by Cainelli and co-workers for the oxidation of alcohols by chromic acid on anion exchange resins.[14]

Experimental Section

In a typical procedure, a solution of CrO_2Cl_2 (10.0 g) in methylene chloride (100 mL) is added with stirring to a slurry of SiO_2–Al_2O_3 (90.0 g, Grace Davison No. 135) in methylene chloride (150 mL). After stirring for an additional 5 min, the yellow-orange solid was collected by suction filtration on a fritted-glass funnel and subsequently dried under reduced pressure. The resulting solid can be used immediately or stored indefinitely if reasonable precautions against moisture are observed.

The following description represents a typical oxidation procedure. Two grams of the above reagent (1.10 mmol of Cr as determined by elemental analysis[15]) are placed in a flask along with 20 mL of methylene chloride and a Teflon-coated stirrer bar. A solution of 1-octanol (0.143 g, 1.10 mmol) in methylene chloride (5 mL) is added and the flask equipped with a drying tube. The resulting mixture is stirred for 5 h before adding 0.5 mL of methanol and filtering. The residual solids are rinsed with two 10-mL portions of methylene chloride and the combined clear, colorless filtrates analyzed directly by GLC. The yield of 1-octanal is 94%; none of the corresponding carboxylic acid is observed. A summary of the results obtained with other representative substrates is presented in Table I.

Registry No.—Chromyl chloride, 14977-61-8.

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Dynamic Carbon-13 Nuclear Magnetic Resonance Spectra of Benzobullvalene and *o*-Toluobullvalene

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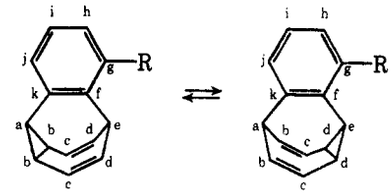
The factors which control the rate of the Cope rearrangement in bullvalene and related compounds are a topic of considerable interest.[1] The elegant work of Oth[2] and Günther[3] has shown that variable temperature ^{13}C NMR is an ideal tool for such investigations. The synthesis and dynamic ^{13}C NMR study of benzobullvalene (1, R = H) and *o*-toluobullvalene (1, R = Me) is now reported.

The synthesis of these compounds was based on Doering's



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rational scheme for the preparation of bullvalene[4] employing the benzyne adduct of tropone[5] as a starting material. Eisenstadt[6] has recently published an analogous procedure. The low- and high-temperature ^{13}C NMR chemical shifts and their assignments are given in Table I. Peaks were assigned on the basis of intensity, chemical shift, multiplicity in off-resonance proton decoupled spectra, and by following their pairwise coalescence as temperature was increased. The assignment of carbons a and e in *o*-toluobullvalene is critical for the assignment of the major isomer for this nondegenerate case. In benzobullvalene, the cyclopropane carbon, 1a or 2e, is upfield of the methine carbon, 1e or 2a, based on the known assignment of bullvalene.[2,3] The introduction of the methyl group in *o*-toluobullvalene results in an upfield shift of 5.9 ppm in the high field peak of minor isomer as the only significant shift change. Based on the well-established,[7] γ-upfield shift of methyl groups, the major isomer is assigned structure 2, R = Me. Based on peak intensities in the low temperature spectrum, the equilibrium constant was found to be 1.6 ± 0.3 at -59 °C. Based on the population averaged chemical shifts at 143 °C, an equilibrium constant of 1.1 ± 0.3 is obtained. The preference for the methyl group on the same side of the molecule as the cyclopropane is consistent with the data recently reported for the methyl group in 9-ethylidenebarbaralene.[8] The reason for this preference remains obscure.

The dynamic parameters for the Cope rearrangement in benzobullvalene were determined by variable temperature carbon-13 NMR. A program[9] employing an equal population two site exchange process was used to calculate the theoretical line shapes. The large spread of chemical shift differences between exchanging carbons permitted observation of line broadening phenomena from -50 to 120 °C. The activation parameters are shown in Table II together with those reported for bullvalene. It is perhaps worth noting that the factor of 2 rate increase (0 °C) induced by replacing a double bond in bullvalene with a benzo group is the smallest structurally induced perturbation on the rate of the degenerate Cope reaction in bridged homotropilidenes.

Our plans to examine a range of substituted benzobullvalenes were thwarted by the observation that the reaction of tropone with 3-chloro- and 3-methoxybenzyne (generated from the 6-substituted anthranilic acids) gave substituted cycloheptatrienylbenzofuran derivatives.

Experimental Section[10]

Proton NMR spectra were recorded on Varian A-60 and XL-100-15 spectrometers in $CDCl_3$. Chemical shifts are reported in δ units from internal Me_4Si. IR spectra were recorded in KBr disks on Perkin-Elmer 257 and 727 spectrometers and mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6D spectrometer. Microanalyses were performed by the Purdue Microanalytical Service. Melting points are uncorrected.

Tropone,[11] 6,7-benzobicyclo[3.2.2]nonatrien-2-one,[12] and 6,7-benzobicyclo[3.2.2]nonatrien-2-ol[13] were prepared by previously published methods. Details of an improved procedure for the preparation of benzobullvalene are given in the microfilm edition. The product had mp 109–110 °C (lit.[6,14] 89, 110–111 °C). Spectral details for the *o*-toluobullvalene intermediates may also be found in the microfilm edition.

Methyl-6,7-benzobicyclo[3.2.2]nona-3,6,8-trien-2-one (I). In a 600-mL beaker equipped with a stirring bar and thermometer 3-methylanthranilic acid (32.0 g, 0.212 mol) was dissolved in dry THF (250 mL). After cooling in an ice bath Cl_3CCO_2H (0.3 g) dissolved in

Table I. Carbon-13 Chemical Shifts of Benzobullvalenes[a,b]

Carbon	Benzobullvalene		o-Toluobullvalene		
	−59 °C	143 °C	(1) −60 °C	(2) −60 °C	140 °C
a	25.0	33.2	25.6	39.6	33.9
b	20.3	77.5	20.2	127.0	78.3
c	126.1	126.1	126.3	126.3	126.5
d	127.2	77.5	126.9	20.4	75.1
e	39.1	33.2	32.1	19.1	26.5
f	(136.7)	137.8			
g	127.0	129.3			
h	126.4[c]	126.4	125.3	126.3	125.6
i	126.0[c]	126.4	129.0	129.3	129.0
j	131.0	129.3	130.8	125.5	128.0
k	(136.7)	137.8			
Me			21.1	21.3	20.2

[a] Chemical shifts are reported relative to internal Me_4Si. At low temperatures, shifts were determined directly, at high temperature shifts were measured relative to solvent and corrected to Me_4Si using the room temperature shift between Me_4Si and solvent. [b] Chemical shifts for bullvalene:[3] a, 20.5; c, 127.2; d, 128.1; e, 30.0. [c] The assignment of pairs of peaks may be reversed.

Table II. Activation Parameters for Cope Rearrangement

Compd	E_A, kcal/mol	A × 10^{13} s^{-1}	k (0 °C), s^{-1}	Ref
Benzobullvalene	11.8	0.37	1350	This work
Bullvalene	13.18	2.37	671	a
	13.9	10	670	b
	11.5	0.13	790	b
	12.8	0.78	416	c

[a] Reference 3. [b] Reference 2. [c] A. Allerhand and H. S. Gutowsky, *J. Am. Chem. Soc.*, **87**, 4092 (1965).

THF (10 mL) was added, followed by the slow addition of isoamyl nitrite (45 mL, 39.2 g, 0.335 mol) over a 5-min period. After warming to 18–25 °C for 1 h, the red precipitate was cooled, collected on a plastic funnel with greased filter paper, washed with excess cold THF, and transferred with a minimum of dry THF to a dry three-neck 500-mL flask equipped with a condenser and N_2 inlet tube. Tropone (20.0 g, 0.189 mol) was added and the reaction flask was immersed in a 35–37 °C oil bath. The reaction should be carefully watched, since the decomposition of the diazonium salt can become very violent with a small increase in temperature. After 8 h the reaction was cooled, concentrated on the rotary evaporator, and filtered over alumina (200 mL) in a 350-mL coarse fritted-disk funnel with ether (1 L). The filtrate was concentrated to 400 mL and dried over $MgSO_4$. Filtration followed by rotary evaporation yielded approximately 35 mL of a black liquid which was vacuum distilled (Hg diffusion pump) to recover unreacted tropone (9.01 g, 45.5%) at 55–58 °C, and the desired ketones I (12.06 g, 32.6%, 59.3% conversion) at 110–114 °C. I slowly crystallized upon refrigeration or the addition of a trace of ether. The solid was partially dissolved in hot pentane and filtered to yield the pure isomer Ia. The recrystallized solid was a mixture of both Ia and Ib: mp 60–65 and 90–95 °C for the mixture, 118–120 °C for Ia; NMR Ia, δ 2.42 (s, 3 H, CH_3), 4.29 (br dd, J = 8.5, 8,0, 1.5, 1 Hz, H-5), 4.96 (d, t, J = 7.5, 1.5, 1.5 Hz, H-1), 5.28 (dq (br ddd), J = 11, 1.5, 1 Hz, H-3), 6.63 (t, d, J = 7.5, 7.5, 7.5 Hz, H-9), 7.00 (ddd, J = 8, 7.5, 1.5 Hz, H-8), 7.10 (br s, 3 H, aromatic), 7.32 (dd, J = 11, 8.5 Hz, H-4); NMR Ib, δ 2.39 (s, 3 H, CH_3), 4.50–4.73 (m, 2 H, H-1 and H-5), 5.26 (br dd, J = 11, 1.5, 1 Hz, H-3), 6.66 (ddd, J = 8, 6.5, 1.5 Hz, H-9), 6.95 (ddd, J = 8, 6.5, 1.5 Hz, H-9), 7.05–7.19 (m, 3 H, aromatic), 7.35 (dd, J = 11, 8.5 Hz, H-4).

Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.65; H, 6.27.

Methylbenzobicyclo[3.2.2]nona-3,6,8-trien-2-ol (II). In a dried 500-mL flask purged with N_2, ketone Ia (1.00 g, 5.1 mmol) was dissolved in ether (300 mL) and cooled in a dry ice–acetone bath. $LiAlH_4$ (2.1 equiv, 0.101 g, 2.68 mmol) was added over a 15-min period with stirring. After 1.5 h an aliquot was filtered and examined by thin layer chromatography using 50% ether–pentane as the eluent. The chromatogram showed two spots which had smaller R_f values than the starting ketone. After 2–2.5 h the reduction was complete and quenched with a 20% aqueous sodium–potassium tartrate solution (15 mL), warmed to room temperature, and diluted with H_2O (100 mL). The phases were separated and the aqueous layer was extracted with more ether (three 50-mL portions). The ether extracts were dried over $MgSO_4$, filtered, and rotary evaporated to give the crude alcohol (1.03 g). Recrystallization from hexane yielded 0.93 g (92%) of IIa. If the mixture of ketones Ia and Ib were reduced, recrystallization recovered 75% of II as a solid, while the remaining 20% was an amorphous oil: mp 106–107 °C (endo isomer IIa only); NMR δ 1.65 (br s, 1 H), 2.45 (s, 3 H), 3.76 (br t, J = 7 Hz, 1 H), 4.14–4.45 (m, 2 H), 5.06 (d, t, J = 10, 3 Hz, 1 H), 6.24–6.64 (m, 2 H), 6.87–7.20 (m, 4 H).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.41; H, 7.12. Found: C, 84.79; H, 7.37.

Methylbenzobarbaralone (IV). (a) Rearrangement of II to III. Methylbenzo[3.2.2]nonatrienol (II) (0.500 g, 2.52 mmol) was dissolved in 33% dioxane–H_2O (150 mL) in a 500-mL flask. $HClO_4$ (70%, 15 mL) was added and stirred for 44 h. An aliquot was quenched in solid Na_2CO_3 and ether and examined by thin layer chromatography using 50% pentane–ether as the eluent. Once the major isomer of II had disappeared, an additional portion of 70% $HClO_4$ (15 mL) was added. After 48 h the reaction was carefully neutralized with small portions of solid Na_2CO_3, diluted with H_2O (100 mL), and extracted with ether (five 50-mL portions). The ether extracts are dried over $MgSO_4$, filtered, and rotary evaporated to give approximately 0.7 g of crude III.

(b) Oxidation of III to IV. Crude alcohol III was stirred with activated molecular sieves in dry CH_2Cl_2 under N_2 for several hours. The CrO_3 (6 equiv, 2.36 g, 23.6 mmol) dried under vacuum over P_2O_5 was added to a stirred solution of dry pyridine (12 equiv, 3.8 mL) and dry CH_2Cl_2 (100 mL) in a flame-dried, three-neck, 300-mL flask purged with N_2. After 15 min alcohol III was added to the homogeneous burgundy colored solution. (If a black insoluble solid was present the oxidizing agent was wet and should be discarded.) After 15 min 2-propanol (15 mL) was added and stirred for 5 min more. The reaction was transferred with ether (100 mL) to a separatory funnel and washed with 5% NaOH (three 100-mL portions) and 5% HCl (three 100-mL portions). If the organic phase was still highly colored, more washings were done with 5% NaOH and 5% HCl. The reaction mixture was finally washed with saturated $NaHCO_3$ (one 100-mL portion) and saturated NaCl (one 100-mL portion) and dried over $MgSO_4$. Filtration followed by rotary evaporation yields 0.373 g (75.4%) of crude ketone IV. Recrystallization from pentane or hexane yielded 59% of a mixture of the isomeric methylbenzobarbaralone (IV) (isomer a, 57%; isomer b, 43%): mp 109–110 °C (mixture of isomers); NMR IVa, δ 2.22–2.88 (m, 2 H, H-1 and H-2), 2.29 (s, 3 H, CH_3), 3.34 (t, J = 8 Hz, 1 H, H-8), 3.98 (br dd, J = 6.5, 2.5 Hz, 1 H, H-5), 5.63–6.09 (m, 2 H, H-3 and H-4), 6.82–7.15 (m, 3 H); NMR IVb, δ 2.22–2.88 (m, 2 H, H-1 and H-2), 2.41 (s, 3 H, CH_3), 3.34 (dd, J = 8, 7 Hz, 1 H, H-8), 3.69 (br dd, J = 6.5, 2.5 Hz, 1 H, H-5), 5.63 (m, 2 H, H-3 and H-4), 6.82–7.15 (m, 3 H).

Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.44; H, 6.44.

Methylbenzobullvalone (V). Methylbenzobarbaralone (IV) 1.81 g, 9.23 mmol) was dissolved in dry ether (200 mL) in a dry 1-L filtering flask immersed in an ice bath with an addition funnel, stirring bar,

and purged under nitrogen. BF_3·OEt_2 (1 equiv, 1.14 mL, 92 mmol) was added and stirred for 15 min. Previously distilled CH_2N_2 (12.75 equiv, 210 mL each of 0.31 and 0.25 M dried over KOH for 1 h) was added over a 1.5-h period to the reaction mixture. After the addition the reaction was quenched with saturated aqueous $NaHCO_3$ (25 mL), filtered, washed with ether (100 mL), and diluted with H_2O (100 mL). The phases were separated and the aqueous layer extracted with more ether (two 25-mL portions). The combined ether extracts were dried over $MgSO_4$. Filtration followed by rotary evaporation gave an oily product which was chromatographed over silica gel (75 g, 80% CH_2Cl_2–hexane) to yield 0.97 g (50.4%) of V and 0.30 g (16.6%) of recovered IV: NMR V, δ 1.8–2.9 (m, 3 H), 2.36 and 2.44 (s, 3 H), 2.29 (m, 2 H), 3.74 and 4.12 (d, J = 9 Hz, 1 H), 5.77 (m, 1 H), 6.13 (m, 1 H), 6.8–7.3 (m, 3 H).

Methylbenzobullvalone Tosylhydrazone (VI). In a dry 50-mL flask purged with N_2, methylbenzobullvalone (V) (0.80 g, 3.8 mmol) and tosylhydrazine (0.70 g, 3.7 mmol) were stirred in dry ether (25 mL). After 57 h the product was filtered and washed with Et_2O (10 mL) to yield 0.428 g. Additional stirring of the filtrate for 36 h gave 10% more product. The total yield of crude VI was 0.478 g (34%), which was 90% one isomer VIa. The ether filtrates were concentrated on the rotary evaporator to give an additional 0.69 g of a puffy yellow solid. NMR indicated that 75% was probably VI. Estimated yield of VI was roughly 70%: mp, turns brown at 137 °C, 142–144 °C dec.

Methylbenzobullvalene (1, R = Me). Freshly distilled isopropylamine (3 equiv, 0.6 mL, 4.2 mmol) was dissolved in ether (100 mL) in a dry three-neck 300-mL flask equipped with a stirring bar and purged under N_2. After cooling the reaction in a dry ice–2-propanol bath, 3 equiv of n-BuLi (2.4 mL of 2.4 M in hexane) was added, and the mixture was warmed to 0 °C. Upon cooling the reaction flask to −78 °C, solid VI (0.217 g, 1.04 mmol) was added and the reaction was slowly warmed to room temperature. After several hours (3–8 h) the reaction was quenched with cold water (50 mL) and separated. The aqueous phase was extracted with ether (three 15-mL portions). The combined ether extracts were washed with 5% HCl (25 mL), saturated $NaHCO_3$ (25 mL), and saturated NaCl (25 mL), and dried over $MgSO_4$. Filtration followed by rotary evaporation gave a white solid: NMR δ 2.26 (s, 3 H); 2.82 (t, J = 9.5 Hz, 1 H), 2.17 (t, J = 9.5 Hz, 1 H), 3.5–4.6 (v br s, 4 H), 5.78 (complex t, 2 H), 6.75–7.20 (m, 3 H); IR (CCl_4) 685 (w), 700 (w), 730 (s), 750 (br s), 800 (s), 810 (sh), 815 (m), 875 (w), 915 (w), 975 (w), 1035 (w), 1095 (w), 1260 (w), 1375 (m), 1410 (w), 1450 (m), 1570 (s), 1580 (s), 1590 (w), 1650 (m), 2870 (w), 2970 (br m), 3030 (s), 3070 (sh) cm^{-1}; MS 195 (7.1), 194 (43.4), 193 (30.7), 192 (7.1), 191 (7.1), 189 (56.7), 180 (15.6), 179 (100), 178 (67.9), 177 (7.1), 176 (5.2), 166 (3.8), 165 (12.7), 153 (3.8), 152 (10.4), 151 (2.8), 142 (3.3), 141 (3.8), 139 (3.8), 129 (3.3), 128 (13.7), 127 (3.8), 115 (6.1), 96 (3.8), 89 (7.6), 77 (2.8), 76 (3.8), 63 (4.3), 51 (3.8), 39 (4.7).

Anal. Calcd for $C_{15}H_{14}$: C, 92.73; H, 7.26. Found: C, 92.44; H, 7.51.

Variable Temperature Carbon-13 NMR Spectra. Proton square wave decoupled[15] carbon-13 spectra were recorded on a modified Varian XL-100-15 spectrometer operating in the Fourier transform mode. The 25.16-MHz excitation frequency was supplied by a Hewlett-Packard Model 8660A frequency synthesizer. Data were collected and calculated on a Nicolet 1080-20 computer. Field-frequency lock was provided by a sample of acetone-d_6 contained in the annulus of a 12-mm tube. The sample itself was placed in a 10-mm tube inside the 12-mm tube. Data points (8K) were collected with a 5-KHz window resulting in 4K real data points after transformation. The excitation pulse length varied from 70 μs (pulse angle 52°) at low temperature to 30 μs (pulse angle 23°) at high temperature. The pulse repetition rate was 1.1 s, and a receiver recovery delay of 200 μs was employed. A minimum of 8192 scans was accumulated in each case. Chemical shifts were calculated from internal tetramethylsilane using the computer calculated frequency separation between peak maxima.

Temperature control was provided by a flow of precooled nitrogen gas using the Varian V4341 temperature controller. Temperature was measured with a Wilmad 5-mm low temperature thermometer and/or a chromel–alumel thermocouple. The temperature sensors were placed at the level of the observation coil immersed in a 12-mm tube containing $CHCl_2CHCl_2$ filled to the same level as the sample. Calibration studies both inside and outside the spectrometer showed that a substantial stem correction (over 10° at low temperature) was required for the thermometer, which varied with the ambient temperature. The thermocouple was used for all reported temperature measurements. Temperatures were recorded before and after data accumulation and were held constant within ±0.5 °C. The absolute temperature is presumed to be accurate to ±1 °C. The samples were prepared by dissolving 0.35 mg of benzobullvalene (0.121 mg of o-toluobullvalene) in 2.5 mL of $CHCl_2CHCl_2$ together with 2–3 drops of tetramethylsilane. No corrections for the temperature dependence of chemical shifts were applied in the calculations.

Registry No.—Ia, 61990-59-8; Ib, 61990-60-1; II, 61990-61-2; III, 61990-64-5; IVa, 61990-62-3; IVb, 61990-63-4; V, 61990-91-8; VIa, 61990-65-6; VIb, 61990-66-7; VIIa, 61990-67-8; VIIb, 62015-28-5; VIII, 34886-96-9; IX, 61990-68-9; X, 61990-69-0; benzobullvalene, 50653-71-9; methylbenzobullvalene, 61990-70-3; 3-methylanthranilic acid, 4389-45-1; tropone, 539-80-0; bullvalene, 1005-51-2.

Supplementary Material Available. An expanded Experimental Section, Tables III–V (11 pages). Ordering information is given on any current masthead page.

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Preparation of Uracil

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Over the last seven decades, uracil, a molecule of interest to organic and biochemists alike, and its derivatives have been prepared by a variety of reactions. Methods of synthetic utility as well as chemical curiosity include synthesis from 2-thiouracil and chloroacetic acid followed by hydrolysis,[1] malic acid and urea in oleum,[2] maleic or fumaric acid and urea in PPA,[3] cyclization of substituted ureiodopropionic acid to dihydrouracil followed by bromination–dehydrobromination,[4] treatment of β-alkoxy acrylamides with ammonia or amines followed by dilute alkali,[5] and palladium salt catalyzed oxidative cyclization of acryloylurea.[6]

This report describes the preparation of uracil by condensing urea and propiolic acid[7] under acid catalysis in refluxing benzene. Uracil-forming reactions run in acidic solvents present formidable problems on plant scale; in this case, the use of organic solvents provides an acceptable alternate. Compared to commercial uracil processes,[1,2] the reaction is