was weighed (yield about 80%). (See Table I for analyses and physical properties.)

Hydrogenolysis of the N-carbobenzyloxy group over 10% palladium on charcoal (0.4 g.) in alcoholic solution containing 1 *N* hydrochloric acid (1 equiv.) was usually complete in 1 hr. The residue obtained after removal of catalyst and solvent was partitioned between ethyl acetate and water (50 ml.:50 ml.), and the aqueous layer was concentrated (reduced pressure) and dried overnight over potassium hydroxide pellets *in vacuo*. After weighing, the residual peptide ester hydrochloride was used directly in the succeeding step. The *t*-butyloxycarbonyl group (used exclusively for compound **6**) was cleaved using hydrogen bromide in trifluoroacetic acid, and this reagent was also used for the selective removal of the carbobenzyloxy group in preference to the benzyl group in the synthesis of compounds **1** and **7**.

The simple extraction procedures described remove starting materials and all obvious by-products (for example the urea and N-acylurea), which would not be the case with such coupling methods as the active ester, the mixed anhydride, the azide, the dicyclohexylcarbodiimide, or solid-phase synthesis. The successive addition of carbobenzyloxy or *t*-butyloxycarbonyl-amino acid units from the C-terminus is a scheme known to minimize racemization.

Although coupling was usually about 80% after 1 hr., it was decided to investigate the synthesis of a peptide derivative by following every reaction to completion, but again without the isolation of intermediates. The model chosen was the protected heptapeptide *t*-butyloxycarbonyl-L-methionyl-γ-*t*-butyl-L-glutamyl-*im*-benzyl-L-histidyl-L-phenylalanyl-δ-trifluoroacetyl-L-ornithyl-L-tryptophylglycine *t*-butyl ester (**8**), which comprises residues 7–13 of β-MSH, but having ornithine instead of arginine at position 11. Again the carbobenzyloxy group was used to protect each introduced amino acid (save for methionine) during coupling reactions and was subsequently removed by hydrogenolysis over palladium on charcoal. All reactions were followed to completion by thin layer chromatography on silica gel with chloroform–methanol (9:1) or with methanol as the solvent. Condensation products were detected using Ehrlich's reagent[4] and/or the *t*-butyl hypochlorite–starch–iodide reagent,[5] and hydrogenolysis products using ninhydrin. For the preparation of the hexapeptide derivative and the heptapeptide derivative it was necessary to use instead of methylene chloride as the solvent acetonitrile and an acetonitrile–dimethylformamide mixture, respectively. The time required for complete coupling varied from 24 to 66 hr. Again at several stages during the synthesis removal of solvent after washing gave crystalline residues. The protected heptapeptide **8** was obtained as a solid residue upon extraction of by-products and removal of solvent. After precipitation from methanol with ether and with water the product crystallized from methanol. Two additional crystallizations afforded the pure protected heptapeptide **8** in 42% over-all yield, m.p. 203–204° dec., $[\alpha]^{24}D$ −21.8° (*c* 1.9, dimethylformamide). *Anal.* Calcd. for $C_{65}H_{86}N_{11}O_{13}SF_3$: C, 59.2; H, 6.57. Found: C, 58.8; H, 6.64. A single Ehrlich-positive spot was observed by thin layer chromatography. Acid hydrolysis gave the amino acids methionine, glutamic acid, *im*-benzylhistidine, phenylalanine, ornithine, and glycine in equivalent amounts, together with some tryptophan.

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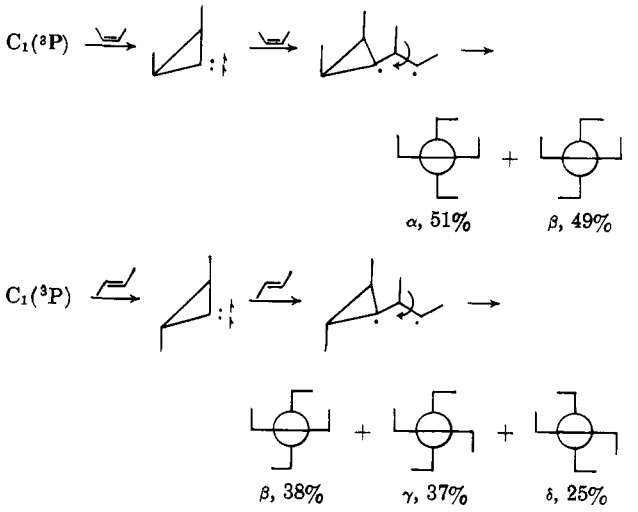
(4) I. Smith, *Nature*, 171, 43 (1953).
(5) D. P. Schwartz and M. J. Pallansch, *Anal. Chem.*, 30, 219 (1958).

Selectivity of Ground-State C_1 and Triplet-State Cyclopropylidene in Olefin Addition Reactions

Sir:

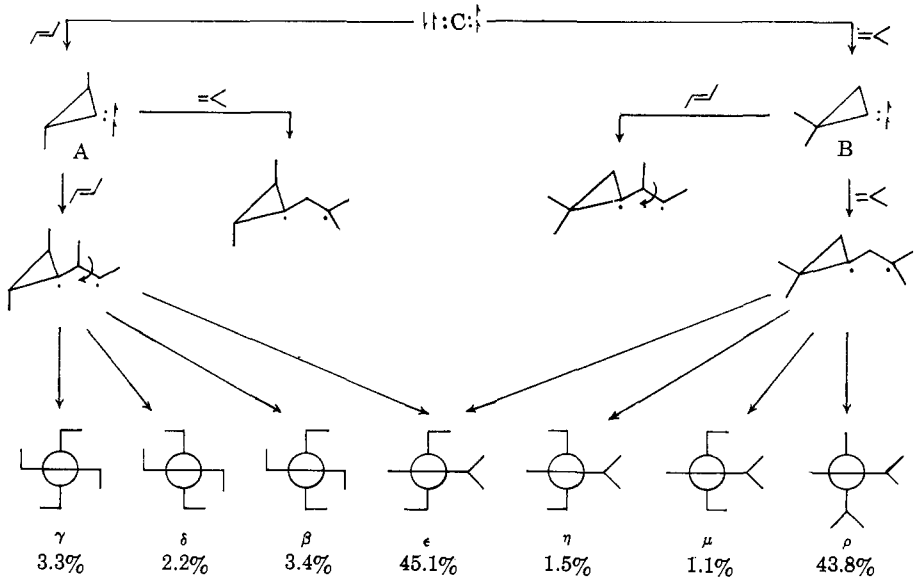
We have reported[1,2] that atomic carbon aged on a paraffin hydrocarbon surface is stable at −196° and reacts with olefins to form spiropentanes. With *cis*- or *trans*-2-butenes spiropentane formation was postulated to occur by a two-step sequence, the first stereospecific and the second nonstereospecific, as expected[3] for the ground state ^3P form of C. This order for the addition steps was required to explain the relative yields of the isomeric products.



An additional consequence of this hypothesis is that butadiene should show greater reactivity than monoolefins in the second step, reaction with a triplet species, and equal or lesser reactivity in the first step, reaction with a singlet species. We wish to report here the results of competition studies which have bearing on this aspect of the problem.

Aged C_1 on a paraffin surface was prepared as described earlier.[1,2] By admitting rapidly a large excess of equilibrated olefin mixture to the cold evacuated sample the matrix was melted by the heat of condensation and reaction occurred in the liquid phase at temperatures in the −100 to −150° range. Addition

(1) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, 87, 1135 (1965).
(2) P. S. Skell and R. R. Engel, *ibid.*, 87, 1135 (1965).
(3) P. S. Skell and A. Y. Garner, *ibid.*, 78, 5430 (1956).



of these mixtures of olefins resulted in product formation under competition conditions and made possible the computation of relative rate constants for both steps of the sequence. The experimental results for a mixture of isobutylene and *trans*-2-butene are summarized in the postulated reaction scheme.

Product ϵ is the only one obtained by two pathways. A separation is possible with the assumption that both triplet cyclopropylidenes would give the same ratio of *cis* to *trans* addition products; product ϵ is obtained

$$\beta/(\gamma + \delta) = (\eta + \mu)/\epsilon_{(via\ B)}$$

90.7% *via* A and 9.3% *via* B.

The competition data are summarized in Table I, showing reactivities for (1) additions to C_1 to form cyclopropylidenes and (2) additions to cyclopropylidenes to form spiropentanes.

Table I

Olefin	Relative rates of olefin additions to :C: (1)	Relative rates of olefin additions to (2)
	1	20
	5	8
	15	10
	30	6
	32	1

The most striking feature of these data is the low reactivity of 1,3-butadiene in the first step, addition to C_1, and the high reactivity in the second step, addition to a cyclopropylidene. For example, in competition with *trans*-2-butene the major products (93%) are those of addition of 1 molecule of 1,3-butadiene and 1 of *trans*-2-butene. The homoadducts of either olefin are small, totaling only 7%.

An explanation of these results can be made as follows: $C_1(^3P)$ displays greater reactivity through its filled and unfilled orbitals than through the half-filled orbitals, and it reacts with conservation of spin angular momentum to make a triplet cyclopropylidene; the triplet cyclopropylidene reacts preferentially with 1,3-butadiene and nonstereospecifically with *cis*- and *trans*-2-butenes.

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Chemical Activation by the Br^{82m} Isomeric Transition. The Half-Life of Br^{82m} [1]

Sir:

Recent reports[2,3] show that radiative neutron capture by Br^{81} (49.5% natural abundance) produces predominantly Br^{82m} rather than the Br^{82} ground state previously assumed, the thermal neutron capture cross sections being 3.0 and 0.3 barns, respectively.[3] The Br^{82m} decays to Br^{82} (36 hr.) by isomeric transition through a highly converted (α_k = 268)[3] 46-kev. level of Br^{82}. The half-life of the isomer has been reported as 4.98 ± 0.12 min.[2] and as 6.20 ± 0.05 min.[3]

Br^{80} atoms born from the isomeric transition Br^{80m} (4.4 hr.) → Br^{80} (18 min.) are activated chemically[4] as a result of the high nuclear charge[5] generated

(1) This work was supported in part by the U. S. Atomic Energy Commission (Contract AT(11-1)-32) and by the W. F. Vilas Trust of the University of Wisconsin.

(2) O. U. Anders, paper presented before the Division of Nuclear Chemistry and Technology at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(3) J. F. Emery, paper presented before the Division of Nuclear Chemistry and Technology at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(4) See, for example: (a) E. Segre, R. S. Halford, and G. T. Seaborg, *Phys. Rev.*, **55**, 321 (1939); (b) D. DeVault and W. F. Libby, *ibid.*, **55**, 322 (1939); (c) J. E. Willard, *J. Am. Chem. Soc.*, **62**, 256, 3161 (1940); (d) J. F. Hornig and J. E. Willard, **75**, 461 (1953); (e) R. M. A. Hahne and J. E. Willard, *J. Phys. Chem.*, **68**, 2582 (1964).

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