glycine residues in the glycylalanine polypeptides studied and found that the glycine residues were more reactive than the alanine residues, thus indicating that the selectivity of the process to glycine residues was preserved from the dipeptides to the polypeptides. The results of these studies are summarized in Table II.

Table II. Selectivity in the Photoalkylation of Polypeptides Containing Glycine and Alanine[a]

Polypeptide	Phe:MePhe[b,d] per residue of respective starting amino acid	Nle:MeNle[c,d] per residue of respective starting amino acid
[L-Ala-Gly-L-Ala]$_n$	30:1	
[(DL-Ala)$_m$(Gly)$_n$] (9:1)	30:1	9:1
[(DL-Ala)$_m$(Gly)$_n$] (77:23)	15:1	14:1
[(DL-Ala)$_m$ (Gly)$_n$] (57:43)	8:1	13:1

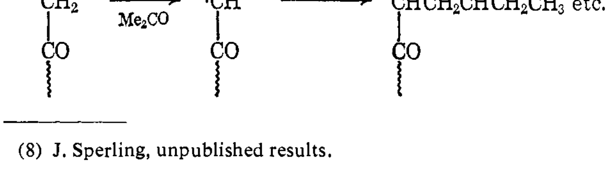
[a] Obtained by multiplying the absolute ratio of the products by the ratio of Ala:Gly in the starting polypeptide. [b] 2-Methylphenylalanine, resulting from alkylation of alanine residues with toluene. [c] 2-Methylnorleucine, resulting from alkylation of alanine residues with 1-butene. [d] The amino acid composition in the product was determined by acid hydrolysis, esterification with 1-butanol followed by trifluoroacetylation, and analysis by glpc [C. W. Gehrke and F. Shahrokhi, *Anal. Biochem.*, **15**, 97 (1966)].

The α-carbon atoms of two adjacent amino acids in polypeptides are in a 1,4 relationship with each other.

$$(\text{-NH}\overset{1}{\text{C}}\text{HR}\overset{2}{\text{C}}\text{O}\overset{3}{\text{N}}\text{H}\overset{4}{\text{C}}\text{HRCO-})$$

This leads to an asymmetric induction process, when one of these α-carbon atoms is chiral, with the chiral center as the asymmetric agent. We have already shown[6] that the generation of a chiral center at the glycine residue in glycylalanine and glycylleucine dipeptides during conversion of that residue to norleucine involves the occurrence of asymmetric induction. We have found that the formation of phenylalanine in the reaction of [L-Ala-Gly-L-Ala]$_n$ with toluene involves the predominant production of the L enantiomer (70%) while the D enantiomer is the minor product (30%). It is noteworthy that in glycylalanine dipeptides hardly any asymmetric induction could be detected in similar reactions with toluene.[8] In the reaction of (L-Pro-Gly-L-Pro)$_n$ and toluene the phenylalanine formed consisted of 68% of the D enantiomer and 32% of the L enantiomer. It is assumed, therefore, that the location of the glycine residue and the conformation of the polypeptide affects the selectivity of the reactions and the asymmetric induction. Work is in progress toward the determination of these relationships.

Spectral determinations indicated that in these photoalkylation reactions acetone serves as the light-absorbing system. Product analysis indicated the involvement of free-radical intermediates.[7] The reaction sequence can thus be formulated as follows.



$$\text{NH(CH}_2\text{)CO} \xrightarrow[\text{Me}_2\text{CO}]{h\nu} \text{NH(}\cdot\text{CH)CO} \xrightarrow{\text{1-butene}} \text{NH(CHCH}_2\dot{\text{C}}\text{HCH}_2\text{CH}_3\text{)CO etc.}$$

The reactions of the polypeptides and toluene follow a similar path involving polypeptide and benzyl free radicals which are generated simultaneously in the reaction mixture. The detailed mechanism is discussed elsewhere.[7]

The application of these reactions for the modification of glycine-containing proteins is in progress.

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(8) J. Sperling, unpublished results.

(9) This work to be submitted to The Feinberg Graduate School of The Weizmann Institute of Science for the Ph.D. in Chemistry.

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Concentration Dependence of the Efficiency of Energy Transfer from $^3(\pi,\pi^*)$ Aromatic Ketones[1]

Sir:

Aromatic carbonyl compounds with low-lying π,π^* triplet states exhibit long triplet lifetimes and low reactivity in photoreduction and Norrish type II cleavage reactions.[2-6] These properties and the high-triplet energies of these compounds make them quite attractive as sensitizers in processes in which chemical reactions of $^3(n,\pi^*)$ sensitizers are undesirable. We wish to report that the efficiency of triplet energy transfer from $^3(\pi,\pi^*)$ aromatic ketones is concentration dependent and to introduce a note of caution concerning the use of such sensitizers as probes of mechanism.

An interest in the use of $^3(\pi,\pi^*)$ sensitizers in the photoaddition of 4,4-dimethyl-2-cyclohexenone to olefins led us to examine *p*-methoxyacetophenone, *m*-methoxyacetophenone, 3,4-methylenedioxyacetophenone, and thioxanthone as sensitizers. Each of the substituted acetophenones has been shown to have a low-lying π,π^* triplet.[2] The photoisomerization of 4,4-dimethyl-2-cyclohexenone to 6,6-dimethylbicyclo[3.1.0]-hexan-2-one (46%) and 3-isopropyl-2-cyclopentenone (54%) was selected as a test system.[7]

The reaction is quenched by di-*t*-butylnitroxide giving a linear Stern–Volmer plot with slope 28.5 ± 1.8 M^{-1} and is sensitized by benzophenone and acetophenone. The yield of products in the sensitized rearrangement does not vary by more than 2% from the direct irradiation. The efficiency of energy transfer from these $^3(n,\pi^*)$ sensitizers is not concentration dependent. The rearrangement thus proceeds *via* a triplet excited state of 4,4-dimethyl-2-cyclohexenone. When sensitizers with low-lying π,π^* triplet states were used, the efficiency of energy transfer was found to be strongly concentration dependent. The results for *p*-methoxyacetophenone, *m*-methoxyacetophenone, 3,4-methylenedioxyacetophenone, and thioxanthone are summarized

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(1) Photochemical Transformations. XXXIV.

(2) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. L. Dusenbery, *J. Amer. Chem. Soc.*, **89**, 5466 (1967).

(3) A. A. Lamola, *J. Chem. Phys.*, **47**, 4810 (1967).

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(6) J. N. Pitts, D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5902 (1968).

(7) O. L. Chapman, Abstracts, Twentieth National Organic Chemistry Symposium, Bloomington, Ind., June 1967, p 127; T. H. Koch, Ph.D. Thesis, Iowa State University, 1968.

Table I. Concentration Dependence of the Efficiency of Energy Transfer

Sensitizer	Concn, M	Φ_0/Φ_{sens}[a]	Φ_{redn}[c]	τ_{rad},[c] sec
p-Methoxyacetophenone	0.10	1.03		
	0.30	1.08	0.04	0.38
	0.65	1.05		
	1.00	1.29		
m-Methoxyacetophenone	0.02	1.04[b]		
	0.10	1.14		
	0.20	1.39	0.006	0.71
	0.60	2.25		
	1.00	3.09		
3,4-Methylenedioxy-acetophenone[d]	0.01	1.40		
	0.05	1.58	0.002	1.20
	0.10	2.31		
	0.20	3.02		
Thioxanthone[d]	0.005	1.65		
	0.01	2.59		

[a] $\Phi_0 = 0.014$ at 43°, 3025 Å, [4,4-dimethyl-2-cyclohexenone] 0.10 M in *t*-butyl alcohol. Quantum yields were measured on a linear apparatus employing a Bausch and Lomb monochromator with the band width (at base) set at 440 Å or less. Samples were carried to 3–5% total conversion. [b] Sensitizer absorbed 95% of light in this case. In all other runs the sensitizer absorbed more than 99% of the light. [c] Data for the substituted acetophenones are taken from ref 2. [d] Higher concentrations were not possible because of solubility limit.

in Figure 1 and Table I. *It is immediately clear from these data that quite erroneous mechanistic conclusions can be drawn from sensitization data in which the concentration dependence of the efficiency of energy transfer has not been studied.*

The reasons for the concentration dependence of triplet energy transfer from π,π^* triplets are not entirely clear. Two possibilities come immediately to mind, excimer formation and self-quenching. In the case of *m*-methoxyacetophenone it is possible that excimers are formed. The wavelength maximum of the phosphorescence of *m*-methoxyacetophenone is concentration dependent and shifts from 445 nm (10^{-4} M in EPA) to 476 nm (5.0 M in EPA). If the excimer has a triplet energy too low for efficient energy transfer to the substrate, competing excimer formation would explain the concentration dependence of Φ_0/Φ_{sens}. Alternatively, short-lived triplet excimers which deactivate to ground state would account for the concentration dependence. This is, in essence, just a mechanism for self-quenching. It is clear from Table I that the degree of concentration dependence of triplet energy transfer observed with the four ketones studied follows the trend of decreasing reactivity in photoreduction and increasing triplet lifetime. Excimer formation could also be a factor in both reactivity and lifetime of π,π^* triplets.

Scheme I

$$S \xrightarrow{h\nu} {}^1S$$

$${}^1S \xrightarrow{k_1} S$$

$${}^1S \xrightarrow{k_2} {}^3S$$

$${}^3S \xrightarrow{k_3} S$$

$${}^3S + K \xrightarrow{k_4} S + {}^3K$$

$${}^3K \xrightarrow{k_5} K$$

$${}^3K \xrightarrow{k_6} \text{products}$$

$${}^3S + S \xrightarrow{k_7} \text{excimer (or 2S)}$$

$$\text{excimer} \xrightarrow{k_8} 2S$$

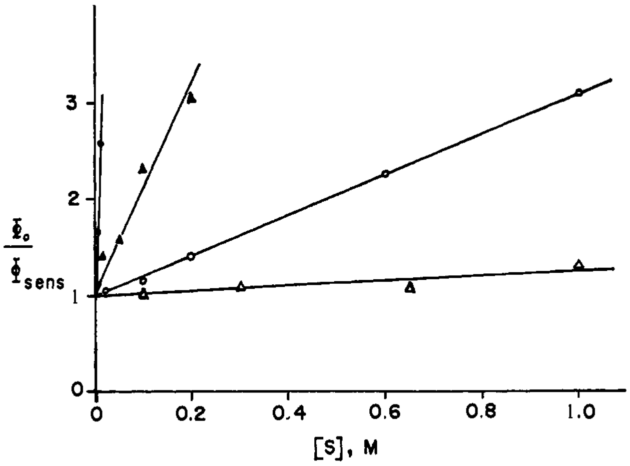

Figure 1. Concentration dependence of the efficiency of energy transfer: △, *p*-methoxyacetophenone; ○, *m*-methoxyacetophenone; ▲, 3,4-methylenedioxyacetophenone; ●, thioxanthone.

The plots shown in Figure 1 are consistent with the mechanism in Scheme I, where S = sensitizer, K = 4,4-dimethyl-2-cyclohexenone, φ = intersystem crossing efficiency for 4,4-dimethyl-2-cyclohexenone, φ' = intersystem crossing efficiency of the sensitizer. Using the steady-state assumption for all excited states, this mechanism leads to the expression

$$\frac{\Phi_0}{\Phi_{sens}} = \frac{\varphi(k_3 + k_4[K] + k_7[S])}{\varphi' k_4[K]}$$

If one assumes that the ratio of the intersystem crossing efficiencies of 4,4-dimethyl-2-cyclohexenone and sensitizer is unity,[8] the slope of the Φ_0/Φ_{sens} *vs.* [S] plots is given by $k_7/k_4[K]$. Using an estimated rate constant (k_4) for the diffusion-controlled triplet energy transfer from sensitizer to 4,4-dimethyl-2-cyclohexenone, it is possible to obtain approximate values for k_7. These values are given in Table II.

Table II. Approximate Values of k_7[a]

Sensitizer	k_7, M^{-1} sec^{-1}
p-Methoxyacetophenone	9×10^7
m-Methoxyacetophenone	8×10^8
3,4-Methylenedioxyacetophenone	4×10^9
Thioxanthone	6×10^{10}

[a] The value of k_4 (3.7×10^9 M^{-1} sec^{-1}) was estimated using the Debye equation, [K] = 0.10 M. Slopes were taken from computer-plotted least-squares lines.

Sensitizer concentration effects have been neglected rather generally in studies of photosensitization. The present results make it clear that these effects can be very significant and that they must be considered. Thus far, the effect has been observed only with ${}^3(\pi,\pi^*)$ sensitizers, but it may not be limited to these cases. Conclusions based on earlier studies in which high concentrations of ${}^3(\pi,\pi^*)$ sensitizers were used with little

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[8] This is a very plausible assumption because both numbers should be between 0.5 and 1.0, probably very close to the latter figure.

or no sensitization observed should be reconsidered. Triplet counting experiments and thus intersystem-crossing efficiencies could also show concentration effects.

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A Reversible Complex of Nitrous Oxide with Cobalt(II) Type-A Synthetic Zeolite

Sir:

Spectroscopically and chemically well-defined complexes have been observed in the Ni^{II}A zeolites.[1] The Ni^{II} ions in a trigonal, almost planar coordination in the zeolitic network combine with various molecules such as olefins, acetylene, cyclopropane, and molecules having a permanent dipole. The Co^{II} ions have now been found to have similar properties, the spectral changes due to the complex formation being particularly striking.

One of the most interesting examples is the adsorption of nitrous oxide on a dehydrated Co^{II}A zeolite which results in a spectral change shown in Figure 1.

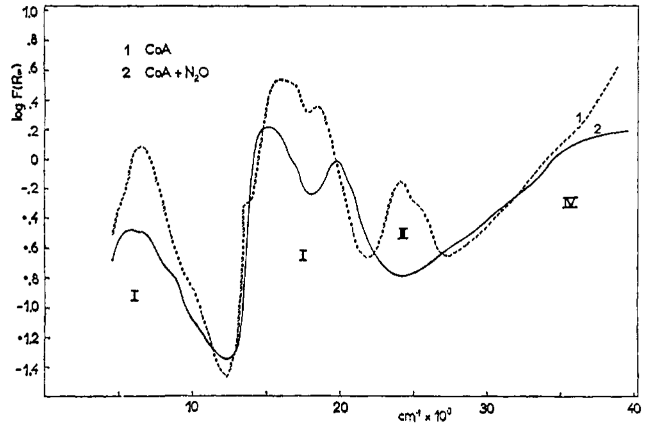

Figure 1. Spectrum of dehydrated, partially exchanged, Co^{II}A zeolite without (curve 1) and with (curve 2) adsorbed nitrous oxide. The Co^{II}A zeolite contained approximately one Co^{II} ion in one large cavity. N_2O was added at a pressure of about 400 Torr. $F(R_\infty) = (1 - R_\infty)^2/2R_\infty$ is proportional to the absorption coefficient (K. Klier, *Catalysis Rev.*, **1**, 207 (1967)) and the wave number on the abscissa axis is given in cm^{-1} 10^{-3}.

In analogy to the Ni^{II}A zeolite, the spectrum 1 is interpreted as that of the Co^{II} ions in an almost planar trigonal coordination to the zeolitic oxygens, the bands I and II being caused by the spin-allowed d_{yz}, $d_{zx} \rightarrow d_{xy}$, $d_{x^2-y^2}$ transitions and the band III, by a $d_{z^2} \rightarrow d_{xy}$, $d_{x^2-y^2}$ transition.[2] The presence of an adsorbed molecule on the *z* axis perpendicular to the plane of oxygen ligands will primarily affect the energy of electrons in the d_{z^2} orbital with the result of shifting the band III to lower energies (Figure 1, curve 2). Since there are no signs of the residual Co^{II}A spectrum 1 in the spectrum 2 of the N_2O–Co^{II}A complex, it is concluded that all cobaltous ions have reacted with one nitrous oxide molecule each. Nitrous oxide can be desorbed by pumping at 50°, whereby the spectrum 1 is completely regenerated. Analysis of the desorbate shows that only N_2O molecules are present under these conditions. Therefore, the N_2O molecule as a whole, and not its fragments, is the reversible ligand to the Co^{II}A zeolite.

At elevated temperature (150°), however, the nitrous oxide molecules decompose over the Co^{II}A zeolite, and an equimolar mixture of $2N_2 + O_2$ is formed. The cobaltous ions are not oxidized during this process but evidently are catalyzing it. Since there is approximately one cobaltous ion in one cavity, the first product of N_2O decomposition must be a nitrogen molecule and an oxygen atom. We propose that this system offers interesting applications in selective oxidation catalysis, having the advantage of both separability of a heterogeneous catalyst from the reactants and uniform energetics of the reactant molecules known so far only in homogeneous catalysis.

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(2) These assignments are meaningful since it has been shown (R. Polak and K. Klier, *ibid.*, in press) that the low symmetry field behaves as a strong ligand field in all relevant cases.

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Alkyl Hex-2-enopyranosid-4-uloses. A New Class of Unsaturated Pyranosides

Sir:

This communication describes some stable, crystalline alkyl hex-2-enopyranosid-4-uloses (**2**), the first reported examples of incorporation of an α,β-unsaturated ketone functionality with high yield into an alkyl pyranoside unit.[1] These molecules are intriguing because the potential they possess for syntheses originating with α,β-unsaturated carbonyl compounds can now be explored as routes to the pharmacologically important branched-chain and amino sugars, the latter being important components of many major antibiotics.[3,4]

The allylic hydroxyl group of recently synthesized **1a**[5] was, as expected, readily oxidized by manganese dioxide[6–8] to ketone **2a** (50% yield; mp 70°; $[\alpha]^{23}\text{D}$ −7.7° (*c* 1.02, $CHCl_3$); λ_{max} (log ϵ) 277 (4.17), 219 mμ (4.09); ν_{max} 5.51, 5.99 μ). The ethyl analog **1b** obtained from **1c**[9,10] by selective benzoylation (*cf.*

(1) Some interesting related systems have been reported,[2] particularly one[2a] which is formally the monoenol ester of an α diketone.

(2) (a) P. J. Benyon, P. M. Collins, P. T. Doganges, and W. G. Overend, *J. Chem. Soc.*, 1131 (1960); (b) E. F. L. J. Anet, *Carbohyd. Res.*, **1**, 348 (1966); (c) E. F. L. J. Anet, *Aust. J. Chem.*, **15**, 503 (1962).

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(8) All new compounds gave satisfactory microanalyses and spectral data.