bromide (33 mmol) in 40 ml of methylene chloride were added at 0°. The reaction mixture was stirred for 2 hr at 0°[7] and then diluted with 15 ml of 6 *N* sodium hydroxide. The olefin formed was extracted into pentane and purified by distillation through a short Vigreux column. The results obtained from several reactions carried out following this general procedure are given in Table II.

Table II. Yields of Products Obtained from Reactions of Cyanogen Bromide with Various Dialkylvinylboranes in CH_2Cl_2

Hydroborating agent[a]	Alkyne	Olefin products (isomeric purity)[a,b]		Yield of trans olefin, %
R_2BH	1-Hexyne	R, H; H, C_4H_9	(96)	69
$R_2'BH$	1-Hexyne	R′, H; H, C_4H_9	(93)	68
$R_2''BH$	1-Hexyne	R″, H; H, C_4H_9	(98)	75[c]
$R_2''BH$	3-Hexyne	R″, H; C_2H_5, C_2H_5		63[d]

[a] R = cyclohexyl, R′ = 2-methylcyclohexyl, R″ = 3-pinanyl. [b] The spectral data for all compounds reported are consistent with the structures proposed. [c] Yield by glpc. Others are isolated yields. [d] The structural assignment is based on the stereochemical result observed in the analogous reaction using 1-hexyne.

It should be noted in connection with the results shown in Table II that in the case using bis(*trans*-2-methylcyclohexyl)borane as the hydroborating agent in formation of the trans olefin product the *trans*-2-methylcyclohexyl group migrates from boron to carbon with retention of configuration. This behavior is similar to that observed in previous work with iodination of the dialkylvinylboranes.[3] Thus, this novel reaction for the conversion of alkynes into di- and trisubstituted olefins of predictable stereochemistry represents a valuable addition to synthetic methodology.

(7) When bis(*trans*-2-methylcyclohexyl)borane was used as the hydroborating agent, the reaction mixture was stirred at 25° for 2 hr.

(8) National Defense Education Act Fellow (Title IV) at the University of California, Davis.

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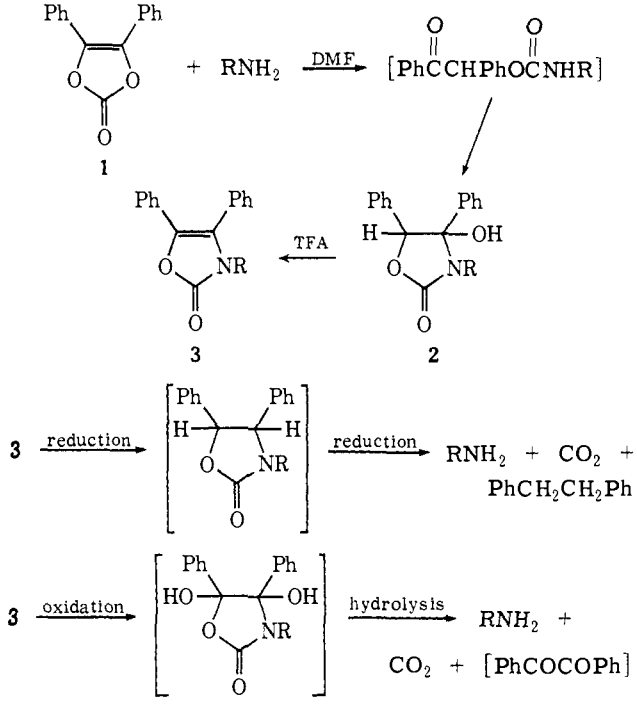
The 4,5-Diphenyl-4-oxazolin-2-one Ring System as an Amine Protecting Group[1]

Sir:

Of the great variety of methods currently available for amino group protection, only a few methods replace both hydrogens of a primary amine function. Although such protection would eliminate or minimize the possibility of a variety of unwanted side reactions, protective groups of this type, which include the phthalimido,[2] arylidine,[3-5] and other groups,[6,7] have generally been of limited utility because of their solvolytic instability, even under mild conditions. We wish to report a novel method of amino group protection by the incorporation of a primary amine nitrogen into the extremely stable and unreactive 4,5-diphenyl-4-oxazolin-2-one ring system.[8] Although the fluorescent and highly crystalline 4,5-diphenyl-4-oxazolin-2-one (Ox) protected derivatives, **3**, are unreactive under the great majority of conditions usually used to remove protective groups, the Ox group may be removed by low-pressure hydrogenolysis, sodium in liquid ammonia reduction, or relatively mild oxidative conditions (Chart I).

Chart I



The Ox derivatives are most conveniently prepared using the cyclic carbonate of benzoin **1**. This reagent may be prepared by treatment of a cooled (5°) stirred mixture of benzoin (1.0 equiv) and phosgene (1.1 equiv) in benzene with distilled *N*,*N*-dimethylaniline (1.0 equiv). After stirring overnight at room temperature, the mixture is filtered from *N*,*N*-dimethylaniline hydrochloride, and the filtrate refluxed for 3 hr to cyclize the initially formed unstable chloroformate. Washing with 1 *N* hydrochloric acid and water, drying over sodium sulfate, and removing the solvent, followed by recrystallization from 95% ethanol, afford the carbonate **1** [mp 75–76°; ir (CCl_4) 1870, 1840 (sh), 1820

(1) Presented in part at the Third American Peptide Symposium, Boston, Mass., June 1972.

(2) J. C. Sheehan and V. S. Frank, *J. Amer. Chem. Soc.*, 71, 1856 (1949).

(3) B. Bezas and L. Zervas, *ibid.*, 83, 719 (1961).

(4) J. C. Sheehan and V. J. Grenda, *ibid.*, 84, 2417 (1962).

(5) E. Gazis, B. Bezas, G. C. Stelekatos, and L. Zervas, *Peptides, Proc. Eur. Symp., 5th, 1962*, 17 (1963).

(6) J. C. Sheehan and E. J. Corey, *J. Amer. Chem. Soc.*, 74, 4555 (1952).

(7) L. A. Carpino, *J. Org. Chem.*, 29, 2820 (1964).

(8) Reviewed in R. Filler, *Advan. Heterocycl. Chem.*, 4, 103 (1965).

cm^{-1}; nmr (CCl_4) δ 7.45 (m); mass spectrum, molecular ion *m/e* 238] in 65–70% yield.

Treatment of a stirred solution of a primary amine or amino acid tetramethylammonium salt (20 mmol) in 20 ml of dimethylformamide with 4.76 g (20 mmol) of **1** produces an intense yellow color which rapidly fades. After stirring for 0.5 hr,[9] the mixture is acidified to pH 1 with 1 *N* hydrochloric acid and extracted with 100 ml of ethyl acetate, and the organic layer is thoroughly washed with water. Drying and solvent removal under reduced pressure give a diastereomeric mixture of hydroxyoxazolidinones (**2**) (ir 1750–1760 cm^{-1}). The mixture may be quantitatively dehydrated to the desired Ox derivative in 20 ml of trifluoroacetic acid over 1–2 hr. Removal of trifluoroacetic acid under reduced pressure and crystallization of the crude product affords pure Ox derivatives in overall yields of 75–85% (Table I). Ox derivatives [ir (KBr) 1750–1760, 1360–1380 cm^{-1}; nmr ($CDCl_3$) δ 7.1–7.3 (s, 5), 7.3–7.5 (m, 5); uv λ_{max} (EtOH) 286–288 mμ, ϵ 1.5 × 10^4; fluorescence spectrum, λ_{max} (EtOH) 390–400 mμ] are stable to aqueous base, refluxing ethanolic hydrazine, ethanolic hydrogen chloride, hydrogen bromide in acetic acid, refluxing trifluoroacetic acid, and anhydrous hydrogen fluoride.[10]

Table I

Ox derivative[a]	Mp, °C[b]	Optical rotation (MeOH)
$OxCH_2CH_2Ph$	123.5–124.5[c]	
Ox-L-Ala	202–204[d]	$[\alpha]^{26}D$ −31.5° (*c* 1.02)
Ox-L-Phe	196–197[d]	$[\alpha]^{25}D$ −176° (*c* 1.02)
Ox-L-Val	234–236[d]	$[\alpha]^{24}D$ −69.3° (*c* 0.99)
Ox-L-Ala-GlyOEt	129.5–130[d]	$[\alpha]^{26}D$ +3.4° (*c* 0.99)

[a] Satisfactory elemental analyses have been obtained for all new compounds. [b] All melting points are uncorrected. [c] Crystallized from 95% ethanol. [d] Crystallized from ethyl acetate–pentane.

The Ox group may be considered as a "protected" *N*-carbobenzoxy-*N*-benzylamine group. It may be removed quantitatively by low-pressure (Parr) catalytic hydrogenation in an organic solvent containing 1 equiv of aqueous acid. Reductions are generally complete within 24 hr using 50 mg of 10% palladium on charcoal for each equivalent of Ox blocked derivative. Similarly the Ox group may be removed in 75–85% isolated yield using sodium in liquid ammonia.

Alternatively the Ox group may be cleaved under oxidative conditions. Oxidation of the oxazolinone double bond to a species equivalent to a dihydroxyoxazolidinone, followed by mild solvolysis, should free the amine function. Treatment of an Ox derivative in trifluoroacetic acid with excess *m*-chloroperbenzoic acid, followed by hydrolytic work-up, affords the free amine in 70% yield.

Simple Ox dipeptide derivatives have been prepared without difficulty using the water-soluble 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride.[11] Removal of the protecting group followed by hydrolysis[12] affords the free peptides in high yield. No racemization has been observed in the preparation of Ox derivatives, stability studies, or coupling or deblocking reactions.[13]

The properties of the 4,5-diphenyl-4-oxazolin-2-ones may lead to alternate applications for the ring system. The fluorescence and stability of Ox derivatives under solvolytic conditions suggest a possible method of peptide N-terminal residue analysis. The N-alkylation of the parent 4,5-diphenyl-4-oxazolin-2-one system under basic conditions[14] may lead to a phthalimide-like method of introducing a nitrogen function. Investigations into these areas and into the scope and limitations of the Ox protecting group are currently in progress.

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(9) The reaction may be conveniently monitored by observing the disappearance of the 1820-cm^{-1} band of the carbonate in the infrared spectrum.

(10) Stability experiments were carried out using Ox-L-Ala as a model. Recovered yields were greater than 95%. Melting point, spectra, and optical rotation were unchanged.

(11) J. C. Sheehan, P. A. Cruickshank, and G. L. Boshart, *J. Org. Chem.*, 26, 2525 (1961).

(12) Hydantoin formation has been noted in the alkaline hydrolysis of Ox peptide esters.

(13) Two-spot method: E. Taschner, A. Chimiak, J. F. Biernat, T. Sokolowska, Cz. Wasilewski, and B. Rzeszotarska, *Peptides, Proc. Eur. Symp., 5th, 1962*, 109 (1963).

(14) R. Gompper, *Chem. Ber.*, **89**, 1748 (1956).

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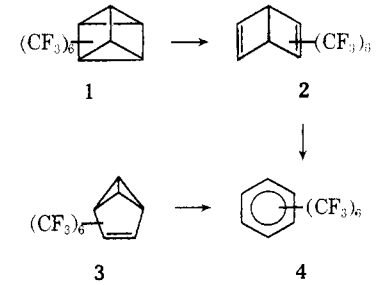
Kinetics and Thermodynamics of $(CCF_3)_6$ Valence Isomer Interconversions

Sir:

As the most complete set[1] of pure benzene valence isomers, the benzene, Dewar benzene, benzvalene, and prismane having the composition $(CCF_3)_6$[2,3] provide a unique opportunity to investigate interrelationships among the four skeletons. Accordingly, the heats of reaction and kinetic parameters have been measured for the thermal isomerizations which connect them, shown in Chart I.

Chart I. Thermal Interconversions of $(CCF_3)_6$ Isomers



(1) Though often ignored in discussions of benzene valence isomers, 3,3′-biscyclopropenyls rightfully belong in this group. An excellent review on $(CH)_n$ valence isomers has just appeared (L. T. Scott and M. Jones, Jr., *Chem. Rev.*, 72, 181 (1972)).

(2) M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *Chem. Commun.*, 202 (1969); *J. Chem. Soc. C*, 1232 (1970). These authors present rate data at 170° for the reactions shown in Chart I.

(3) D. M. Lemal, J. V. Staros, and V. Austel, *J. Amer. Chem. Soc.*, 91, 3373 (1969).