with L = P(p-tolyl)$_3$, where $K_4 \sim 4 \times 10^{-4}$ M in benzene at 25°. The dimer obeys Beer's law and has a ^{31}P spectrum consisting of a non-first-order doublet of triplets. The large doublet splitting is assigned to J_{PRh} while the small triplet splitting may be due to J_{PRhRh} or J_{PRhRhP}; in any event the spectrum is inconsistent with a monomeric species RhClL$_2$. In the presence of 0.01 M or higher added L, solutions of RhClL$_3$ complexes do obey Beer's law, showing that equilibrium 4 is forced to the left under these conditions. There was no evidence for RhClL$_4$ formation even in 0.5 M L.

Our studies show that RhCl[P(C$_6$H$_5$)$_3$]$_3$ and RhH$_2$Cl[P(C$_6$H$_5$)$_3$]$_3$ are the major species present in solutions of tris(triphenylphosphine)rhodium chloride and hydrogen. Reactions 3 and 2 represent the first two steps in the "hydride" route[1,7] to hydrogenation, the subsequent step presumably being coordination of the olefin to the site vacated by P$_1$. This mechanism is in harmony with the basic postulate that, in general, only 16- and 18-electron complexes are present in homogeneous reactions catalyzed by group VIII transition metal complexes, other species being energetically unfavorable.[8] A similar sequence of reactions obeying this rule can be written for the "unsaturate" route.[1,7] Detailed studies of various other aspects of the olefin hydrogenation system are currently being investigated.

Acknowledgment. We are indebted to Professor J. H. Noggle of the University of Delaware for the use of their Bruker HFX-90 spectrometer in obtaining Fourier transform ^{31}P spectra on dilute solutions of RhCl[P(C$_6$H$_5$)$_3$]$_3$, to G. Watunya for obtaining the cw spectra in Figures 1 and 2 on a similar spectrometer, and to D. W. Reutter for the Cary 14 spectra.

(8) C. A. Tolman, accepted for publication in *Quart. Rev., Chem. Soc.*

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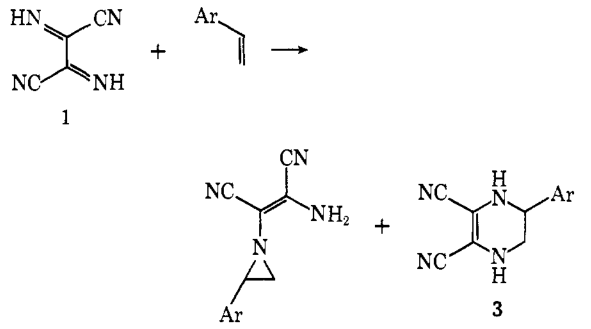
Hydrogen Cyanide Chemistry. II. Reactions of Diiminosuccinonitrile with Olefins

Sir:

Diiminosuccinonitrile (DISN), prepared by base-catalyzed addition of hydrogen cyanide to cyanogen, has been found to be a highly reactive and versatile intermediate, particularly valuable in the synthesis of new heterocycles through condensation and displacement reactions.[1] We now wish to report that the 1,4-diazabutadiene (HN=C—C=NH) system[2] of this polyfunctional reagent behaves like a zwitterionic nitrenium ion toward sufficiently nucleophilic olefins and furthermore the reaction products depend highly on the electronic character of the olefin substituents.

Styrene and p-halostyrenes reacted with DISN in acetonitrile at room temperature to give 2-amino-3-(2-arylaziridin-1-yl)maleonitrile (**2a–c**) in 50–80% yield,[3,4] whereas the more electron-rich p-methoxystyrene and 2-vinylfuran gave 5-aryl-2,3-dicyano-1,4,5,6-tetrahydropyrazine (**3e** and **3f**) in 60–80% yield.[3,5] While in the latter cases the reaction was complete within a day and no aziridine could be detected; DISN was still present in the former reactions even after several days, but no tetrahydropyrazine was detected in the reaction mixture. p-Methylstyrene gave both types of products, **2d** and **3d** (eq 1).



(1)

	2	3
	yield, %[3]	
a, Ar = C$_6$H$_5$	58	
b, Ar = p-ClC$_6$H$_4$	51	
c, Ar = p-FC$_6$H$_4$	79	
d, Ar = p-CH$_3$C$_6$H$_4$	62	1.3
e, Ar = p-CH$_3$OC$_6$H$_4$		60
f, Ar = 2-furyl		81

That the aziridine formation proceeds with retention (>98%) of olefin stereochemistry was demonstrated by the reaction of cis- and $trans$-β-methylstyrene[6] with DISN. It was previously reported[1] that the cycloaddition of cis-1,2-dimethoxyethylene with DISN to 2,3-dicyano-5,6-dimethoxy-1,4,5,6-tetrahydropyrazine also occurs with retention of stereochemistry.

Mechanistically, we postulate that DISN interacts with sufficiently nucleophilic olefins in such a manner that the 1,4-diazabutadiene is progressively polarized to a zwitterionic nitrenium ion (see **5**) as the transition state is approached. This novel polarization is probably assisted by generation of the highly resonance stabilized dicyanovinylamide ion. Since nitrenium ions[7] are isoelectronic with carbenes, **5** is expected to give zwitterionic aziridinium ion **4**[8] with retention of olefin stereochemistry (eq 2). Migration of a hydrogen atom from the ring nitrogen to the amido nitrogen

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(1) R. W. Begland, A. Cairncross, D. S. Donald, D. R. Hartter, W. A. Sheppard, and O. W. Webster, *J. Amer. Chem. Soc.*, **93**, 4953 (1971).

(2) The system has been virtually unknown and very little studied; see G. Tuchtenhagen and K. Rühlman, *Justus Liebigs Ann. Chem.*, **711**, 174 (1968).

(3) All reactions were carried out in acetonitrile in the presence of excess olefins at room temperatures except where noted otherwise. The yields are not optimized. All new compounds gave correct elemental analyses and consistent spectral (iv, uv, nmr) data.

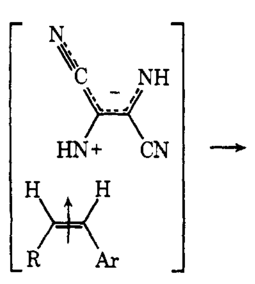
(4) Typically, **2a** showed uv$_{max}$ (C$_2$H$_5$OH) 300 nm (ϵ 14,200); nmr (CDCl$_3$) δ 2.50 (d, 1, J = 4 Hz, $trans$-CH$_2$), 2.66 (d, 1, J = 7 Hz, cis-CH$_2$), 3.12 (d of d, 1, J = 4, 7 Hz, CH), 4.55 (br, 2, NH$_2$), 7.33 (s, 5, arom).

(5) Typically, **3e** showed uv$_{max}$ (C$_2$H$_5$OH) 324 nm (ϵ 10,300), 224 (21,800); nmr (CD$_3$CN–D$_2$O) δ 2.96 (d of d, 1, J = 12.5, 6.6 Hz, $trans$-CH$_2$), 3.38 (d of d, 1, J = 12.5, 3.2 Hz, cis-CH$_2$), 4.11 (d of d, 1, J = 6.6, 3.2 Hz, CH), 3.81 (s, 3, OCH$_3$), 7.11 (AB, 4, arom). The tetrahydropyrazines (**3**) are readily converted to the corresponding 5-aryl-2,3-dicyanopyrazines.

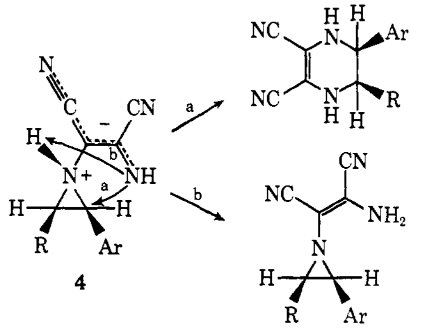
(6) The reaction of cis-β-methylstyrene required reflux in acetonitrile.

(7) Nitrenium ions have been shown to add to double bonds: P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970); also see W. Nagata, S. Hirai, K. Kawata, and T. Aoki, *J. Amer. Chem. Soc.*, **89**, 5045 (1967).

(8) Although DISN is believed to be transoid,[1] **4** is assumed to possess a maleonitrile side chain. It is not clear how and when this isomerization occurs; however, DISN is readily converted to diaminomaleonitrile (DAMN) derivatives in many reactions[1] and DAMN is thermodynamically more stable than diaminofumaronitrile: Y. Yamada, N. Nagashima, A. Nakamura, and I. Kumashiro, *Tetrahedron Lett.*, 4529 (1968).

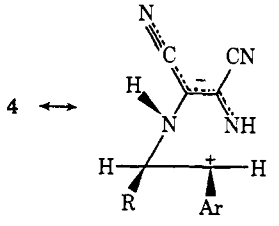


5



(2)

results in the formation of aziridines. A sigmatropic $_\sigma 2_s + _\pi 4_s$ migration of the carbon bearing an aryl group to the amido nitrogen, on the other hand, can give rise to 2,3-dicyano-1,4,5,6-tetrahydropyrazines with retention of olefin stereochemistry. Consistent with this mechanism is the observation that as the electron-donating power of the aryl group increases, the reaction becomes more facile and the formation of dicyanotetrahydropyrazine becomes more favorable. The latter may be expected because the bond between the ring nitrogen and the carbon-bearing aryl group in **4** becomes weaker as the resonance contribution of **4a** to the zwitterionic aziridinium ion **4** increases (eq 3). This two-step stereospecific formation of 2,3-dicyano-1,4,5,6-tetrahydropyrazine, however, cannot be differentiated from the direct 2 + 4 cycloaddition between DISN and olefins by presently available data. Reactions of DISN with other olefins and a detailed discussion of the mechanism will be reported upon completion of this work.



(3)

4a

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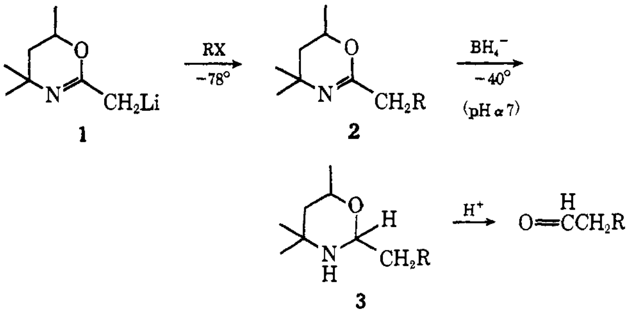
Dihydro-1,3-oxazines. XV. A Two-Carbon Homologation of Alkyl Halides to Aldehydes Using a Novel Ketene *N*,*O*-Acetal

Sir:

The alkylation of 2-methyldihydro-1,3-oxazines *via* their lithio salt **1** at −78° has been shown to provide suitable precursors **2** which were converted under pH-controlled borohydride reduction to masked aldehydes **3** and ultimately to aldehydes by acidic cleavage.[1] Although many examples were provided to demonstrate the utility of this sequence,[2] it still suffers from several disadvantages: (a) successive low-temperature steps are required for the formation of **2** and **3**, (b) the use of alkyllithium reagents which are not universally available, and (c) isolation of **2** and **3** which results in loss of material and time.



We describe in this preliminary report a significant and efficient modification of the sequence which originates from the methiodide salt (**4**)[3] of the readily available starting oxazine **5**. The methiodide salts have been used earlier to prepare ketones by addition of organometallic reagents to the C=N link followed by hydrolytic cleavage.[4] In this instance, however, **4** was smoothly transformed into the ketene *N*,*O*-acetal[5] **6** [91%; bp 94–95° (30 mm); ir 1625 cm^{-1}; nmr (benzene) δ 3.08, 3.69 (d, $J = 2$ Hz) assigned to the vinyl protons] which was highly sensitive to moisture, rapidly forming the amino ester **9**. The ketene *N*,*O*-acetal was also successfully prepared (87%) by the base-catalyzed cleavage of the methiodide salt **8** (mp 136.5–138°) obtained by treating the acetone adduct **7**[6] with methyl iodide (dimethylformamide, 70°). It was felt that **6** would behave as a highly nucleophilic enamine due to its unusual high-field vinyl proton signals. This suggests considerable contribution from canonical form **6a** to its ground-state structure.[7] Due to the unstable nature of **6** and its difficulty in handling, we found that it may be conveniently prepared *in situ*. Thus, by treating the methiodide salt **4** in dimethylformamide with sodium hydride (2 equiv) followed by the addition of an alkyl halide, the elaborated oxazinium salt **10** was rapidly produced. The latter is immediately neutralized by the second equivalent of sodium hydride present to the ketene *N*,*O*-acetal **11** and treated with an ethanolic solution of sodium borohydride forming **12**.

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(1) A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzer, *J. Amer. Chem. Soc.*, **91**, 763 (1969).

(2) For preparative details, see J. M. Fitzpatrick, G. R. Malone, I. R. Politzer, H. W. Adickes, and A. I. Meyers, *Org. Proc. Prep.*, **1**, 193 (1969).

(3) Prepared by stirring a mixture of 5 and 4.0 equiv of methyl iodide in the dark for 20 hr. Filtration and washing with ether produced a 92% yield of 4: mp 156–158°; ir (KBr) 1610 cm^{-1} (O$\cdots$C$^+\cdots$NCH$_3$).

(4) A. I. Meyers and E. M. Smith, *J. Amer. Chem. Soc.*, **92**, 1084 (1970).

(5) Ketene *N*,*O*-acetals of the type H$_2$C=CORNR$_2$ have been previously prepared by base-catalyzed neutralization of the adduct from *N*,*N*-dimethylacetamide and triethyloxonium fluoroborate [H. Meerwein, W. Florian, N. Schon, and G. Stopp, *Justus Liebigs Ann. Chem.*, **641**, 1 (1961)]. Alkylation of amide acetals to homologated amides has been reported to arise from ketene *N*,*O*-acetals which were presumed to be intermediates [T. Oishi, M. Nagai, and Y. Ban, *Tetrahedron Lett.*, **4**, 497 (1968); T. Oishi, S. Murakami, Y. Sakurai, H. Nakakimura, and Y. Ban, Abstracts of the Third International Congress of Heterocyclic Chemistry, B, Sendai, Japan, 1971, p 125].

(6) A. I. Meyers, A. Nabeya, H. W. Adickes, J. M. Fitzpatrick, G. R. Malone, and I. R. Politzer, *J. Amer. Chem. Soc.*, **91**, 764 (1969).