an AB quartet (J = 10.0 Hz) centered at τ 8.31. The strong upfield shift of H_2 (relative to H_5) can be attributed to long-range shielding by the π electrons of the phenyl ring.⁹ The H₁-H₆ bridgehead-bridgehead longrange coupling in 4 was determined by the preparation of 7-phenyltricyclo[$3.2.0.0^{2,6}$]heptan-7-ol-1- d_1 (5) via the irradiation of exo-5-benzoylbicyclo[2.1.1]hexane-5endo- $d_1(6)$.¹⁰

The nmr spectrum of the monodeuterated compound (5) showed a coupling constant of 2.70 Hz between the deuterium and the bridgehead hydrogen. Since hydrogen-hydrogen coupling is as great by a factor of 6.55 as deuterium-hydrogen coupling,¹¹ the value obtained is essentially identical with that encountered in the bicyclo[1.1.1]pentane system (*i.e.*, J = 18.0 Hz)^{12,13} indicating that the geometries of both ring systems are essentially the same.

Thermal decomposition of 4 at 150° afforded a mixture of 2(33%) and 3(67%). The formation of these products can best be accounted for by a thermal cleavage of the bridgehead C-C bond followed by ring opening of the diradical (path a) or by a 1,5-H transfer step (path b). The formation of 3 and 4 from the irradia-



tion of 2 may be considered to be analogous to the Norrish type II cleavage and cyclobutanol formation observed with the irradiation of aliphatic ketones containing γ -hydrogens.¹⁴ The behavior of the diradical generated by thermolysis of 4 is essentially the same as that encountered in the Norrish type II process and once again illustrates the reverse hydrogen transfer step of 1,4 diradicals. 15-17

The quantum yield for disappearance of ketone $(\Phi = 0.06)$ is considerably lower than that of related acyclic phenyl ketones¹⁸ and its value is not significantly enhanced with added *t*-butyl alcohol. The photolysis is readily quenched by the addition of piperylene, in agreement with a $n-\pi^*$ triplet as the reactive excited state. Since the quantum yield is independent of solvent, the low efficiency cannot be attributed to disproportionation of the 1,4 diradical.¹⁸ The low efficiency must be related instead to some molecular feature of 2 which re-

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(10) The monodeuterated bicyclo ketone 6 was prepared from the photolysis of syn-7-chlorodiazonorcamphor in D₂O followed by removal of the 7-chloro substituent with lithium metal and conversion of the

(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolu-tion Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 188.

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(15) P. J. Wagner, J. Amer. Chem. Soc., 89, 5898 (1967); Tetrahedron Lett., 1753 (1967).

(16) A. Padwa and E. Alexander, J. Amer. Chem. Soc., 90, 6871 (1968).

(17) N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, 91, 7551 (1969).
 (18) P. J. Wagner and H. N. Schott, *ibid.*, 91, 5383 (1969).

tards formation of the biradical and allows direct radiationless decay to compete with chemical reaction of the triplet. We suspect that the inefficiency of the photoprocess is due to the unfavorable geometry required for internal hydrogen abstraction. The preferred transition state for internal hydrogen transfer is one in which carbon, hydrogen, and the nonbonding electron on oxygen can approximate a linear configuration.¹⁹ These stereoelectronic requirements cannot be readily met with the above ketone.

It is interesting, at this point, to compare the photoefficiency of 2 with that of cyclobutyl phenyl ketone (7) ($\Phi = 0.03$). The cyclobutane ring is quite flexible and exhibits a dynamic ring-bending equilibrium which allows for conformation equilibration of monosubstituted cyclobutanes.²⁰ It was previously argued that one possible source of inefficiency in the cyclobutyl phenyl ketone system was the low concentration of the conformer having the benzoyl group in the pseudoaxial position.² Bicyclo ketone 2 is an appropriate model for the reactive conformer of 7, since the benzoyl group is now locked into the axial position. If the inefficiency of 7 was totally due to the low population of the reactive conformer, then we would expect that 2 would be similar to valerophenone in terms of photoefficiency.²¹ This is certainly not the case and suggests that the inefficiency of both 2 and 7 are related to the poor stereoelectronic features of these ketones.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant No. GP-9385).

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(20) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *ibid.*, **69**, 2483 (1947).

(21) It has been pointed out that the quantum efficiency of type II photoelimination is not directly related to triplet-state reactivity for phenyl ketones that undergo significant disproportionation from the 1,4 diradical.²² However, ketones 2 and 7 show no significant solvent effects and consequently it is assumed that quantum efficiency and triplet reactivity of these ketones are closely related.

(22) P. J. Wagner and A. E. Kemppainen, J. Amer. Chem. Soc., 90, 5896 (1968).

(23) Fellow of the Alfred P. Sloan Foundation, 1968-1970.

Albert Padwa,23 Walter Eisenberg

Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214 Received February 6, 1970

Dibenzopentalenyl Dianion. A Perturbed [12]Annulene Dianion

Sir:

Perturbation theory predicts that dibenzo[cd.gh]pentalene (I) should be an unusually good example of the periphery electronic model which describes this system as a perturbed [12]annulene.^{1a,b} SCF calculations² confirm this prediction; these calculations suggest that the first excited triplet state lies only 0.3 eV above the ground state! In this communication we wish to report the synthesis of the first derivative of this molecule, dilithium dibenzo[cd,gh]pentalenide (II). The properties of this derivative clearly support the periphery model as

^{(1) (}a) B. M. Trost and G. M. Bright, J. Amer. Chem. Soc., 89, 4244 (1967), and references therein; (b) P. Kinson and B. M. Trost, Tetrahedron Lett., 1075 (1969).

⁽²⁾ We express our gratitude to Dr. Howard E. Simmons for carrying out a SCF-PPP calculation on this system.

Chart I. Intermediates in the Synthesis of Dilithium Dibenzopentalenide

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a reasonable description of such systems. Furthermore, this dianion on the basis of the above model is expected to give and experimentally does give a good correlation of nmr chemical shifts with charge density in contrast to a recent report dealing with other polycyclic dianions.³



Figure 1. Nmr spectrum of dianion II.

Chart I shows those compounds on the synthetic route to the dianion II.⁴ 4,5-Methylenephenanthrene (III) on treatment with iodic acid in aqueous acetic acid and dioxane affords a 68% yield of 4,5-methylene-9,10phenanthraquinone (IV): mp 260° dec; ir (CHCl₃) 1680 cm⁻¹. Treatment of this material with *p*-toluenesulfonylhydrazide followed by chromatography on silica gel affords a 68% yield of 9-diazo-10-keto-4,5methylenephenanthrene (V): mp 180–181° dec; ir (CHCl₃) 2100, 2080, 1632, 1610 cm⁻¹. Photolysis of the diazo ketone at 3500 Å in the presence of *t*-butylamine followed by tlc affords the corresponding Wolff

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rearrangement amide VI (ir (CHCl₃) 3425, 1670 cm⁻¹) in 2% yield. The low yield in this reaction is both interesting and frustrating in view of the observed propensity for the Wolff rearrangement to occur under electron-impact conditions.^{1b} Acid hydrolysis of the amide produces a 90% yield of 4,8-dihydrodibenzo-[cd.gh]pentalene-4-carboxylic acid (VII) [mp 222.0-223.5°; ir (CHCl₃) 1703 cm⁻¹; nmr τ (CDCl₃) -0.30 (1 H, bs), 2.56, 2.65, 2.83 (6 H, ABC pattern broadened by allylic methine and methylene coupling, $J_{ab} = J_{ac} =$ 7.6 Hz, $J_{bc} = 1.5$ Hz), 4.43 (1 H, s), 5.69 (2 H, s)] which on copper quinoline decarboxylation affords 4,8-dihydrodibenzo[cd,gh]pentalene (VIII), mp 137.5-138.3° [nmr τ (CCl₄) 2.79, 2.97 (6 H, A₂B pattern broadened by methylene coupling, $J_{ab} = 7.6$ Hz), 5.87 (2 H, s)] in 73% yield.



Figure 2. Plot of dianion nmr chemical shifts vs. charge density.

Treatment of dihydrodibenzopentalene (5.5 mg, 0.031 mmol) in THF- d_8 (0.3 ml) with *n*-butyllithium in hexane at -78° followed by warming to room temperature affords the dibenzopentalenyl dianion, whose nmr is shown in Figure 1. Inverse addition of the dianion-containing solution to D₂O produces dihydrodibenzopentalene (IX) with 99% d_2 incorporation (mass spectrum) in the 4 and 8 positions (nmr).

Figure 2 is a plot of the nmr chemical shift of the protons of several perturbed [12]annulene dianions⁵ vs.

⁽³⁾ R. G. Lawler and V. Ristagno, J. Amer. Chem. Soc., 91, 1534 (1969). The discrepancy in the charge density-chemical shift correlation for the compounds reported can be ascribed to an incorrect ring current adjustment. In some of the molecules considered by Lawler and Ristagno, a paramagnetic ring current for the dianion would be expected—a suggestion that would account for the abnormally high shifts. For dianions possessing $(4n + 2) \pi$ electrons in a monocyclic array, a good correlation is anticipated: see above; T. Schaefer and W. G. Schneider, Can. J. Chem., 41 966 (1963); R. S. Schneider and E. F. Ullman, Tetrahedron Lett., 3249 (1969).

⁽⁴⁾ All new compounds showed satisfactory analytical data.

⁽⁵⁾ For the nmr spectrum of the as-indacene dianion see T. J. Katz, V. Balogh, and J. Schulman, J. Amer. Chem. Soc., 90, 734 (1968). We are indebted to Professor K. Hafner for providing us a copy of the nmr spectrum of s-indacene prior to publication.

the Hückel charge density of the corresponding carbon atom in which the excess charge density is restricted to the periphery of the molecule. Such a plot produces a reasonably straight line as shown even without correcting for differential ring current effects. Most surprising is the fact that the points for dilithium dibenzopentalenide (II) fall almost exactly on this line. Table I

Table I. Charge Distribution

Position	δ	Experimental	НМО	SCF
1	5.340	1.34	1.33	1,29
2	6.245	1.16	1.16	1.18
3	6.670	1.06	1.04	1.06

compares the charge densities obtained from this plot with the Hückel and SCF calculated values. Excellent agreement is observed. Such agreement provides strong evidence that all the excess negative charge resides on the periphery of the molecule with effectively little, if any, charge delocalized over the central double bond. This charge distribution strongly supports the peripheral electronic model description of the dibenzopentalene system.

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- (6) Alfred P. Sloan Foundation Fellow.
- (7) National Institutes of Health Predoctoral Fellow.

Barry M. Trost,⁶ Philip L. Kinson⁷ Department of Chemistry, University of Wisconsin Madison, Wisconsin 53706 Received January 22, 1970

Substitution Kinetics of Alkylbis(dimethylglyoximato)aquocobalt(III) in Aqueous Solution¹

Sir:

In view of recent interest concerning the kinetics of some alkyl-cobalt (III)^{2,3} complexes and the similarity between certain dimethylglyoxime complexes of cobalt and vitamin B_{12} ,⁴ we wish to present a preliminary report of our investigation into the substitution reactions of various alkylbis(dimethylglyoximato)aquocobalt(III) complexes. The overall reaction studied is

$$RCo(DH)_2OH_2 + L \xrightarrow{k_t} RCo(DH)_2L + H_2O$$
(1)

where [DH] represents the dimethylglyoximato monoanion, $[ON=C(CH_3)C(CH_3)=NOH]^-$, R = methyl, ethyl or isopropyl, $L = SCN^{-}$, N_3^{-} , py, CN^{-} , or NH_3 , and k_f is the second-order ligation rate constant expressed in M^{-1} sec⁻¹.

The rate data were collected in aqueous solution at 10° and unit ionic strength by means of stopped-flow spectrophotometry.⁵ Formation quotient data were

collected under the same conditions by use of a Carv 14 spectrophotometer. Direct exposure to room lights was avoided during these measurements. The method of preparation of these complexes is that described by Schrauzer.6

In agreement with previous observations made by Schrauzer,⁴ we find the cobalt-carbon bond to be stable under the conditions employed in this study.⁷ Cyclic reactions such as the following were carried out to show that the observed rapid reaction 1 is indeed substitution of the aquo group by L, leaving the cobalt-carbon bond intact.

$$\begin{array}{ccc} CH_{3}Co(DH)_{2}OH_{2} & \xrightarrow{SCN^{-}} & CH_{3}Co(DH)_{2}SCN^{-} & + & H_{2}O \\ & + & & & \\ Ag^{+} & & & \\ AgSCN \end{array}$$
(2)

The regeneration of the aquo starting material was demonstrated spectrophotometrically. Retention of the planar bis[dimethylglyoximato] configuration has been demonstrated by previous authors in other dimethylglyoxime complexes.8

Table I is a summary of thermodynamic and kinetic data for reaction 1 when $R = -CH_3$. The pH of these reaction solutions was such that hydrolysis of the nucleophile was negligible and deprotonation of the complex did not occur. For a wide range of charged and un-

Table I. Rate and Formation Quotient Data for Ligation Reactions of CH₃Co(DH)₂OH₂^a

L	$k_{\rm f}, M^{-1}{ m sec}^{-1}$	K, M ⁻¹
SCN ⁻ N ₃ - Py CN- NH ₃ OH-	49.6 34.7 29.9 14.0 3.1	$9.6 \times 10 2.04 \times 10^{2} 4.81 \times 10^{3} 10^{6} 3.64 \times 10^{3} 2.7 \times 10$

^a Data collected at 10° and unit ionic strength (NaClO₄).

charged nucleophiles, L, the second-order ligation constants only vary by approximately a factor of 10. However, the cobalt center demonstrates a great deal of thermodynamic discrimination between nucleophiles, as is shown in the 10⁵ variation in formation quotients.

This narrow range of rate constants for the methyl complex on reaction with various nucleophiles is an indication that the detailed nature of the ligand substitution process is that of a dissociative interchange mechanism.⁹ That is to say that L group participation in the transition state is not as significant as rupture of the cobalt-aquo bond. However, our data do not strictly preclude the possibility of an extreme dissociative mechanism in which H₂O behaves as a more efficient nucleophile than L. Plots of pseudo-first-order rate constants as a function of nucleophile concentration show no sign of curvature in the range of concentrations

⁽¹⁾ A brief comment on the lability of these compounds was included in a paper presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., 1969.

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