followed by the excess dipolarophile, and the reaction product was separated by fractional vacuum distillation. Thus, the following compounds were obtained.

5-Vinyl-3-cyano-4,5-dihydro-1,2-oxazole (V) was obtained as an oil, bp 53° (0.3 mm), $n^{20}\text{D}$ 1.4852, yield 50%. *Anal.* Calcd for $C_6H_6N_2O$: C, 59.01; H, 4.95; N, 22.94. Found: C, 59.25; H, 5.07; N, 23.02.

3,5-Dicyano-4,5-dihydro-1,2-oxazole (VI) had bp 87° (0.3 mm), $n^{25}\text{D}$ 1.4920, mp 45–46°,[12] yield 53%. *Anal.* Calcd for $C_5H_3N_3O$: C, 49.59; H, 2.50; N, 34.70. Found: C, 49.43; H, 2.64; N, 34.79.

5-Phenyl-3-cyano-4,5-dihydro-1,2-oxazole (VII) had bp 102–106° (0.1 mm), $n^{24}\text{D}$ 1.5553, mp 40°,[12] yield 61%. *Anal.* Calcd for $C_{10}H_8N_2O$: C, 69.75; H, 4.68; N, 16.27; mol wt, 168. Found: C, 69.94; H, 4.83; N, 16.24; mol wt, 177 (osmometric, acetone).

3-Cyano-4,5-dicarbomethoxy-1,2-oxazole (VIII) had bp 102–106° (0.35 mm), $n^{22}\text{D}$ 1.4797, mp 28°,[12] yield 27%. *Anal.* Calcd for $C_8H_2N_2O_5$: C, 45.72; H, 2.88; N, 13.33. Found. C, 45.59; H, 2.79; N, 13.53.

3-Cyano-5-phenyl-1,2-oxazole (IX) had mp 88–89° [from petroleum ether (bp 35–45°)], yield 40%. *Anal.* Calcd for $C_{10}H_6N_2O$: C, 70.58; H, 3.55; N, 16.46. Found. C, 70.74; H, 3.54; N, 16.29.

When aqueous sodium carbonate was replaced in the above reactions by triethylamine, working at temperatures between −17 and +10° under anhydrous conditions as described by Huisgen,[13] none of the adducts V–IX could be obtained, although III was easily decomposed by the triethylamine.

Polymeric Cyanogen N-Oxide (XII).—Compound III (5.6 g) was dissolved in 100 ml of H_2O and filtered, and the filtrate was diluted with 150 ml of H_2O. After 4 hr at 25–30°, 300 mg of XII was filtered off. Within the next 2 hr saturated sodium bicarbonate solution was added dropwise at a rate to maintain pH 6. After 12 hr an additional amount of the polymeric nitrile oxide XII (1.2 g) was filtered off. The crude XII was apparently amorphous, but could be obtained microcrystalline by precipitation from an acetone solution with water. It could not be dried completely at room temperature; at elevated temperatures violet decomposition occurred. Therefore, the analytical data are not entirely satisfactory, but leave no doubt about the composition of the product.

Anal. Calcd for $(C_2N_2O)_5$: C, 35.31; H, 0.00; N, 41.19; mol wt, 340. Found (for two different preparations). C, 35.50, 35.96; H, 0.30, 0.33; N, 39.43, 39.36; mol wt, 308, 377.

We found our preparations not so explosive as described;[4] when XII was heated in a test tube over the open flame only deflagration occurred; a blow with a hammer did not detonate the polymer. Compound XII is insoluble in water and nonpolar organic solvents, but it is easily soluble in methanol, ethanol, acetone, or ethyl acetate.

5-Phenyl-1,2-oxazolecarboxylic Acid (XI).—The cyano compound IX (333 mg) was refluxed for 30 min with 4 ml of 30% aqueous sodium hydroxide, the solid cake was dissolved by addition of water (20 ml) and ethanol (20 ml), and refluxing was continued for another hour. Ethanol and water were then slowly distilled off until the remaining volume in the flask was reduced to approximately 15 ml. The sodium salt of XI which is little soluble in excess sodium hydroxide separated at this point. After cooling the thick slurry was acidified with concentrated hydrochloric acid. The acid XII was filtered and washed with little cold water, redissolved in 2 *N* ammonia (10 ml), filtered from little insolubles, and reprecipitated by concentrated hydrochloric acid, yield 81%. The product was found identical with an authentic sample[8] by infrared spectrum and mixture melting point (162°).

5-Phenyl-4,5-dihydro-1,2-oxazole-3-carboxylic Acid (X).—The acid X was obtained from the nitrile VIII in an analogous fashion as above and identified by comparison with a specimen prepared according to the literature.[7]

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[12] The substance crystallized only after prolonged storage in the refrigerator.

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The Enhanced Intensity of the n → π* Transition as Evidence for Orbital Interaction in β-Silyl Ketones[1a]

W. KENNETH MUSKER AND RANDOLPH W. ASHBY

Department of Chemistry, University of California,
Davis, California

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The possibility of intramolecular interactions between a trimethylsilyl group and a nonadjacent donor resulting in expanded octet σ bonding of silicon has led previous investigators[1b-4] to search for experimental confirmation. Neither infrared analysis of silicon substituted ketones[1b,2] nor pK_A comparisons of silicon containing amines[3] or carboxylic acids[4] with their carbon analogs have yielded evidence for the interaction. Brook[5] reported the spectral properties of some triphenylsilyl substituted ketones, but noted no intramolecular interaction.

Since the enhancement of the extinction coefficient of the n → π* transition in ketones has been attributed to intramolecular orbital interactions, we directed our attention to an ultraviolet study of simple β- and γ-substituted silyl ketones. We found that the ultraviolet absorption spectrum of 1-trimethylsilyl-2-propanone (VIII) and 1-trimethylsilyl-2-butanone (IX) in several solvents exhibited an enhanced extinction coefficient for the n → π* transition, *i.e.*, four to five times greater than values for 2-pentanone (I), 4,4-dimethyl-2-pentanone (II), or 1-methoxy-2-propanone (V) and in the same range as β,γ-unsaturated ketones (see Table I).[6-11]

It should be recalled that ketone carbonyl groups ordinarily exhibit a low intensity (ϵ <30) absorption between 270 and 310 mμ. The low intensity is attributed to the fact that excitation of a lone pair np oxygen electron to the carbonyl π* orbital is symmetry forbidden.[12,13]

Examination of the intensity of the n → π* transition of related ketones (Table I) suggests that alkyl substitution and steric and inductive effects cannot account for the high intensity absorption of these β-silyl ketones. For example, 4,4-dimethyl-2-pentanone (II) and 2,2,4,4-tetramethyl-3-pentanone (III), compounds for which a steric effect would be expected, have normal extinction coefficients (ϵ ~20), and, indeed, comparable with those of 2-pentanone (I). Inductive effects can be similarly

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[1] (a) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965, p 42-O. (b) L. H. Sommer, "Stereochemistry Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 12.

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TABLE I

$n \rightarrow \pi^*$ TRANSITIONS OF SUBSTITUTED KETONES

Ketone	Sol-vent[a]	λ_{max}, mμ	ϵ_{max}	Ref
2-Pentanone (I)	CY	280	18	6
	ET	276	20	6
4,4-Dimethyl-2-pentanone	CY	287	20	6
(II)	ET	284	24	6
2,2,4,4-Tetramethyl-3-pentanone (III)	HX	296	21	6
1,1,1-Trifluoro-2-propanone (IV)	HP	278	40	7
1-Methoxy-2-propanone (V)	CY	282	13	8
	ET	278	15	8
2-Methyl-1-penten-4-one (VI)	IO	290	77	9
1-Phenyl-2-propanone (VII)	CY	289	108	8
	ET	285	150	8
1-Trimethylsilyl-2-propa-	CY	283	81	This work
none (VIII)	ET	276	114	This work
1-Trimethylsilyl-2-butanone	CY	279	93	This work
(IX)	ET	276	121	This work
1-Trimethylsilyl-3-butanone	CY	283	24	This work
(X)	ET	279	40	This work
Bicyclo[2.2.1]hepten-2-one (XI)	CY	304	290	10
Bicyclo[2.2.1]hepten-7-one (XII)	IO	275	33	11
α-Triphenylsilylacetophenone (XIIIa)	ET	310 (sh)[b]	328	5
α-Triphenylmethylacetophenone (XIIIb)	ET	323	95	5
β-Triphenylsilylpropiophenone (XIVa)	ET	311 (sh)	131	5
β-Triphenylmethylpropiophenone (XIVb)	ET	314	84	5

[a] CY = cyclohexane; IO = isooctane; ET = ethanol; HX = hexane; HP = heptane. [b] sh = shoulder.

discounted on the basis of the low extinction coefficient of the $n \rightarrow \pi^*$ transition of 1-methoxy-2-propanone (V) and 1,1,1-trifluoro-2-propanone (IV).

Inspection of ketones exhibiting enhanced extinction coefficients (VI, VII, XI) reveals a common ability on the part of a substituent to interact with the carbonyl group.[14] Labhart and Wagniére[15] attributed β,γ-unsaturated ketone extinction coefficient enhancement to the specific interaction between the nonbonding oxygen p orbital and the ground-state olefinic π orbitals. Perhaps the clearest evidence for a correlation between the intensity of the $n \rightarrow \pi^*$ transition and carbonyl interaction was described by Cookson[11] in a comparison study of the isomeric bicyclo[2.2.1]heptenones. The 7-keto isomer XII, in which oxygen p-orbital nodal planes and olefinic π orbital are orthogonal and the overlap integral zero, exhibits a normal extinction coefficient for an $n \rightarrow \pi^*$ transition. However, the same orbitals of the 2-keto isomer XI are oriented such that they can interact, and an intense $n \rightarrow \pi^*$ transition is observed.

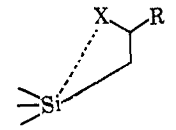
Noting enhanced extinction coefficient values for 1-phenyl-2-propanone (VII) and assuming a freely rotating system, Marsocci and MacKenzie[8] visualized interaction between the carbonyl carbon p orbital and the benzenoid carbon p orbital, as originally suggested by Cookson.[16a] The extinction coefficient of 1-phenyl-3-butanone could be calculated[8] (calcd ϵ 35, found ϵ 32) knowing only the experimental value of ϵ for 1-phenyl-2-propanone and equating the probability factors of the interacted conformations of the two molecules.[17]

It is believed that the observed intensification of the $n \rightarrow \pi^*$ transition in β-silyl ketones arises primarily from a perturbation of the carbonyl group by the silicon d orbitals which results in a mixing of s and np orbital character of the carbonyl oxygen and making this electronic transition more allowed.[13] Alternatively the π^* state could be perturbed by d-orbital interaction but this possibility seems less probable.

Additional evidence for intramolecular interaction based on the lowering of the infrared stretching frequency of the carbonyl band (1698 cm^{-1} in CCl_4) and on the C^{13} nmr spectrum has been reported.[18]

While it is true that α-trimethylsilylacetophenone (XIIIa) exhibits a greater $n \rightarrow \pi^*$ transition intensity than its carbon counterpart,[5] and we feel that interaction can contribute to the effect, it is noted that there is considerable band overlap between 250 and 350 mμ which could contribute to the intensity.

This interaction may be of general importance in providing a pathway for decomposition of organosilanes *via* a four-centered activated complex.[1b]



Experimental Section

1-Trimethylsilyl-2-propanone was prepared by the method of Hauser and Hance[19] and **1-trimethylsilyl-3-butanone** was synthesized by the procedure of Sommer and Marans.[20] 1-Trimethylsilyl-2-butanone was synthesized by a modification of the procedure outlined by Hauser and Hance[19] for the synthesis of β-silyl ketones. The Grignard reagent formed from chloromethyltrimethylsilane was treated with propionic anhydride and the isolation of the silyl ketone was carried out in the usual way:[19] bp 74–75° (60 mm), n^{25}_{D} 1.4240. *Anal.* Calcd for $C_7H_{16}SiO$: C, 58.25; H, 11.20. Found:[21] C, 57.97; H, 11.23.

All compounds were purified by gas–liquid partition chromatography [5-ft Silicone SF-96 on Chromosorb W or 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb W] prior to ultraviolet analysis.

The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, Model 14, using matched 1-cm cells and calibrated with potassium chromate. Matheson spectroquality cyclohexane was used and anhydrous ethanol was purified by an accepted procedure.[22]

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A Novel Reaction of Substituted Purines and Pyrimidines[1]

ALFREDO GINER-SOROLLA AND AARON BENDICH

Division of Biological Chemistry, Sloan-Kettering Institute for Cancer Research, and Sloan-Kettering Division, Graduate School of Medical Sciences, Cornell University Medical College, New York, New York 10021

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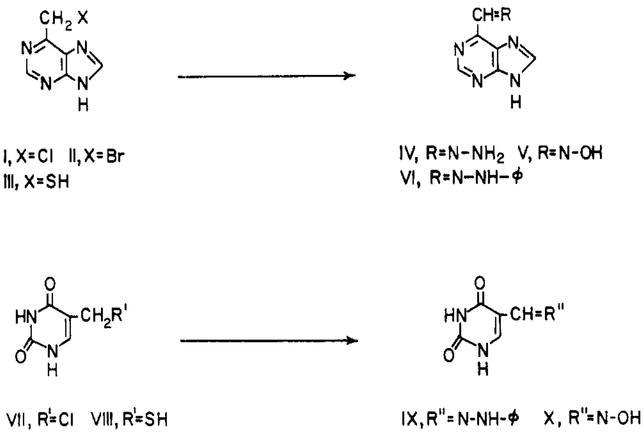
We have found that derivatives of aldehydes are obtained when halogeno- and mercaptomethylpurines or -methyluracils (substituted in the 6 or 5 positions, respectively) are allowed to react with hydrazine, hydroxylamine, or phenylhydrazine. When analytically pure 6-chloromethylpurine[2] (I) was refluxed for 4 hr with a fivefold excess of 10% hydrazine in ethanol, the known purine-6-carboxaldehyde hydrazone[3] (IV) was formed in 94% yield, with evolution of ammonia (Scheme I). A similar transformation resulted with 6-bromomethyl-[2] (II) and 6-mercaptomethylpurine[4] (III). The reaction between the substituted methylpurine derivative (I, II, III) and the hydrazine solution starts after 20 min of refluxing, and is usually complete in 3 to 4 hr; prolonged treatment alters neither the reaction product nor its yield. Since equimolecular amounts of 6-chloromethylpurine and hydrazine provided only a 28% yield of IV, it appears that an excess of hydrazine is essential for the completion of the reaction. Solutions of hydrazine sulfate, buffered at pH 7, gave very poor yields of the hydrazone (IV). As previously observed,[5] an excess (20 equiv or more) and prolonged treatment (10–15 hr) with concentrated hydrazine (64–95%) in water or ethanol reduces hydrazone IV to 6-methylpurine, but, at the lower hydrazine concentration mentioned above, there is little conversion of IV to 6-methylpurine. Reaction of 6-chloromethylpurine (I) with hydroxylamine or with phenylhydrazine provided purine-6-carboxaldehyde oxime (V) or phenylhydrazone (VI) in 37 and 62% yield, respectively. With thiosemicarbazide and 6-chloromethylpurine (I), a solution showing the characteristic ultraviolet spectrum of the known[3] thiosemicarbazone obtained. Purine-6-carbinol,[6] 6-methylpurine 1-N-oxide[7] and alkyl or alkylaryl S-substituted mercaptomethylpurines did not react either with hydrazine or phenylhydrazine.

SCHEME I



I, X=Cl II, X=Br III, X=SH

IV, R=N-NH$_2$ V, R=N-OH VI, R=N-NH-ϕ

VII, R'=Cl VIII, R'=SH

IX, R''=N-NH-ϕ X, R''=N-OH

In an extension of this reaction to pyrimidine derivatives, we have converted 5-chloro- (VII) and 5-mercaptomethyluracil[8] (VIII) into the known[9] 5-uracilcarboxaldehyde phenylhydrazone (IX) in 39 and 47% yield, respectively, by reaction with phenylhydrazine. 5-Mercaptomethyluracil and ethanolic hydroxylamine gave an almost quantitative yield of the corresponding oxime (X). Similar treatment of either the chloro- or the mercaptomethyluracil derivatives with hydrazine and thiosemicarbazide failed to yield the corresponding aldehydo derivatives. The hydrazone could not be synthesized from 5-uracilcarboxaldehyde upon reaction with hydrazine; attempts to prepare the hydrazone by reaction of the thiosemicarbazone (prepared from 5-uracilcarboxaldehyde[9]) with hydrazine also failed. Such transformations have been achieved in excellent yield using purine-6-carboxaldehyde thiosemicarbazones.[6]

This conversion of a substituted methylpurine or pyrimidine with hydrazine, hydroxylamine, and phenylhydrazine resembles the reported reaction of phenacyl bromides with hydrazine.[10] It is known that substituted benzyl chlorides upon treatment with hydrazine are not converted into aldehyde derivatives.[11]

Attempts to transform 6-chloromethylpurine, 6-aminomethylpurine,[12] or 5-chloromethyluracil into the corresponding aldehydes with hexamethylenetetramine, according to the Sommelet method,[13] failed. Similar negative results have been reported with several heterocyclic derivatives.[14]

The reaction between the methylpurine derivatives and hydrazine may involve the steps shown in Scheme II. Compound XI, the initial reaction product of 6-

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