

The studies on the scope and limitation of the catalytic reaction of alkyl esters¹⁸ as well as the further application of the new methodology for the formation of a carbon-transition metal bond are in progress.

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Registry No. 2, 933-05-1; 3, 84454-49-9; 4, 19066-22-9; 5, 5745-61-9; 6, 3620-18-6; 7, 61490-90-2; 8 (R = Me), 53282-55-6; 8 (R = Et), 7030-75-3; 9, 84454-50-2; 10 (isomer 1), 65167-91-1; 10 (isomer 2), 65138-39-8; 11 (isomer 1), 84472-74-2; 11 (isomer 2), 84472-75-3; 12, 84454-51-3; 13 (isomer 1), 84454-52-4; 13 (isomer 2), 84454-53-5; 14 (isomer 1), 84454-54-6; 14 (isomer 2), 84454-55-7; 15 (isomer 1), 84454-56-8; 15 (isomer 2), 84454-57-9; 16 (isomer 1), 84472-76-4; 16 (isomer 2), 84498-61-3; 17 (isomer 1), 84454-58-0; 17 (isomer 2), 84454-59-1; 18, 84454-60-4; HSiMe₃, 993-07-7; HSiEt₃, 617-86-7; HSiEt₂Me, 760-32-7; Co₂(CO)₈, 10210-68-1; CO, 630-08-0; cyclohexanol acetate, 622-45-7; 4-chlorocyclohexanol acetate, 84454-61-5; 2-hexanol acetate, 5953-49-1; 2-norbornanol acetate, 34640-76-1; 4-methyl-2-oxetanone, 3068-88-0; 5-methyldihydro-2-furanone, 108-29-2; 5-pentyldihydro-2-furanone, 104-61-0.

Supplementary Material Available: GLC data and characterization of 7-18 (12 pages). Ordering information is given on any current masthead page.

(18) The present catalytic reaction so far is limited to secondary alkyl esters. Primary alkyl esters gave a mixture of several products. In the case of tertiary alkyl acetates, no incorporation of carbon monoxide was observed.

Benz[*b*]homoheptalene. Consequences of Ring Fusion between Benzene and a Bridged [12]Annulene

Lawrence T. Scott* and Mark A. Kirms

Department of Chemistry, University of Nevada
Reno, Nevada 89557

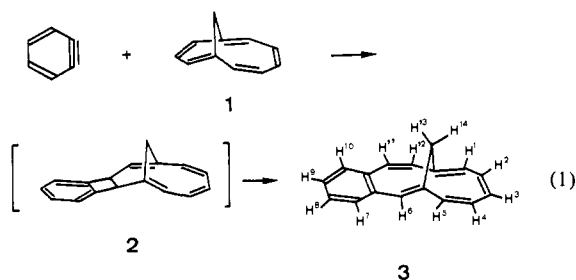
Harald Günther* and Henning von Puttkamer

Universität—Gesamthochschule Siegen, FB8, OC II
Postfach 210209, D-5900 Siegen 21, Germany

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We have recently discovered¹ that addition of an electron-deficient acetylene to homoazulene (1)² results in ring expansion of 1 to generate the homoheptalene ring system.³ This novel route to structurally interesting [12]annulene derivatives has now been extended to a remarkably simple synthesis of benz[*b*]homoheptalene (3)³ as illustrated in eq 1. Thus benzyne (generated



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(2) Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216-5220 and references cited therein. Homoazulene (1) may also be named 1,5-methano[10]annulene or bicyclo[5.3.1]undeca-1,3,5,7,9-pentaene.

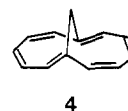
(3) Homoheptalene (4) may also be named 1,7-methano[12]annulene or bicyclo[5.5.1]trideca-1,3,5,7,9,11-hexaene. Benz[*b*]homoheptalene (3) may also be named 3,4-benzo-1,7-methano[12]annulene or 3,4-benzobicyclo[5.5.1]trideca-1,3,5,7,9,11-hexaene.

Table I. Some Properties of Benz[*b*]homoheptalene (3)

mp	53-54 °C
¹ H NMR	(400 MHz, CD ₃ CN) perimeter δ(1) 5.90, δ(2) 5.73, δ(3) 5.66, δ(4) 5.61, δ(5) 6.22, δ(6) 6.47, δ(11) 6.16, δ(12) 6.06; benzo ring δ(7) 6.96, δ(8) 7.14, δ(9) 7.12, δ(10) 6.78; bridge δ(13) 4.52, δ(14) 4.43.
¹³ C NMR	(CDCl ₃) δ 145.9, 143.3, 138.7, 137.5, 136.3, 133.3, 132.9, 132.7, 130.9, 130.6, 130.4, 129.9, 128.5, 127.4 (2 C), 126.9, 31.2.
IR (KBr)	2995, 1475, 1445, 842 (s), 812, 775, 763, 727 (s), 707, 678, 640 (s) cm ⁻¹
UV(CH ₃ CN) λ _{max}	226 (sh), 274, 379 nm

in situ from excess benzenediazonium-2-carboxylate at 80 °C in 1,2-dichloroethane⁴) reacts with homoazulene to produce the stable orange hydrocarbon 3 in 51% yield, presumably via an initial [2 + 2] cycloadduct (2). The previously unknown title compound (3) incorporates both a benzene ring (4*N* + 2 π electrons) and a [4*N*]annulene derivative into a single bicyclic π system, and we report here several consequences of that unusual union. Table I summarizes some of the properties of benz[*b*]homoheptalene.

The parent homoheptalene molecule 4 was first prepared in an



elegant ten-step synthesis by Vogel et al. nearly a decade ago.⁵ The π system of this bridged [12]annulene, unlike that in benzene, was found to deviate significantly from planarity⁶ and to be characterized by alternating short and long bonds.^{5,6} Nevertheless, ¹H NMR spectroscopy reveals that hydrocarbon 4 shares with other [4*N*]annulenes the ability to support an induced *para*-magnetic ring current:⁷ the methylene bridge protons of 4 resonate at abnormally low field (δ 6.1), whereas the protons attached to the perimeter resonate at relatively high field (δ 5.1-5.8).⁵ Ring puckering and bond alternation undoubtedly reduce the ring current to a level below that in a pure [12]annulene,⁸ as predicted by theory,⁷ but some cyclic conjugation still remains. The same structural features likewise reduce the instability ("anti-aromaticity") normally associated with [4*N*]annulenes⁹ and thereby endow homoheptalenes with an ideal balance between paratropicity and isolability.

Fusion of a benzene ring onto one bond of a [4*N* + 2]annulene causes bond-length alternation, weakens the ring current, and diminishes the resonance energy in the annulene ring.¹⁰⁻¹³ The consequences of uniting a benzene ring with a [4*N*]annulene, however, have been difficult to assess experimentally, owing to the lack of stable [4*N*]annulene/benzannulene pairs.^{10,14} The

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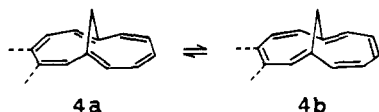
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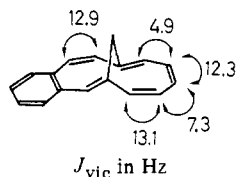
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synthesis of hydrocarbon **3** accordingly provides a unique opportunity for direct NMR comparison between a paratropic [4*N*]annulene (**4**) and a monobenzo derivative thereof (**3**).

One important aspect of this comparison concerns the effect of benzannulation on the dynamic π -bond shift observed previously in the parent compound.⁵ Of the two valence isomers **4a** and **4b**,



the latter is now highly favored, as can be seen by examining the vicinal H,H coupling constants obtained from a 400-MHz ¹H NMR spectral analysis of **3**.



These values, in fact, correspond quite closely to those estimated for **4** at -135 °C,⁵ where the π -bond shift is slow on the NMR time scale (average difference <0.6 Hz). Thus, the geometric features of the [4*N*] perimeter must be comparable for the two compounds, and one may expect paratropic behavior also for the benzannulated system **3**. Indeed, several aspects of the ¹H NMR chemical shift data in Table I attest to the presence of a paramagnetic ring current in the [12]annulene moiety of **3**: (1) The bridge protons resonate at 2.2 ppm lower field than those of an atropic model.¹⁵ (2) The benzo protons show the relation $\delta_\alpha < \delta_\beta$, which is typical for benzo rings fused to paratropic systems.¹² (3) Even the benzo β -protons are shielded by 0.23 ppm relative to $\delta(\text{benzene})$. (4) The signals for the "olefinic" protons H-(1)-H(4) appear upfield by 0.6-0.9 ppm from the reference value for cyclic conjugated olefins (6.5 ppm^{14b}).

It is equally apparent, however, that the benzene ring in **3** has caused a marked reduction of the paramagnetic ring current in the 12-electron π system relative to that in the parent homoheptalene **4**. The bridge protons in **4** resonate at even lower field than those in **3** by ca. 1.6 ppm,¹⁶ and the "olefinic" protons in **4** resonate at higher field than those in **3** by ca. 0.4 ppm. Using a value of 2.2 ppm for the CH₂ resonance in an atropic system¹⁵ and $\delta(\text{CH}_2)$ of **4**, we estimate that **3** sustains 50-60% of the paramagnetic ring current effect present in **4**. Thus, benzannulation reduces the paramagnetic ring current of this [4*N*]annulene by approximately the same percentage that benzannulation reduces the diamagnetic ring current of several rigid [4*N*+2]annulenes.^{10,11} Quantitative effects of benzannulation on other [4*N*]annulenes have previously been reported only for dehydro systems.¹⁴ The present study consequently represents an important step toward broadening our understanding of electron delocalization in bicyclic π systems.

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Registry No. 1, 65754-71-4; **3**, 84537-62-2; **4**, 40985-77-1; benzyne, 462-80-6.

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(16) The possibility that this difference in $\delta(\text{CH}_2)$ between **3** and **4** might result mainly from through-space shielding by the benzene ring in **3** can be rejected on the following grounds: (1) the small shift difference between H(13) and H(14), with H(13) at the low-field side; (2) the location of the CH₂ protons in the deshielding rather than the shielding region of the simple anisotropy cone for benzene, as indicated by models.

Emission Spectroscopic Properties of Dioxorhenium(V) Complexes in Crystals and Solutions

Jay R. Winkler and Harry B. Gray*

Contribution No. 6666 from the Arthur Amos Noyes Laboratory California Institute of Technology Pasadena, California 91125

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It is surprising how little attention has been paid to the emission spectroscopic behavior of transition-metal oxo complexes,^{1,2} particularly in view of the widespread interest in their electronic structures.³⁻¹⁰ Our interest in exploring excited-state oxygen atom transfer chemistry has led us to examine dioxorhenium(V) systems, and we have discovered that several of these complexes possess relatively long-lived emissive excited states in solution.

The electronic absorption spectrum of *trans*-ReO₂L₄^z exhibits a weak band maximizing between 400 and 450 nm (L = CN⁻, z = -3, λ_{max} 404 nm; L = pyridine (py), z = +1, λ_{max} 415 nm; L = 1/2en, z = +1, λ_{max} 450 nm).¹¹ Straightforward electronic structural considerations suggest that the band be assigned to ¹E_g(b_{2g})¹(e_g)¹ ← ¹A_{1g}(b_{2g})² and that a less intense lower energy shoulder be attributed to the transition to ³E_g.¹²

Luminescence is observed from crystalline samples containing *trans*-ReO₂L₄⁺ (L = pyridine, pyridine-*d*₅, 4-picoline, and 4-*tert*-butylpyridine), Re¹⁸O₂(pyridine)₄⁺, and ReO₂(CN)₄³⁻. The emission maxima are all near 650 nm at 300 K, and at low temperature a great deal of vibrational fine structure is resolved. The 5 K single-crystal emission spectrum of K₄ReO₂(CN)₄ is very complex but does display a progression (865 cm⁻¹) corresponding to the symmetric Re-O stretching vibration. The 5 K emission spectrum of crystalline *trans*-[ReO₂(py)₄]BPh₄ is much less complex and exhibits progressions in a 900-cm⁻¹ Re-O stretching mode as well as a 185-cm⁻¹ vibration that probably corresponds to the symmetric Re-py stretching coordinate (Figure 1). A Franck-Condon analysis of this emission spectrum indicates a 0.1-Å excited state distortion of each Re-O bond (Re-O = 1.86 Å (¹A_{1g}), [ReO₂(py)₄]Cl·2H₂O).¹³ Both the estimated distortion and the relatively long radiative lifetimes (Table I) are consistent with an assignment of ³E_g as the emissive excited state.¹²

Perdeuteration of the pyridine ligands in *trans*-ReO₂(py)₄⁺ increases the excited-state lifetime in crystals by more than a factor of 4 (Table I). Oxygen-18 substitution, however, does not lead to a similar increase in lifetime. These data are consistent with a weak coupling model for radiationless decay in these systems where the rates of nonradiative deactivation are sensitive to the frequencies of the highest energy vibrations (C-H) in the molecule.¹⁴ Chemical modification of the equatorial pyridine ligands (4-picoline, 4-*tert*-butylpyridine) shortens the excited-state lifetime by a factor of 3.

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(12) The ligand field levels in *trans*-ReO₂L₄^z would be expected¹⁰ to be ordered b_{2g}(xy) < e_g(xz, yz) < b_{1g}(x² - y²) < a_{1g}(z²), with a ¹A_{1g}(b_{2g})² ground state. The e_g orbitals possess π^* (ReO₂) character, and as a result the Re-O bonds in both the ¹E_g and ³E_g states should be slightly weaker than in the ground state.

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