The results are outlined in Tables I and II. The cleavage reaction is general and, under this particular set of conditions, depends on the nature of the residues adjacent to the cysteinyl residue and on the nature of the S-acyl group. In Table II the glutamic acid formed gives a measure of the specific cleavage and the glycine formed corresponds to the concurrent nonspecific cleavage. In agreement with the intramolecular mechanism we have proposed, it is seen that the extent and specificity of the cleavage depends on the stability of the anion (R^-) formed.

Table I. Cleavage of Model Tripeptides as the S-(4-Nitrophenyloxycarbonyl) Derivatives

Cysteine tripeptides[a]	% cleavage[b]
Cbz-Glu$_\gamma$-Cys(SH)-Gly-OH	30
Cbz-Phe-Cys(SH)-Gly-OH	73
Cbz-Ala-Cys(SH)-Gly-NH_2	53
Cbz-Ala-Cys(SH)-Gly-OH	50

[a] The thiol peptides were acylated *in situ* with 4-nitrophenyloxycarbonyl chloride at pH 7. [b] Yield of cleavage is calculated from the carbobenzyloxy amino acid liberated after 90 min at pH 8.1, 50°, from 5 μmoles of peptide/ml of buffer.

Table II. Effect of Various S-Acyl Groups on the Cleavage of Cbz-Glu$_\gamma$-Cys(SH)-Gly-OH[a]

Thiol derivatives[b]	% glutamic acid formed (specific fission)	% glycine formed (nonspecific fission)
4-$NO_2C_6H_4OCO$	30	2
C_6H_5SCO	47	3
n-C_4H_9SCO	10	3
$(CH_3)_2NCO$	7	5
C_6H_5CO	1	3
H	3	5

[a] The hydrolysis was at pH 8.1, 50°, 90 min, at 5 μmoles of peptide/ml of buffer. The concentrations of glutamic acid and glycine in the reaction mixture were determined after decarbobenzoxylation. [b] Acylations were carried out at pH 7.

To date very little is known of the properties of 2-ketothiazolidinecarboxylic acids[12] or their peptide derivatives. However, 2-imino analogs have been described briefly.[4]

In order to investigate the properties of product IV, in one experiment the pH 8 buffer used for cleavage of the peptide derivatives listed in Table II was 0.2 *M* N-ethylmorpholine acetate[13] (instead of the usual 1.0 *M* potassium hydrogen carbonate); this was subsequently removed by lyophilization to yield a salt-free product. This material after paper chromatography gave new spots which were ninhydrin negative but chlorine–tolidine positive.[14] As previously, treatment of the reaction product with hydrogen bromide in acetic acid gave glutamic acid (identified on paper chromatograms). Oxidation of the reaction product with performic acid gave β-sulfoalanylglycine which was converted to the corresponding DNP derivative and hydrolyzed to DNP-cysteic acid and glycine. These products were all identified with authentic specimens by paper ionophoresis at pH 1.8 (1.0 *M* formic acid) and at pH 2.3 (6% acetic acid). All these observations confirm that the cleavage occurs at the N-acyl bond attached to the cysteine residue.

The elimination step B and the hydrolysis step C must compete with alternative modes of hydrolysis (*e.g.*, of the acylated thiol II to regenerate thiol I and possibly opening of the thiazolidine ring III), and these will decrease the yield of specific fission. So far we have used only one arbitrarily chosen set of hydrolysis conditions (pH 8, 90 min, 50°). Further studies will be required in order to find the optimal conditions for a general cleavage process.

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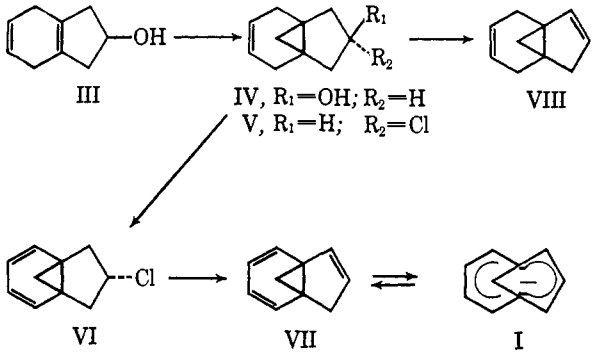
1,5-Methanocyclononatetraenyl Anion

Sir:

We wish to report the preparation of a new stable 10π electron anion, 1,5-methanocyclononatetraenyl anion (I). I is the methano-bridged derivative of the previously reported aromatic cyclononatetraenyl anion[1] and completes the series of methano-bridged 10π electron aromatic species: neutral compound,[2a] carbonium ion,[2b] and anion.



Synthesis of I proceeded from 2-indanol[3] (II) *via* Birch reduction with sodium in liquid ammonia to give, in 74% yield, 4,7-dihydroindan-2-ol[4] (III), bp 93° (1 mm), in complete analogy to the reaction with indane to give 4,7-dihydroindane.[5] The structure of III was confirmed spectroscopically by its lack of

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absorption between 220 and 360 mμ and the presence of two vinyl protons at τ 4.34 in its nmr spectrum.

Treatment of III with methylene iodide and excess zinc-copper couple[6] gave IV[4] in 60% yield after recrystallization from hexane, mp 69–70°. Analyses of the crude reaction product by vpc indicated there was less than 5% of other compounds produced in the reaction. The same reaction conducted on the acetate of III when subjected to vpc analyses showed at least four major products. This dramatic directing effect by hydroxyl in the placement of the cyclopropane ring has precedent[7] and suggests that in IV the cyclopropane ring and hydroxyl are in a *cis* relationship.[7,8] The structure of IV was confirmed by its nmr spectrum which displayed the following protons at τ values relative to TMS: vinyl, 4.57 (multiplet), 2H; α to hydroxyl, 5.69 (pentuplet), 1H; allylic methylene, 7.80 (multiplet), 4H; aliphatic methylene, 8.13 (doublet), 4H; cyclopropane, 9.14, 1H and 9.50, 1H (doublets, J = 4.5 cps).

The epimeric chloride V was obtained stereospecifically by treatment with thionyl chloride in ether in the presence of tri-*n*-butylamine.[9] The chloride V,[4] bp 63–64° (1 mm), was homogenous to vpc on several columns and displayed an appropriate nmr spectrum with the two cyclopropane protons at τ 9.50 and 9.68 (doublets, J = 5.0 cps).

Treatment of V with 1 mole of bromine in dichloromethane at −78° and bisdehydrobromination of the resulting crude dibromide with excess potassium *t*-butoxide in *t*-butyl alcohol gave VI[4] in over-all 56% yield, bp 70–71° (1 mm). That VI was indeed a norcaradienyl derivative was clear from its ultraviolet absorption spectrum: λ_{max} (cyclohexane) 245 mμ (ε 2100), 255 (2100), and 273 (2300), which is characteristic of this type chromophore.[10] The nmr spectrum of VI had the following protons at the τ values indicated: vinyl, 4.04 (multiplet), 4H; α to chlorine, 6.17 (multiplet), 1H; aliphatic methylene, 7.1–8.1 (multiplet), 4H; cyclopropane, 8.75, 1H and 10.16, 1H (doublets, J = 5.0 cps).

The dehydrochlorination of VI required a less hindered base, 15% methanolic potassium hydroxide, and gave the triene VII[4] in 50% yield, bp 64–65° (10 mm), λ_{max} (cyclohexane) 270 mμ (ε 2100) and 258 mμ (ε 2000), with the following nmr spectrum: vinyl, τ 3.92 (multiplet), 5H; vinyl, 4.68 (double triplet), 1H; allylic methylene, 7.35 (multiplet), 2H; cyclopropane, 8.53, 1H and 9.90, 1H (doublets, J = 3.5 cps).

The anion I was produced immediately by treatment of VII with a solution of sodium methylsulfinyl anion[11] in dimethyl sulfoxide under nitrogen at room temperature.[12] An nmr spectrum of I in dimethyl sulfoxide-d_6 displayed protons at τ 2.94 (double doublet, J = 2.0 and 5.5 cps), 2H; 3.98 (multiplet), 5H; 10.45 (doublet, J = 7.5 cps), 1H; and 10.95 (doublet, J = 7.5 cps), 1H.[13] Quenching of I with water regenerated VII in excellent yield and demonstrated the reversible nature of the transformation of I to VII.

The low-field resonance of the ring protons[14] combined with the strong shielding of the methylene protons[16] located above the ring indicates the presence of a ring current and suggests that I is a 10π electron aromatic system. Further studies are in progress.

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(12) Under identical conditions the hydrocarbon VIII, prepared by dehydrochlorination of V, was unreactive.
(13) The τ values were measured using the peak attributed to protonated dimethyl sulfoxide as an internal standard.
(14) The nmr spectrum of indenyl anion[15] in dimethyl sulfoxide-d_6 taken in this laboratory shows protons at τ 2.72 (double doublet, J = 3.0 and 5.5 cps, 2H), 3.52 (multiplet, 3H), and 4.1 (doublet, J = 3.0 cps, 2H).
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(16) The increase in the *gem*-coupling constant from 3.0 to 7.5 cps in VII and I, respectively, is consistent with the change from cyclopropane to methylene bridge type protons.[17]
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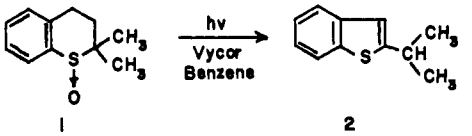
The Photochemical Rearrangement of a Sulfoxide

Sir:

Although the photoracemization of optically active aryl alkyl and aryl aryl sulfoxides, together with the photodecomposition of these sulfoxides and alkyl alkyl sulfoxides, has been reported,[1] there have been to the best of our knowledge no reported instances of rearrangements of sulfoxides upon irradiation. We now wish to report the photoinduced rearrangement of a sulfoxide.

A 10^{-2} *M* benzene solution of 2,2-dimethylthiachroman 1-oxide (**1**) on irradiation under a dry nitrogen atmosphere using a 200-w Hanovia medium pressure mercury arc lamp with a Vycor filter gave as the major product 2-isopropylbenzothiophene (**2**),[2] which was isolated by alumina chromatography of the reaction mixture after removal of the benzene solvent.



1 2

The structure of **2** was suggested by the physical data: mol wt 176 and empirical formula $C_{11}H_{12}S$, confirmed by high-resolution mass spectrometry; nmr peaks ($CDCl_3$) at δ 1.33 (6H doublet, J = 6.5 cps, $(CH_3)_2$–CH–), 3.25 (1H multiplet, $(CH_3)_2$–C*H*), 6.98 (1H singlet, (–S–C=CH–)), and 7.10–7.82 (4H multiplet, aromatic protons). An authentic sample of 2-isopropylbenzothiophene was prepared from benzothiophene by the unequivocal procedure described by

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