A Study of the Response of Bullvalenylcarbinyl p-Anisoate to Solvolysis and of Bullvalenyldiazomethane to Thermal Activation

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Cyanobullvalene has been prepared and transformed into bullvalenylcarboxaldehyde and carbinol. Upon treatment with bases under a variety of conditions, the tosylhydrazone was converted into bullvalenyldiazomethane, which was found to undergo intramolecular cyclization to afford the isomeric pyrazole more rapidly than loss of nitrogen. No evidence could be gained for intervention of the carbene. During attempts to convert the carbinol into its tosylate (**3b**), rearrangement to isomeric alcohol **13** occurred. This same compound arose as the exclusive solvolysis product of the *p*-anisoate derivative (**3c**) and mechanistic rationalization for its formation is given. The valence tautomers of **3b** and **3c** which are capable of leading directly to **13** are seen to be positionally isomeric with that of aldehyde **2** which accounts for acid-promoted rearrangement of the latter exclusively into **7** and **8**. This is taken to mean that bond reorganization of carbonium ion intermediates in the bullvalenyl series can be initiated from different valence isomers, a phenomenon which probably is highly dependent upon the nature of the carbocation center and its method of generation.

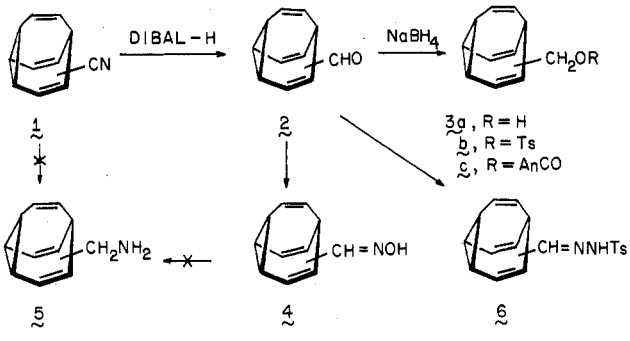
Subsequent to the synthesis of bullvalene[2-5] and the experimental realization of Doering's prediction[6] that this hydrocarbon enjoys an unparalleled capacity for rapid and reversible Cope rearrangement which scrambles completely (via 1,209,600 possible isoenergetic valence isomers!) the constituent cyclopropyl, vinyl, and bridgehead carbon atoms, a good deal of attention has been accorded the preparation of substituted bullvalenes.[7,8] The majority of this effort is due to Schröder and Oth, whose main purpose has been to elucidate the capability of a given group to partition itself by means of the available valence tautomerism channels between the several widely differing chemical environments.[9] These studies point up the uniquely distinctive property of the individual carbon atoms in bullvalene, viz., that they are subject to ready interconversion between four sites of nonidentical chemical character.

Several years ago, we developed an interest in investigating the capability of bullvalene and semibullvalene to function as neighboring groups in a wide range of chemical reactions. The specific question posed was: were a $-CH_2^+$, -CH:, $-N_2^+$, or other reactive functionality to be generated adjacent to a ring carbon atom of such highly fluxional molecules, would subsequent reaction occur from an sp^3 (bridgehead), $sp^{2.25}$ (cyclopropyl), or sp^2 (olefinic) hybridized state?[10] Several investigations involving nonfluxional dibenzosemibullvalene derivatives as model compounds have already been completed.[11] In this paper, we wish to delineate our more recent attempts to elucidate the chemical reactivity of of the bullvalenylcarbinyl cation and bullvalenylcarbene systems.[12]

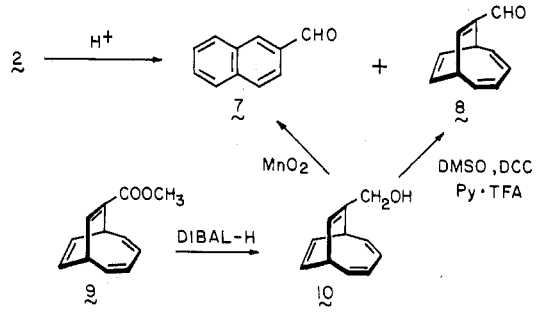
Results and Discussion

Reaction of bromobullvalene with sodium dicyanocuprate[13] in refluxing dimethylformamide solution conveniently afforded the unrearranged cyano derivative **1** in 80% yield. At 108°, the ^1H NMR spectrum ($CDCl_3$) of **1** comprised only a coalesced singlet ($W_{1/2}$ = 7.5 Hz) appearing at δ 4.45. Cooling to −35° sufficed to reveal the expected three sets of signals: a doublet at δ 6.76 (1 H) due to the vinyl proton β to cyano together with multiplets centered at δ 5.97 (4 H) and 2.56 (4 H) arising from the olefinic and cyclopropyl–aliphatic protons, respectively. Reduction of **1** with 1 equiv of diisobutylaluminum hybride (DIBAL-H) gave aldehyde **2** (67%), subsequent reduction of which with ethanolic sodium borohydride led to the desired alcohol **3a** (83%).[14]

Attempts to reduce **1** or oxime **4** with lithium aluminum hydride resulted in the generation of complex product mixtures. Examination of their ^1H NMR spectra showed clearly that the bullvalene ring system was no longer intact. No evidence was found for the formation of amine **5**. Comparable difficulties were encountered during lithium aluminum hydride reduction of **2**.



Aldehyde **2** was seen to be very prone to acid-catalyzed rearrangement. When exposed to a solution of *p*-toluenesulfonic acid in benzene at room temperature for 12 hr, **2** underwent conversion exclusively to 2-naphthaldehyde (**7**).



At shorter exposure times (1 hr), a mixture of **7** and **8** (72:28) was obtained, which proved to be inseparable by standard chromatographic techniques. The product ratio was determined by relative integration of the aldehydic proton absorptions in the ^1H NMR spectrum. The 2,4-dinitrophenylhydrazones of these aldehydes did prove separable by fractional crystallization. That derived from **8** was shown to be identical with a sample prepared from authentic aldehyde, synthetic entry to which was gained from the known ester **9**.[15] Reduction of **9** with 2 equiv of DIBAL-H followed by oxidation under Moffatt conditions gave **8**. Treatment of **9** with but 1 equiv of DIBAL-H at low temperature gave rise to a mixture of **9** and **10**. Upon oxidation

Table I
LIS ^{1}H NMR Data for 13 (δ, 60 MHz, $CDCl_3$)

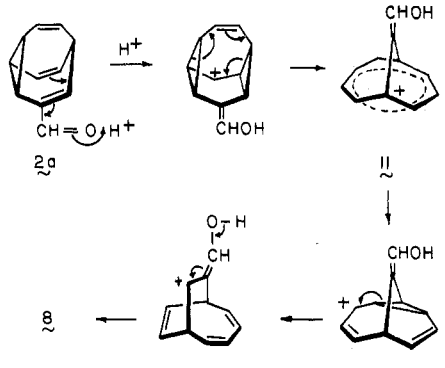
Mol % Eu(fod)$_3$	H_1	H_2	H_3	H_4, H_7	H_8, H_{10}	H_6	H_6'	H_5	H_9
0	*a*	4.12	*a*	*a*	*a*	4.80	5.00	*a*	*a*
9.9	*a*	*a*	*a*	*a*	*a*	5.13	5.38	4.12	*a*
19.4	*a*	10.00	9.52	7.58	6.78	5.38	5.70	4.70	8.63
28.9	9.07	12.73	11.27	8.47	7.22	5.68	6.05	5.32	9.83
39.2	*a*	15.25	12.85	9.08	7.58	5.95	6.35	5.87	10.80
48.5	11.90	17.10	13.92	9.95	7.83	6.13	6.55	6.23	11.62
59.6	12.90	18.85	14.75	9.90	8.07	6.27	6.72	6.50	12.15

[a] Not individually discernible owing to peak overlap.

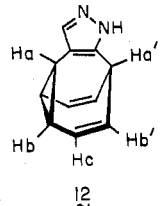
of **10** with manganese dioxide, 2-naphthaldehyde was obtained.

An interesting feature of this acid-catalyzed rearrangement is that only one each of the possible bicyclo[4.2.2]decatetraene carboxaldehydes and naphthaldehydes are produced. This can be concisely rationalized in terms of reaction through valence isomer **2a,** protonation of which leads initially to bishomotropylium ion **11**[16] (Scheme I). The isomerization of **8** to 9,10-dihydro-2-naphthaldehyde[5a] and subsequent air oxidation would give **7.** Significantly, were protonation of the other three valence tautomers of **2** to operate and bond reorganization of a comparable type to follow, exclusive access to **7** and **8** would not likely be gained.

Scheme I



Synthesis of tosylhydrazone **6** could be realized successfully by heating an ethanol solution containing equimolar quantities of **2** and tosylhydrazine on a steam bath for 20 min *in the absence of acid.* Upon cooling, **6** crystallizes from solution and can be isolated in 44% yield. Decomposition of **6** in glyme or ethylene glycol using *n*-butyllithium or sodium alkoxide as base resulted in the formation of a single compound in 34–42% yield. The same product was isolated from pyrolysis of the sodium salt of **6.** Its mass spectrum shows a parent ion at *m/e* 170 which corresponds to a molecular formula of $C_{11}H_{10}N_2$. In addition, the ^{1}H NMR spectrum clearly shows the presence of a homotropilidene structure,[17] and the ir spectrum contains an >NH absorption. In light of these data and ample precedent for conversion of vinyl diazo compounds to pyrazoles,[18] the substance was formulated as **12.**



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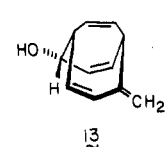
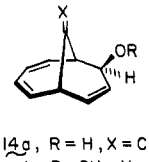
Combustion analysis of **12** indicated it to contain water of crystallization to the extent of one molecule of water per three molecules of the pyrazole. This was confirmed by Fourier transform ^{1}H NMR analysis at 90 MHz of a portion of the analytical sample. At the low concentration level of the sample the one >NH proton and the water of crystallization appeared at the same chemical shift as H_a, $H_{a'}$, H_b, and $H_{b'}$ resulting in a total area of 7.47 relative to protons H_c (2.00). This comprises a surplus of 0.47 proton attributable to the water of crystallization (calcd 0.67). When deuterium oxide was added, the relative areas changed to 5.70:2.00.

No evidence was gained for generation of the desired bullvalenylcarbene species even when recourse was made to low-temperature photochemical methods.

Attempts to prepare tosylate **3b** by stepwise addition of *n*-butyllithium and *p*-toluenesulfonyl chloride to alcohol **3a** led instead to isolation of a new alcohol, shown by mass spectrometry to be isomeric with **3a.** ^{1}H NMR analysis indicated the presence of six olefinic protons (m centered at δ 6.0), an exo methylene group (d, J = 2.0 Hz, at 5.00 and d, J = 2.0 Hz, at 4.78), a proton α to the hydroxyl group (m, 4.11), two bridgehead protons (m, 3.32), and the OH functionality (br s, 1.98). A lanthanide-induced shift study of this new alcohol showed clearly that the exo methylene is fixed so as to be distant from the hydroxyl group (see Table I and Figure 1). These data eliminate **14a** as a possiblity. In addition, little similarity is seen between the features of this LIS study and the one described by Willcott for **14b.**[19] On the other hand, structure **13** is fully consistent with



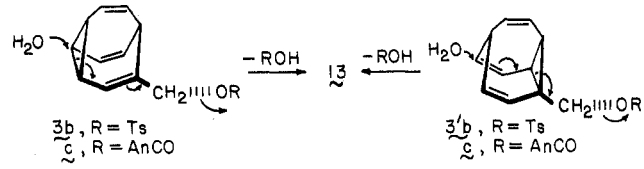
13



14a, R = H, X = CH_2
b, R = CH_3, X = H_2

these data and its formation is easily rationalized at the mechanistic level. Thus, attack by water as depicted in Scheme II during ionization of **3b** or **3'b,** probably under control by steric and electronic factors, affords **13** directly. Since water was precluded during tosylate formation, the solvolysis likely occurred during isolation (preparative TLC was utilized).

Scheme II



3b, R = Ts
c, R = AnCO

3'b, R = Ts
c, R = AnCO

Hydrolysis of the *p*-anisoate **3c** in 70:30 (v/v) acetone–water at 125° (sealed tube) for 24 hr also gave **13** (85% yield based upon recovered **3c**) as the only product.

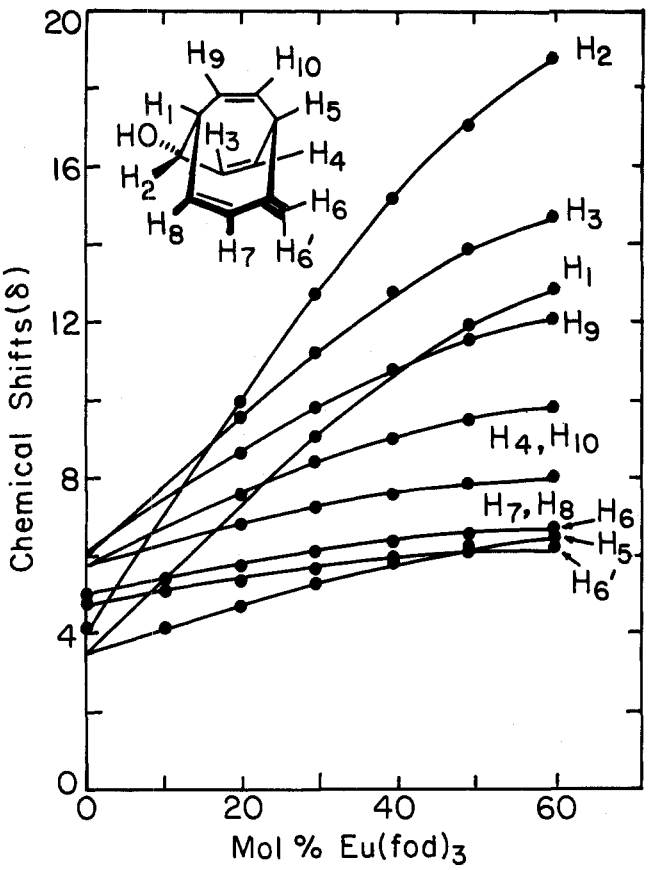


Figure 1. Plot of chemical shift vs. mol % $Eu(fod)_3$ for **13**.

Our finding of high levels of contrasting selectivity in the acid-catalyzed rearrangement of **2** and in the solvolysis of **3b** and **3c** permits us to suggest that rearrangement reactions of potential carbonium ion centers on the bullvalene backbone, e.g., **15** and **16**, appear capable of initiation from

15 16

different valence tautomeric forms. We propose that the ultimate course taken will likely depend upon the nature of the cationic center, its method of generation, and to some extent the timing of the transition state along the reaction coordinate. That several pathways are open is not surprising; what is now needed is additional experimental information that would assist in formulating on an a priori basis the mechanistically most favorable reaction channel available to a new bullvalene derivative.

Experimental Section

Proton magnetic resonance spectra were obtained with Varian A-60A and Jeolco MH-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined with Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative VPC work was done on a Varian Aerograph A90-P3 instrument equipped with a thermal conductivity detector.

Cyanobullvalene (1). A mixture of 4.36 g (20.5 mmol) of bromobullvalene,[7b] 1.01 g (20.5 mmol) of sodium cyanide, 1.84 g (20.5 mmol) of cuprous cyanide, and 200 ml of freshly distilled dry dimethylformamide was refluxed under nitrogen for 8 hr. The reaction mixture gradually turned brown and then black. After cooling to room temperature, the black solution was transferred to a separatory funnel with 500 ml of 10 *N* sodium cyanide solution and 500 ml of ether. The ether layer was washed with water (2 × 1000 ml) and brine (1 × 1000 ml), dried over magnesium sulfate, filtered, and evaporated in vacuo. The resulting yellow oil was purified by column chromatography on silica gel (elution with 25% ether–hexane). The colorless oil so obtained was crystallized from 4 ml of ethanol at −30° to give 2.62 g (82%) of **1**: mp 60–60.5°; ν_{max} (KBr) 2190 cm^{-1}; δ_{TMS} ($CDCl_3$) (−35°) 6.76 (d, 1 H, olefinic β to CN), 5.97 (m, 4 H, olefinic), and 2.56 (m, 4 H, cyclopropyl and aliphatic); δ_{TMS} ($CDCl_3$) (108°) 4.45 (s, $W_{1/2}$ = 7.5 Hz).

Anal. Calcd for $C_{11}H_9N$: C, 85.13; H, 5.85. Found: C, 85.27; H, 6.16.

Bullvalenylcarboxaldehyde (2). A solution of 1.00 g (6.44 mmol) of **1** in 50 ml of dry benzene was stirred magnetically at room temperature and 5.6 ml of 26% diisobutylaluminum hydride in hexane (1.1 equiv) was added via syringe. The temperature of the reaction mixture was raised to 40° using a warm water bath and stirring was maintained for 0.5 hr. The solution was cooled in ice and residual active hydride was quenched by careful addition of 2.0 ml of methanol followed by 2.0 ml of water. After being stirred for 1 hr, the mixture was filtered through a pad of Celite and the filtrate was dried over magnesium sulfate, filtered, and evaporated in vacuo to yield an orange oil. This material crystallized slowly from benzene–hexane to give 0.678 g (67%) of **2** as a yellowish solid: mp 153–159°; ν_{max} (KBr) 2830, 1629, 1610 cm^{-1}; δ_{TMS} ($CDCl_3$) 9.05 (s, 1H, –CHO) and 4.50 (very br, 9 H).

Bullvalenylcarboxaldehyde Oxime (4). To 0.50 g (7.2 mmol) of hydroxylamine hydrochloride dissolved in 3 ml of water was added 2 ml of 10% sodium hydroxide solution followed by 100 mg (0.63 mmol) of **2** and 5 ml of ethanol. The mixture was heated on a steam bath for 15 min. The solid which was initially present quickly dissolved upon warming. Subsequent cooling deposited a pale green solid which was collected by suction filtration, taken up in hot ethanol, and treated with Norit. To the filtrate was added 5 ml of water and the total volume was reduced to 10 ml on a steam bath. Slow cooling yielded 98 mg (85%) of **4** as white needles: mp 184–185° (from ethanol); ν_{max} (KBr) 3230, 1620, 1290, 972, 953, 938, and 824 cm^{-1}; δ_{TMS} [$(CD_3)_2$ CO] 7.41 (s, 1 H, >CH=N–), 4.38 (very br, 9 H), and 2.78 (br s, 1 H, hydroxyl).

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.02; H, 6.44; N, 7.82.

Bullvalenylcarbinol (3a). A mixture of 510 mg (3.22 mmol) of **2**, 200 mg (5.0 mmol) of sodium hydroxide, and 1.46 g (38.3 mmol) of sodium borohydride in 50 ml of ethanol was stirred for 24 hr at room temperature and then added to 500 ml of water and 100 ml of ether. The ether layer was separated, washed with water and brine, and dried over magnesium sulfate. After removal of the ether in vacuo, the resulting yellow oil was chromatographed on silica gel (elution with 50% ether–hexane) to give 428 mg (83%) of **3a** as a pale yellow oil. The analytical sample was obtained by preparative VPC at 170° (6 ft × 0.25 in. 5% SF-96 on Chromosorb G): ν_{max} (KBr) 3320 and 1015 cm^{-1}; δ_{TMS} ($CDCl_3$) 4.35 (very br, 9 H), 4.02 (s, 2 H, methylene), and 1.88 (br, s, 1 H, hydroxyl).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.32; H, 7.73.

Bullvalenylcarboxaldehyde Tosylhydrazone (6). A mixture of 316 mg (2.00 mmol) of **2** and 372 mg (2.00 mmol) of tosylhydrazine in 10 ml of ethanol was heated on a steam bath for 20 min. The hot solution was filtered and allowed to cool to room temperature. The tosylhydrazone crystallized as pale yellow needles. After further cooling at −30°, the needles were collected to give 290 mg (44%) of **6**: mp 151° dec; ν_{max} (KBr) 1355, 1328, 1300, and 1160 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.52 (m, 6 H, aromatic, >CH=N–, and >NH), 4.50 (very br, 9 H), and 2.40 (s, 3 H, methyl).

Anal. Calcd for $C_{18}H_{18}N_2O_2S$: C, 66.23; H, 5.56; N, 8.58. Found: C, 66.61; H, 5.61; N, 8.47.

Acid-Catalyzed Rearrangement of 2. To 6.3 ml of a solution of *p*-toluenesulfonic acid in benzene (1.0 mmol/ml) was added 50 mg (0.63 mmol) of **2** and the mixture was stirred at room temperature for 12 hr. Addition of the solution to water (30 ml) and extraction with ether (10 ml), followed by washing of the organic layer with water and saturated sodium bicarbonate solution, drying over sodium sulfate, and removal of solvent in vacuo gave 29 mg (58%) of 2-naphthaldehyde (**7**). This product was identified by ^1H NMR comparison with a known sample, and by means of its 2,4-DNP derivative, mp 269–270.5° (lit.[20] mp 270°).

When the duration of reaction was limited to 1 hr, a mixture of two aldehydes was detected by ^1H NMR after the above work-up; these were determined to be **7** and **8** in a ratio of 72:28 as determined by the relative areas of their aldehyde absorptions in the ^1H NMR spectrum, 31 mg (62%).

Use of *p*-toluenesulfonic acid-d_1 gave identical results and showed no deuterium incorporation. These two aldehydes could not be separated by TLC and although separation could be achieved on a gas chromatograph equipped with an SF-96 (10%) column at 155°, the collected material that should have corresponded to **8** was found on a preparative scale to still be contaminated with **7**. Rearrangement was apparently also taking place in the exit port.

Reduction and Oxidation of 9. To an ice-cold solution of 100 mg (0.53 mmol) of **9**[15] in 5 ml of dry ether under argon was added via syringe 0.92 ml (1.17 mmol) of diisobutylaluminum hydride (26% by weight, 1.27 mmol/ml) in hexane. This clear solution was stirred at 0° for 1 hr, then treated with 0.5 ml of methanol and 0.5 ml of water. After 1 hr, the aluminum salts were removed by filtration through Celite and the gel was washed with three 20-ml portions of ether. The combined filtrates were dried over sodium sulfate and evaporated in vacuo. The residue was chromatographed on a short Florisil column (elution with 20% ether–carbon tetrachloride) to give **10** as a clear oil: δ_{TMS} ($CDCl_3$) 5.25–6.20 (m, 7 H, olefinic), 3.91 (s, 2 H, methylene), 2.85–3.43 (m, 2 H, bridgehead), and 2.88 (br, s, 1 H, hydroxyl). This oil was transferred to a 10-ml flask and 1 ml of dry dimethyl sulfoxide, 1 ml of dry benzene, 358 mg (1.74 mmol) of dicyclohexylcarbodiimide, 60 μl (0.74 mmol) of pyridine, and 30 μl (0.40 mmol) of trifluoroacetic acid were added. This solution was stirred magnetically for 24 hr at room temperature, at which point it was poured into 15 ml of ether to which was added 240 mg (2.67 mmol) of oxalic acid in 6 ml of methanol. After an additional 30 min, water (10 ml) was introduced, and the organic layer was separated and washed sequentially with water and saturated sodium carbonate solution, dried over sodium sulfate, and evaporated in vacuo. Thin layer chromatography showed that incomplete oxidation had taken place. Elution with 25% ether–hexane showed a minor component (i.e., **8**) and a major one (**10**). Isolation of **8** by preparative TLC gave 9 mg (11% from **9**) which was spectroscopically identical with **8** obtained from acid-catalyzed rearrangement of **2**. The 2,4-dinitrophenylhydrazine derivatives of **8** prepared by the two routes were also identical by infrared and TLC.

Oxidation of **10** with manganese dioxide gave 2-naphthaldehyde (**7**).

Pyrolysis of the Sodium Salt of Bullvalenylcarboxaldehyde Tosylhydrazone (6). A stirred solution of 163 mg (0.50 mmol) of **6** in 2 ml of dichloromethane (which had been stored over sodium hydroxide pellets) was treated with 21 mg (1 molar equiv) of 47% sodium hydride suspension. Gas evolution started immediately and ceased after 3 min. The solvent was removed in vacuo and the pyrolysis apparatus was assembled. The system consisted of the reaction flask, a bent adaptor leading into a straight vacuum adaptor, and a receiver. When a vacuum of 0.01 mmHg had been attained, the apparatus was lowered such that the reaction flask became immersed in a salt bath preheated at 200° and the receiver was cooled in a Dry Ice–isopropyl alcohol bath. Within a few seconds bubbling was noted in the reaction flask and deposition of a yellow oil was seen in the cooler portions of the bent adaptor. No change in the pumping speed was noted, indicating that no nitrogen was being evolved. After approximately 2 min, activity was no longer evident in the reaction flask, and a gray solid remained. The yellow oil crystallized upon scratching. After preparative thick layer chromatography, there was isolated 34 mg of the pyrazole **12** as a white solid: mp 83–87°; ν_{max} (KBr) 3360 and 3180 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.35 (s, 1 H, >CH=N–), 5.80 (m, 2 H, olefinic), 4.10 (m, 4 H, olefinic ⇌ cyclopropyl), 3.27 (t, J = 8.5 Hz, 1 H, cyclopropyl ⇌ aliphatic), and 3.05 (t, J = 8.5 Hz, 1 H, cyclopropyl ⇌ aliphatic); calcd for $C_{11}H_{10}N_2$ m/e 170.0844, found 170.0847.

Anal. Calcd for $(C_{11}H_{10}N_2)_3 \cdot H_2O$: C, 74.97; H, 6.10. Found: C, 74.65; H, 6.27.

Base-Induced Decomposition of 6. To a stirred solution of 3 equiv of the base in 5 ml of dry solvent under nitrogen was added 1 equiv of **6** in one portion. This mixture was then heated in a 125° oil bath for 10 min. The only observable change was a darkening of the reaction mixture. This was then cooled in ice and rinsed into a separatory funnel with 80 ml of water and 25 ml of ether. The ether layer was washed with water, dried over sodium sulfate, filtered, and evaporated in vacuo. The resulting oil was chromatographed on a short column of silica gel (elution with 75% ether–hexane). The only isolated product was the pyrazole **12** (Table II).

Bullvalenylmethyl *p*-Anisoate (3c). To a solution of 158 mg (0.99 mmol) of **3a** in 3 ml of 2,6-lutidine was added 171 mg (1.00 mmol) of *p*-anisoyl chloride in 2 ml of 2,6-lutidine. A precipitate formed immediately and the mixture was placed in the refrigerator for 18 hr. The orange reaction mixture was added to 40 g of ice and water and the precipitate was collected by suction filtration, washed with 30 ml of cold water, and dried in air. Preparative TLC (elution with 75% ether–petroleum ether) yielded 151 mg (52%) of **3c** as an off-white solid. The second component was identified as *p*-anisoyl anhydride. Recrystallization from hexane gave pure **3c** as white prisms: mp 85–86°; ν_{max} (KBr) 1720, 1610, 1275, 1260, 1710, and 1110 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.92 and 6.83 (AA′BB′, 4 H, aromatic), 4.59 (s, 2 H, methylene), 4.30 (very br, 9 H), and 3.80 (s, 3 H, methoxyl).

Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.45; H, 6.23.

Solvolysis of 3c. A 0.375-in. glass tube was charged with 107 mg (0.36 mmol) of **3c** and 1.0 ml of 70:30 (v/v) acetone–water and sealed 20 cm from the bottom under vacuum while being cooled in a Dry Ice–isopropyl alcohol bath. The sealed tube was allowed to warm to room temperature, then totally immersed in an air bath at 125°. After 10 min the tube was removed and inverted a few times to dissolve the molten ester at the bottom. The tube was subsequently replaced and heated for 24 hr. After cooling in a Dry Ice–isopropyl alcohol bath the tube was opened and the yellowish reaction mixture was added to 40 ml of water and extracted with ether (2 × 20 ml). The combined ether layers were washed with water (30 ml) and saturated sodium carbonate solution (30 ml), dried over sodium sulfate, and evaporated in vacuo to yield a yellow oil which upon preparative TLC purification was separated into its two components: R_f 0.73, 24 mg. Recovered **3c**: R_f 1.40, 38 mg. Rearranged alcohol **13** (85% based on recovered **3c**), white needles: mp 77–77.5° (from pentane); ν_{max} (neat) 3380 and 1015 cm^{-1}; δ_{TMS} ($CDCl_3$) 6.00 (m, 6 H, olefinic), 5.00 (d, J = 2.0 Hz, 1 H, exo methylene), 4.78 (d, J = 2.0 Hz, 1 H, exo methylene), 4.11 (m, 1 H, >CHO), 3.32 (m, 2 H, bridgehead), and 1.98 (br s, 1 H, hydroxyl); calcd m/e 160.0888; found, 160.0890.

Attempted Preparation of 3b. To a magnetically stirred solution of 212 mg (1.32 mmol) of **3a** in 5.0 ml of dry tetrahydrofuran under nitrogen at 0° was added 0.63 ml (1 equiv) of 2.10 M *n*-butyllithium. The clear solution yellowed upon addition of the *n*-butyllithium; no other change was noted after 0.5 hr. To this was added 250 mg (1.32 mmol) of *p*-toluenesulfonyl chloride. After 0.5 hr, solvent was removed in vacuo, 2 ml of dichloromethane was added, and the resulting suspension was filtered. Only one spot was seen by TLC (R_f 0.81, 50% ether–hexane). Isolation by preparative TLC gave **13** (52 mg, 24%).

Table II
Decomposition of Bullvalenylcarboxaldehyde Tosylhydrazone (6)

Mmol of 6	Solvent	Base	% yield of 12
0.80	Diglyme	*n*-BuLi	37
0.46	Ethylene glycol	*n*-BuLi	33
0.86	Diglyme	$NaOCH_3$	42

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Registry No.—**1**, 54934-08-6; **2**, 54934-09-7; **3a**, 54934-10-0; **3c**, 54934-11-1; **4**, 54934-12-2; **6**, 54934-13-3; **7**, 66-99-9; **9**, 20061-12-5; **10**, 54934-15-5; **12**, 54934-16-6; **13**, 54934-17-7; bromobullvalene, 27576-96-1; sodium cyanide, 143-33-9; cuprous cyanide, 544-92-3; tosylhydrazine, 1576-35-8; *p*-anisoyl chloride, 100-07-2; bullvalenyldiazomethane, 54934-14-4.

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N^3,O^4-Ethylene-1-methyluracilium Methanesulfonate. A Uracil-Derived Heteronuclear Stabilized Cation[1]

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The preparation and properties of N^3,O^4-ethylene-1-methyluracilium methanesulfonate, a heteronuclear stabilized cation, and its interconversions with 3-(β-methanesulfonyloxyethyl)-1-methyluracil were studied. The former was shown to have three sites for reactions with nucleophilic reagents: the β carbon of the ethylene moiety and C-4 and C-6 of the pyrimidine ring. Products resulting from attack at the β position were observed with DMSO, water, alcohols, benzoate, chloride, diethylamine, and pyridine. A strong rate dependence on solvent was noted with chloride ions. Products resulting from attack at C-4 were observed with water, hydroxide, alcohols, alkoxide, and isopropylamine. Diethylamine was the only reagent which led to a product resulting from attack at C-6 of the cation. Oxygen-18 experiments verified the sites at which the uracilium salt reacted with hydroxide and water. Although the N^3,O^4-ethylene-1-methyluracilium cation bears a net positive charge, deuterium exchange reactions were not observed. Mechanisms are proposed to account for the products of the various reactions which were investigated.

N^3,O^4-Ethylene-1-methyluracilium mesylate (**1**, Scheme I) was isolated during the course of the synthesis of 3-(β-mesyloxyethyl)-1-methyluracil[2] (**2**). This uracilium salt is an exceptionally stable member of the class of compounds referred to as heteronuclear stabilized cations.[3,4] Two examples of resonance-stabilized cations having the pyrimidine nucleus have been observed, but only in solution.[5]

Delocalization of the positive charge over several atoms of cation **1** enhances stability and provides multiple sites for chemical reactions. Furthermore, one of its resonance structures is analogous to that postulated as a rationalization for the carbanion mechanism of H-6 exchange in pyrimidines.[6]

In most cases where salts of heteronuclear stabilized cations have been isolated, the anions have been nonnucleophilic species such as ClO_4^-, BF_4^-, or SbF_6^-. By contrast, the anionic portion of salt **1** is sufficiently nucleophilic under certain circumstances to enable the salt to revert to its covalent isomer.

Results and Discussion

3-(β-Hydroxyethyl)-1-methyluracil (**3**) was obtained in high yield by a three-step synthesis starting with 2,4-diethoxypyrimidine.[7] Mesylation of **3** gave a 90% yield of ester **2** and a small amount of 3-(β-chloroethyl)-1-methyluracil (**4**). The structure assigned to **2** is supported by the ultraviolet absorption spectrum, which is essentially identical with that of **3**[8] and of 1,3-dimethyluracil.[9] The infrared spectrum of compound **2** is that of a typical 1,3-disubstituted uracil: ν (C_2=O) 1700, ν (C_4=O) 1660, ν (C=C) 1620 cm^{-1} and absorptions due to uracil nucleus vibrations at 1415–1440 and 1450–1490 cm^{-1}.[10] In fact, the infrared spectra of all of the compounds (**2, 3, 4, 6, 8, 11,** and **12**) which have the uracil nucleus exhibit these characteristic absorption bands. In general, these compounds also absorb in regions characteristic of the functional groups which are substituents on the N-3 ethyl side chain; e.g., compound **2** absorbs at 1185 and 1345 cm^{-1}.[11] The ^{1}H NMR resonances of H-5, H-6, and NCH_3 in ester **2** are essentially the same as those in **3**, while the methylene resonances are shifted downfield, as expected. The resonance due to the protons in the methanesulfonyl group is in the same region as that of other methanesulfonate esters.[12] The ester was soluble and relatively stable in nonpolar solvents (e.g., chloroform, ethyl acetate, and acetone) and it migrated like a covalent compound in thin layer chromatography on silica gel.