration. There is the possibility that the anti anion suffers a destabilizing interaction between the lone pair on nitrogen and the pair of π electrons at the α carbon.[19] Such a lone-pair-π-repulsive effect has a precedent, though its magnitude could not be quantitatively assessed.[20]

Behavior analogous to the lithiated ketimines has been well established for a number of metalated butenes. The careful work of Schlosser[22] showed a preference for the cis configuration of the butenyl anion (in tetrahydrofuran) which increased as the metal changed in the order Li, Mg, K, Cs. In contrast, measurement of this cis ⇄ trans equilibrium in the gas phase[23] shows a slight excess of trans over cis, reflecting a small steric effect dominating a small "electronic effect". The divergent results in the gas phase were quite logically assessed as an indication of the profound importance of solvent effects on the equilibrium. It may well be that the stereoselectivity of reactions of lithiated imines will be best accounted for by differential solvation effects.[24]

The above conclusion raises the question as to whether the current arguments, orbital symmetry and chelation, have a primary influence on the stereoselectivity observed in oximes, hydrazones, and nitrosamines. Rather, these systems may owe their stereoselectivity of alkylation to the same factor responsible for the syn selectivities of lithiated ketimines. Further work towards elucidation of this factor is in progress.

Table I. Syn-Anti Stereoselectivity in Imine Alkylations



reactant	% syn product[a]	% syn at equilibrium	% yield of ketone[b]
2a, n = 0	≥98	18	64
2b, n = 1	≥99[c]	21	81
2c, n = 2	≥99	31	87
2d, n = 3	≥99	23	85
2e, n = 7	≥99	17	95[d]

[a] The figure given is based on the ^{13}C NMR spectrum of product after completion of 1000 transients at which time 1% anti isomer would be detectable. In two instances (n = 0, 7) 5% anti isomer was observed and, after each additional 1000 scans, was observed to increase. The figures quoted were obtained by extrapolation to zero time of sample preparation. [b] Hydrolysis (NH_4Cl-$NaHCO_3$ buffer) and distillation gave pure ketone as established by NMR, VPC, TLC, and IR. [c] Use of allyl bromide gave 2-allylketimine (≥99% syn) which provided a 94% yield of 2-allylcyclohexanone on hydrolysis. Alkylation with 3-bromo-1-chloropropane gave, after hydrolysis, an 81% yield of 3-chloropropyl derivative. [d] Yield of crude methyl derivative by ^1H and ^{13}C NMR.

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(14) The rates were measured by monitoring the integrals of the two methyl absorptions over a period of 20 min. Separate ^1H NMR measurements on a sample of **1** partially deuterated in the syn position in Me_2SO-d_6 in the absence of base showed that, in this solvent, the half-life for inversion is 2 h. Thus, under the conditions of integral measurements, the effect of a "lateral shift" would be small (and would only cause a slight diminution in selectivity). The assignment of absorptions to *syn*- and *anti*-methyl protons was made previously[13] by three independent methods.
(15) The ^{13}C NMR spectra clearly indicated the stereochemistry of the alkylation products. The syn and anti α carbons of ketimines exhibit a 10–11-ppm difference in shieldings with the syn carbon appearing at higher field, as has been observed for oximes, oxime ethers, hydrazones, and nitrosamines.[16] Axial substituents were clearly identifiable by the γ-shielding effect. Confirmatory proof that the syn carbon was at higher field was obtained as follows. A sample of **1** was selectively deuterated in the syn position in Me_2SO-d_6–*tert*-butyl alcohol-*O*-*d*, as indicated by the ^1H NMR NMR and then immediately examined by ^{13}C NMR. The high-field methyl signal (δ 18.7) was no longer visible above the noise, while the lower field methyl absorption (δ 29.4) remained a singlet.
(16) The carbon shieldings in cyclohexanone ketimines revealed stereochemically dependent substituent effects of an α-methyl group which were essentially identical with those of oxime ethers and nitrosamines.[8b]
(17) This highly strained ketone has been reported as one component (48%) in a mixture of diastereoisomers: F. Johnson, *Tetrahedron*, **30**, 3241 (1974).
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(19) Interaction of the lone pair on nitrogen with the trans C–C bond via donation into an empty σ^* orbital should be more important in the starting material, thereby favoring anti lithiation.
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(24) One influence of solvent on these organometallics would be to perturb the state of aggregation about which there is no direct evidence. We have observed (R. R. Fraser and F. Akiyama, unpublished results) that the formation of the anion with butyllithium–tetramethylethylenediamine or –hexamethylphosphoramide had no effect on the syn selectivity.

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Structure and Triboluminescence of Polymorphs of $(Ph_3P)_2C$

Sir:

Hexaphenylcarbodiphosphorane[1] ($(Ph_3P)_2C$) has attracted recent interest because of its triboluminescent properties,[2,3] its structure-bonding relationships,[4,5] and its organometallic chemistry.[6] During our spectroscopic studies of its triboluminescence (TL), we found that triboluminescent crystals lose their TL upon standing. Further investigation revealed that single crystals of the non-TL polymorph could be obtained from solution by slow crystallization. The crystal structure of the non-TL phase, its differences from the previously reported[4] phase, and its implication to the triboluminescence mechanism are reported here.

Nontriboluminescent, moisture sensitive, yellow diamond-shaped crystals of ~0.20 by 0.16 mm were cleaved from needles grown by slow cooling of a diglyme solution in an insulated container. X-ray diffraction data collected at −160 °C under a stream of cold, dry nitrogen indicated the orthorhombic space group $P2_12_12_1$; $a = 11.184\ (4)$, $b = 12.956\ (4)$, $c = 19.410\ (5)$ Å; $V = 2812.5$ Å^3; $Z = 4$; $d_{calcd} = 1.267$ g/cm^3. Data were collected on a Syntex $P\bar{1}$ automated diffractometer with monochromatic Mo Kα radiation up to a 2θ maximum of 47°; 1776 reflections of $I > 3\sigma$ were used in the solution and refinement of the structure ($R_{final} = 0.041$). No correction for crystal absorption was made ($\mu = 1.38$ cm^{-1}). In addition to the low temperature structure determination, diffraction data were collected at room temperature and refined to a final R factor of 0.059. Crystal decomposition was observed in this case with a decrease in standard reflection intensities of ~30%. However, the crystal and molecular structures were essentially the same as those observed at low temperature.[7]

The previously reported phase of hexaphenylcarbodiphosphorane contains two different molecular forms in a monoclinic $C2$ unit cell ($\beta = 95.1°$).[4] Bond length and bond angle differences between the molecular structures of the nontriboluminescent molecule reported here (crystal A, Figure 1) and the two molecules of the previous structure (BI and BII) are shown in Table I. Torsion angles, defined as C–P–P–C, range from 25.0 to 27.5° in the nontriboluminescent structure compared with the previously reported[4] range of 5.5 to 8.3°.

Table I. Hexaphenylcarbodiphosphorane: Molecular Data

molecule	P=C=P angle, deg	distance, Å		
		C=P	P···P	P–C(Ph)
$(Ph_3P)_2C$ (A)[a]	134.4	1.610	2.968	1.853
$(Ph_3P)_2C$ (A)[b]	131.7 (3)	1.635 (5)	2.984	1.831
$(Ph_3P)_2C$ (BI)	130.1 (6)	1.633 (4)	2.961	1.837
$(Ph_3P)_2C$ (BII)	143.8 (6)	1.629 (3)	3.097	1.832
$(Ph_3P)_2CH^+$	128.2 (3)	1.702 (5)	3.063	1.808

[a] Room temperature. [b] Low temperature.

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