Table I. Typical Aerosol Fluorination Reaction Parameters[a]

starting compound	fluorine flow, mL/min		helium diluent, mL/min		reaction temp, °C		main helium carrier, mL/min	hydrocarbon throughput mmol/h	overall[b] stoichiometry hc:F_2	percent F_2 concn, final stage	reaction time,[c] s	product distribution % collected	product yield % theoretical
	reactor	mod 1	reactor	mod 1	reactor	mod 1							
		mod 2		mod 2		mod 2							
3,3-dimethyl-2-butanone	10	20	150	150	−40	−30	600	2.8[e]	1:52	3.6	49	23	12
		30		150		10							
2,2,4,4-tetramethyl-3-pentanone	20	20	150	150	−30	−20	600	2.9[e]	1:67	4.8	49	71	9[d]
		40		150		10							

[a] See ref 1 and 25 for the significance of these parameters. [b] One milliliter/minute of F_2 delivers 2.44 mmol/h of F_2. [c] Reactor volume/total flows; reactor volume = 1355 mL. [d] Product is *F*-2,2,5-trimethyl-3-hexanone. [e] Total carrier flow through evaporator 550 mL/min (500 mL/min primary, 50 mL/min secondary).

C_4F_7; 69 (75) CF_3: [EI] 447 (1) $C_9F_{17}O$, M − F; 247 (37) C_5F_9O; 219 (43) C_4F_9; 69 (100) CF_3. ^{19}F NMR (1% $CFCl_3/CDCl_3$) ϕ_A −61.61 ppm (t of m), ϕ_B −109.32 (hexadec of doublets), ϕ_C −184.26 (m), ϕ_D −71.82 (t of d); $J_{AB} = J_{BD} = 10.26$ Hz, $J_{AD} = 0.88$ Hz, $J_{AC} = 0$, $J_{BC} = 4.40$ Hz, $J_{CD} = 6.10$ Hz. Anal. Calcd for $C_9F_{18}O$: C, 23.19; F, 73.37. Found: C, 22.33; F, 71.16.

1-Fluoro-2,2,4,4-tetramethyl-3-pentanone, $(CH_3^A)_3CC(O)C(CH_2^BF^C)(CH_3^D)_2$: IR ($cm^{-1}$) 2980 (m), 2950 (s), 2900 (m), 2870 (m), 1680 (s), 1475 (s), 1360 (s), 1290 (s), 970 (s). Major mass cations were [m/e (relative intensity) formula]: [CI] 161 (4) $C_9H_{18}OF$, M + H; 103 (28) C_5H_8OF; 101 (46) C_5H_6OF; 59 (100) C_2FO: [EI] 69 (30) C_5H_9; 57 (23) C_4H_9; 44 (71) C_2H_4O; 32 (100) CH_2F. ^{19}F NMR (1% $CFCl_3/CDCl_3$/0.2% $CHCl_3$) ϕ_C −221.76 ppm (t); ^1H NMR δ_A +1.24 ppm (s), δ_B = +4.40 (d), δ_D +1.29 ppm (s); J_{CH_2F} = 47.4 Hz.

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Registry No. 3,3-Dimethyl-2-butanone, 75-97-8; 2,2,4,4-tetramethyl-3-pentanone, 815-24-7; *F*-3,3-dimethyl-2-butanone, 88995-83-9; 3-(difluoromethyl)-*F*-3-methyl-2-butanone, 88995-84-0; 3,3-bis(difluoromethyl)-*F*-2-butanone, 88995-85-1; *F*-2,2,5-trimethyl-3-hexanone, 88995-86-2; 1-fluoro-2,2,4,4-tetramethyl-3-pentanone, 88995-87-3.

Isotriquinacene

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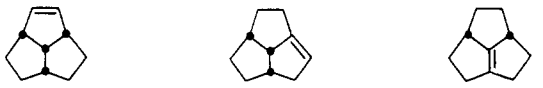
Recent activity at the theoretical level by McKervey[2] as well as Schleyer[3] and at the experimental level by deMeijere[4] has called attention to the strain relationships between the three all-cis tricyclo[5.2.1.$0^{4,10}$]decenes. The energetic costs associated with positioning the double bond at a bridgehead location as in **2** or a double bridgehead site as in **3** are 4.1 and 16.3 kcal/mol, respectively, relative to **1**.



1 **2** **3**

This ordering of stabilities holds particular fascination in the area of triquinacene chemistry where the only tricyclo[5.2.1.$0^{4,10}$]decatriene reported to date, viz. triquinacene (**4**),[5-9] is unique in having no bridgehead double

4 **5** **6**

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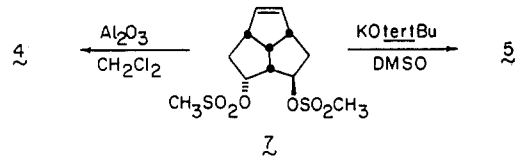
bond. A number of years ago, a facile synthesis of 5[10] was uncovered in this laboratory. This finding, which forms the subject of this note, may serve to stimulate renewed interest in acepentalene (6), the most fully dehydrogenated, strained, and electronically perturbed member of this class of molecules.[5]

As Deslongchamps and co-workers first pointed out,[8] dimesylate 7 in dichloromethane solution readily undergoes twofold elimination when slurried with activated alumina at room temperature to give 4 in moderate yield. We have



observed that substitution of potassium *tert*-butoxide in anhydrous dimethyl sulfoxide leads instead to a product mixture highly enriched in the less thermodynamically stable 5 in 69% crude yield (5:4 = 96:4). Following purification by preparative vapor-phase chromatography, 5 was isolated as a colorless oil, which, while relatively stable in dilute solution or under an inert atmosphere, polymerized on standing in air at room temperature for several hours. Its ^1H and ^{13}C NMR spectra (see Experimental Section) are fully consistent with the unsymmetrical nature of the triene.

In the belief that 5 is formed under kinetically controlled conditions, attempts were made to induce its isomerization to 4 with activated alumina. However, reaction times up to 48 h led to no detectable double-bond isomerization (error limits ±1%). Isotriquinacene was thereby shown not to be a precursor of triquinacene under the Deslongchamps conditions. These results constitute an interesting dichotomy concerning the manner in which the two reagents in question enter into formal E_2 elimination chemistry. Such differences may be more widespread than heretofore appreciated in conformationally rigid systems[11] and may offer insightful opportunities for developing proper synthetic strategies toward strained olefins.

Experimental Section

Tricyclo[5.2.1.0^{4,10}]deca-1,5,8-triene (Isotriquinacene, 5). To a solution of 7[8] (2.0 g, 6.2 mmol) in dry dimethyl sulfoxide (40 mL) was added potassium *tert*-butoxide (2.2 g, 19 mmol) in one portion. The reaction flask was purged with nitrogen and stirred at room temperature for 24 h. The dark reaction mixture was poured into water (150 mL) extracted with ether (3 × 100 mL), dried, and evaporated to leave 560 mg (69%) of triene mixture as a reddish oil. VPC analysis (15% Carbowax 20M on Chromosorb P, 100 °C, 10 ft × $^1/_8$ in) showed the mixture to be comprised of 4% of 4 and 96% of 5 (assuming the same detector response for the isomers). Preparative VPC isolation (5% SE-30 on Chromosorb P, 130 °C, 6 ft × $^1/_4$ in.) afforded 5 as a colorless liquid; ^1H NMR (270 MHz, $CDCl_3$) δ 6.21 (dd, J = 5.7 and 0.5 Hz, H_9), 6.07 (dd, J = 5.7 and 2.8 Hz, H_8), 5.54 (dt, J = 5.4 and 0.6 Hz, H_6), 5.41 (dt, J = 5.4 and 1.9 Hz, H_5), 5.37 (dt, J = 3.7 and 2.2 Hz, H_2), 3.78 (m, H_{10}), 3.45 (m, H_7), 3.16 (dq, J = 5.8 and 2.0 Hz, H_4), 3.00 (m, exo-H_3), 2.55 (ddd, J = 16.6, 3.7, and 2.0 Hz, endo-H_3); ^{13}C NMR ($CDCl_3$) ppm 155.87 (s), 139.16 (d), 136.09 (d), 128.43 (d), 127.91 (d), 117.94 (d), 59.92 (d), 52.01 (d), 47.72 (d), 42.73 (t).

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 91.84; H, 8.08.

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Registry No. 5, 89032-66-6; 7, 42501-47-3; potassium *tert*-butoxide, 865-47-4.

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(10) Tricyclo[5.2.1.0^{4,10}]deca-1,5,8-triene, the proposed colloquial name for which is isotriquinacene.

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Biologically Oriented Organic Sulfur Chemistry. 23. A Hydrodisulfide from a Sulfonamide Derivative of Penicillamine[1]

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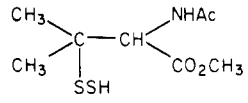
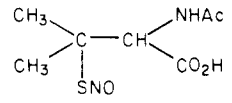
Hydrodisulfides (RSSH) are important intermediates in several biochemical and chemical systems. For example, they play essential roles in enzyme-catalyzed reactions[2] and are formed in the oxidation of phosphorothioates to phosphates (e.g., of parathion, p-$O_2NC_6H_4OPS(OEt)_2$, to paraoxon, p-$O_2NC_6H_4OPO(OEt)_2$) by cytochrome P-450.[3] In previous work,[4] a hydrodisulfide (1) derived from the



1



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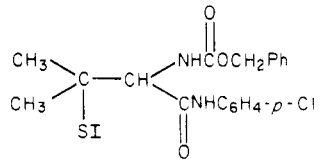

3

methyl ester of *N*-acetylpenicillamine was prepared in the hope that, as had been found with a thionitrite (2)[5] and a sulfenyl iodide (3),[6] the hydrodisulfide would be relatively stable. We hoped that 1 thus might provide a product that would make the corresponding thiol a useful trap for sulfur atoms generated either photochemically from carbonyl sulfide[7] or from the oxidation of phosphorothioates with

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