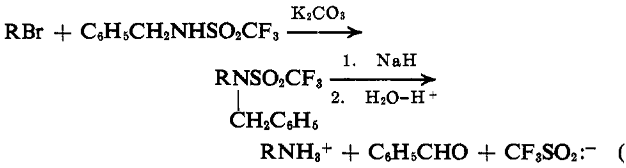
The third case (**c**) was unreactive to refluxing 3 days with NaH in dimethylformamide. This elimination of triflinate from triflamides provides a basis for a useful new "Gabriel synthesis" of primary amines, outlined in eq 5 and carried out for R = $C_6H_5CH_2$ and *n*-C_7H_{15}



$$\mathrm{RBr} + \mathrm{C_6H_5CH_2NHSO_2CF_3} \xrightarrow{\mathrm{K_2CO_3}} \underset{\displaystyle \mathrm{CH_2C_6H_5}}{\mathrm{RNSO_2CF_3}} \xrightarrow[\text{2. } \mathrm{H_2O{-}H^+}]{\text{1. NaH}} \mathrm{RNH_3^+} + \mathrm{C_6H_5CHO} + \mathrm{CF_3SO_2{:}^-} \quad (5)$$

in 70–80% overall yields.

Comparable elimination of triflinate from carbon was also observed in the preparation of chalcone in high yield by stirring $C_6H_5COCH_2CH(C_6H_5)SO_2CF_3$ (mp 134°)[2] in acetonitrile with potassium carbonate (36 hr) or simply on pyrolysis (neat) at 160°. The potassium triflinate formed in all these eliminations was isolated in near quantitative yield as a stable acetone- or water-soluble salt (KSO_2CF_3, mp 180° dec; ir 8.7, 9.3, 9.9 μ).

Elimination of sulfinates from hydrazine derivatives is characteristic of several reactions like the McFadyen–Stevens aromatic aldehyde synthesis or the Cava diazo ketone preparation from α-diketone monohydrazones. Under much milder conditions the corresponding triflic derivatives undergo these reactions. The *N'*-trifylbenzhydrazide ($C_6H_5CONHNHSO_2CF_3$, mp 159–160°)[2] decomposes smoothly in boiling triethylamine (89°) to afford benzaldehyde and an 80% yield of nitrogen (determined manometrically), while brief boiling of the lithium salt in dimethylformamide at 100° yielded 75% of the 2,4-dinitrophenylhydrazone of benzaldehyde. Furthermore, the triflated hydrazide also afforded benzaldehyde (40%) simply by distillation at 170°.

The conversion of benzil monohydrazone to azibenzil was carried out by triflation with $(CF_3SO_2)_2O$ and triethylamine (1 mol) in methylene chloride at −78°; on warming to about 0° and addition of excess triethylamine, the diazo ketone is quickly formed in over 80% yield.

Finally, as the triflamides appear in most ways to be desirable, stable amine derivatives or protecting groups for synthesis, their direct removal was examined. First, removal from a primary amine is easily effected by phenacylation and elimination as described above. Thus, aniline is recovered from its triflamide ($C_6H_5NHSO_2CF_3$) by stirring overnight with *p*-bromphenacyl bromide and potassium carbonate in acetone and working up with mild acid hydrolysis (80% recovery). In addition we have found triflamides of secondary amines to be quantitatively and rapidly reduced to the parent amine with lithium aluminum hydride in boiling ether. The primary triflamides are quite stable under these conditions, however, since the stable salt is formed first, but they may be reduced in minutes with sodium bismethoxyethoxyaluminum hydride ("Red-Al") in boiling benzene,[7] also nearly quantitatively.

These initial studies imply a broad range of synthetically useful, clean, and practical reactions of triflamides as well as attractive potential for normally stable, easily removed amine protecting groups. Many of these applications are under further study in our laboratory, as is a comparable survey of the reactions of the trifyl group attached to carbon (the "triflones," CF_3SO_2C).

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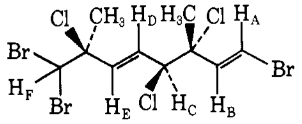
[7] E. H. Gold and E. Babad, *J. Org. Chem.*, 37, 2208 (1972), found reduction of primary toluenesulfonamides moderately successful at higher temperatures and much longer time.

(3*R*,4*S*,7*S*)-*trans,trans*-3,7-Dimethyl-1,8,8-tribromo-3,4,7-trichloro-1,5-octadiene, a Novel Monoterpene from the Sea Hare, *Aplysia californica*

Sir:

The sea hare, *Aplysia californica*, is a large shell-less opistobranch which is commonly found intertidally, feeding on red algae. Analysis of the digestive (midgut) gland of *Aplysia* showed a high concentration of bromine,[1] which has subsequently been attributed to the presence of a large number of halogenated terpenes derived from compounds found in the algae ingested by the sea hare.[2] Most of the halogenated terpenes were obviously related to known algal metabolites but the algal source of the title compound is unknown.

The ether-soluble portion (31 g) of an ethanolic extract of the digestive glands from adult sea hares[3] was subjected to chromatography on Florisil. Elution with 20% benzene in petroleum ether gave the highly halogenated monoterpene **1** (2 g): $C_{10}H_{12}Br_3Cl_3$;[4] mp 54°, $[\alpha]^{23}\mathrm{D}$ −50.2° (*c* 1.0). The mass spectrum[5] showed no molecular ion but had peaks corresponding to the loss of chlorine ($M^+ - 35, 37$) and bromine ($M^+ - 79, 81$). The nmr spectrum[5] indicated the presence of two tertiary methyl groups, two trans-disubstituted olefinic functions, one of which was adjacent to a methine proton, and a second methine proton. In order to definitively elucidate the structure, a single-crystal X-ray diffraction analysis was undertaken.



Transparent needles, obtained from methanol recrystallization, belong to the monoclinic crystal class with $a = 5.934\ (6)$, $b = 12.061\ (3)$, and $c = 11.141\ (3)$ Å, and $\beta = 82.1\ (2)°$.[6] An observed density of 2.00 g/cm³ requires two molecules per unit cell which on the basis of the known optical activity and systematic absences (0*k*0 missing if $k = 2n + 1$) indicated the space group $P2_1$. All data in the *hkl* and $\bar{h}kl$ octants (1450 reflections) were collected on a fully automated Hilger-Watts diffractometer using Zr-filtered Mo Kα

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(1) L. Winkler, *Veliger*, **11** (3), 268 (1969).

(2) D. J. Faulkner and M. O. Stallard, manuscript in preparation.

(3) Six individuals (5.7 kg) were collected intertidally at La Jolla.

(4) A satisfactory elemental analysis was obtained.

(5) Mass spectrum: *m/e* 439, 441, 443, 445, 447 ($M^+ - Cl$), 395, 397, 399, 401 ($M^+ - Br$); base peaks 167, 169, 171 $(C_4H_5BrCl)^+$. 220-MHz nmr spectrum: ($CDCl_3$) δ 1.75 (s, 3 H), 1.95 (s, 3 H), 4.51 (d of d, H_C), 5.76 (s, H_F), 6.08 (m, H_D), 6.11 (AB d, H_E), 6.43 (AB d, H_B), 6.55 (AB d, H_A).

(6) A right-handed coordinate system was maintained throughout the structural analysis.

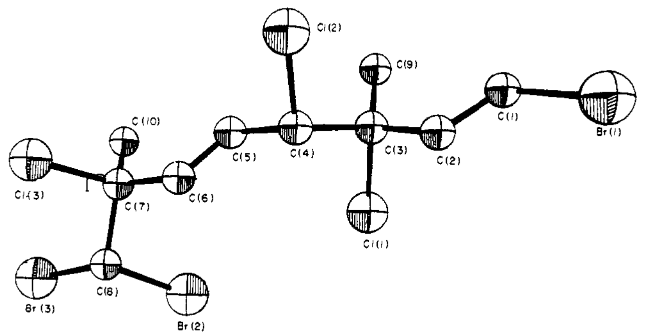

Figure 1. A computer-generated perspective drawing of the title compound.

radiation (0.7107 Å). During the data collection the crystal yellowed and periodically checked standard reflections declined $\sim$10% in intensity. After Lorentz, polarization, and background correction 1091 reflections were judged observed ($F_o \geq 3\sigma(F_o)$). Normalized structure factors were computed in the usual fashion and phase angles were assigned to the 160 E values larger than 1.40 by a multiple solution, weighted tangent formula scheme.[7] The phased three-dimensional E synthesis revealed the six heavy atom positions and the subsequent electron density synthesis revealed the ten remaining carbon atoms. Full-matrix least-squares refinements smoothly converged to an unweighted crystallographic residual of 0.10.[8] At this stage anomalous scattering factor corrections were made for the heavy atoms and refinement continued to weighted residues of 0.081 and 0.077 for the structure and its mirror image, respectively. A computer-generated drawing of the structure with the significantly lower residual is shown in Figure 1.[9] All bond distances and angles agree well with generally accepted values.[10] The molecules are extended with the molecular axis roughly parallel to b. There are no unusually short intermolecular contacts.

As can be seen in the figure the double bonds C-1–C-2 and C-5–C-6 are trans.

The tribromotrichloromonoterpene **1** is the first member of a unique series of monoterpenes containing a vinyl bromide function. A second halogenated monoterpene is currently under investigation. Two sesquiterpenes containing both bromine and chlorine have been isolated from red algae of the genus *Laurencia*;[11] both have subsequently been found in *Aplysia californica* digestive gland extracts. This terpene represents the most highly polyhalogenated naturally occurring substance found to date. It appears that *Aplysia* naturally performs the complex task of concentrating halogen-containing compounds from algae.

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(8) W. R, Busing, K. O. Martin, and H. A. Levy, ORFLS, U. S. Atomic Energy Commission Report No. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(9) (a) C. K. Johnson, ORTEP, U. S. Atomic Energy Commission Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; (b) W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

(10) O. Kennard and D. G. Watson, "Molecular Structures and Dimensions," Crystallographic Data Centre, Cambridge, England, 1970.

(11) J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *J. Amer. Chem. Soc.*, 93, 3774 (1971); *Tetrahedron Lett.*, 195 (1972).

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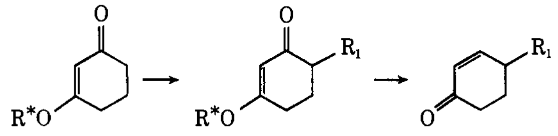
Spiroannelation of Enol Ethers of Cyclic 1,3-Diketones. A Simple Stereospecific Synthesis of β-Vetivone

Sir:

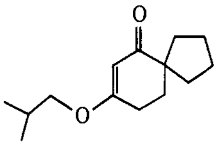
We have reported[1] that enol ethers of 1,3-cyclohexanediones can be alkylated *via* their kinetic enolates (**1** → **2**). The resulting alkylated products can then be transformed by conventional methods to 4-alkyl-Δ^2-cyclohexenones (**2** → **3**).



1 **2** **3**

We now report on the use of this method for the synthesis of spiroannelated cyclohexenones.

The isobutyl enol ether of 1,3-cyclohexanedione (**1**), R* = isobutyl,[2] was added at $\sim -60°$ to a solution of 3 equiv of lithium diisopropylamide in tetrahydrofuran containing 3 equiv of hexamethylphosphoramide. Addition of 2.5 equiv of 1,4-dibromobutane was followed by stirring at room temperature for 48 hr. Work-up then gave after evaporative distillation (90–111° (0.1 mm)) and purification on silica gel (5% ethyl acetate in benzene) the spiroannelated enol ether **4** (m/e 222.1589; nmr δ 5.3 (1 H, s), 3.16 (2 H, d), 1.5–2.0 (11 H), 1.0 ppm (6 H, d)) in about 35% conversion (44% yield).



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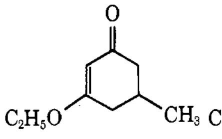

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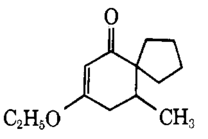

6

Similarly, the ethyl enol ether of 5-methyl-1,3-cyclohexanedione (**5**)[3] gave the spiroannelated enol ether **6** (m/e 208.1436; ir 6.04, 6.19 μ; nmr δ 0.97 (3 H, d, J = 6 Hz), 5.2 ppm (1 H, s)) in $\sim$36% conversion (50% yield).

The application of this synthesis of 4,4-spiroannelated cyclohexenones to a stereospecific synthesis of β-vetivone[4] (**12**) from **5** demonstrates its usefulness. The

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