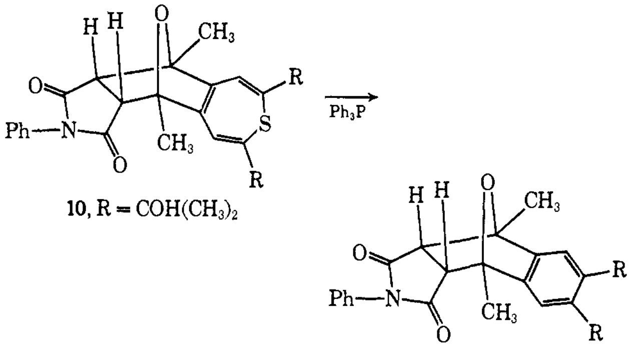
and shows only a single absorption maximum at $\lambda_{max}^{CH_3OH}$ 381 nm (ϵ 444) as well as strong end absorption and tailing to 500 nm in the visible.



10, R = COH(CH$_3$)$_2$

11, R = COH(CH$_3$)$_2$

Solutions of thiepin **10** in dimethylformamide or chloroform may be heated for prolonged periods without noticeable decomposition. When triphenylphosphine is added, however, rapid decolorization of these solutions occurs and the sulfur-free endo adduct **11**, mp 275°, is formed in 93% yield along with triphenylphosphine sulfide (87% yield). Adduct **11** exhibits singlet proton resonance at δ 1.60 and 1.70 (methyls of the isopropyl groups), 2.03 (bridgehead methyl groups), 3.56 (protons α to the imide carbonyl groups), and 7.10 (benzene ring protons). Broad singlet resonance for the hydroxyl group occurs at δ 5.52 and complex multiplets for the imide phenyl protons appear at 6.20–6.45 (2 H, ortho protons) and 7.20–7.55 (3 H, meta and para protons).

Paramagnetic ring current properties have been observed for annulated thiepins similar to **6** and **9**.[12] The thiepin ring protons of **10** occur at higher field values (δ 6.50) than the corresponding protons of the furanothiepin **9** (δ 6.80). In addition, the ortho protons of the imide phenyl group in heterocycle **10** occur at lower field values (δ 6.70–7.00) than the comparable protons of adduct **11** (δ 6.20–6.45). This behavior is consistent with the supposition that thiepin **10** might possess a paramagnetic ring current.[12]

Further work on heterocycle **10**, including an X-ray crystal-structure determination, is in progress.

Acknowledgment. We are grateful for support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation.

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(12) For a more detailed discussion of this phenomenon, see ref 7 and 10.

(13) National Science Foundation Trainee Fellow, 1969–1970.

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Electron Spin Resonance Identification of Oxygen Adducts of Cobalt(II) Complexes[1]

Sir:

Cobaltous complexes of simple amines such as triethylenetetramine bind molecular oxygen reversibly.

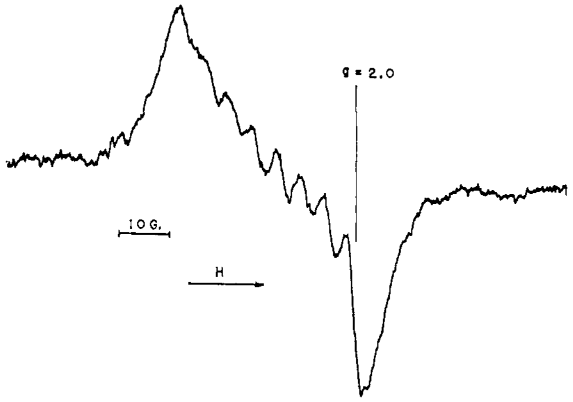

Figure 1. Esr spectrum of oxygenated aqueous solution (pH 5.6) of cobalt(II) and polyethylenimine (0.4%). The spectrum was taken 45 sec after oxygenation.

During the oxygenation process free radicals are produced, as indicated by the initiation of polymerization of vinyl monomers.[2] The initiating species was proposed to be a peroxy cobalt radical. Peroxy metal species appear to be the initial intermediates in metal-catalyzed autoxidation such as occurs in biochemical systems.[3,4]

In the present communication we wish to report the identification by electron spin resonance of the free radical species produced by the addition of molecular oxygen to a variety of cobalt–amine complexes. Esr spectra have been obtained previously for the cobalt compounds vitamin B_{12r} and cobaloximes(II)[5] and for some specific cobalt Schiff bases[6] in organic solvents at low temperatures when oxygen is introduced. Our systems, on the other hand, involve aqueous solutions of simple amines at room temperature.

Aqueous solutions of diethylenetriamine, triethylenetetramine, tetraethylenepentamine, polypropylenimine, and polyethylenimine (number-average molecular weight, 40,000), each at a concentration of 0.4%, were adjusted to pH 5.6 and deoxygenated by purging with helium. The acidification was carried out with the noncomplexing perchloric acid. Cobaltous nitrate was then added to give a final concentration of 10^{-3} *M*. The solutions were subsequently oxygenated by bubbling oxygen through for 15 sec. Esr measurements were performed with a Varian E-3 spectrometer, using an aqueous cell, 45 sec after the oxygenation.

A typical esr spectrum is illustrated in Figure 1. It was found that the larger was the ligand in the homologous series the greater was the signal. All solutions exhibited at room temperature a characteristic spectrum consisting of a well-resolved eight-line hyperfine structure with an isotropic splitting constant of 13.1 G, which is very close to that found for the monomeric oxygen adducts of cobalt(II) Schiff bases.[6] This corresponds to the interaction of an unpaired electron with a single ^{59}Co nucleus of spin $^7/_2$ and demonstrates that the para-

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(1) Supported by the Ford Foundation on Grant No. 690-0106.

(2) N.-L. Yang and G. Oster, *J. Polym. Sci., Part B*, **7**, 861 (1969).

(3) S. Fallab, *Angew. Chem.*, **79**, 500 (1967).

(4) A. H. Mehler in "Oxygenases," O. Hayaishi, Ed., Academic Press, New York, N. Y., 1962, p 123.

(5) J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, **91**, 2775 (1969); G. N. Schrauzer and L. P. Lee, *ibid.*, **92**, 1551 (1970).

(6) B. M. Hoffman, D. L. Siemente, and F. Basolo, *ibid.*, **92**, 61 (1970).

magnetic species contains only one cobalt atom. The observed g value, namely 2.026, indicates that the species is a peroxy radical,[7] but its unequivocal identification of molecular geometry would require esr studies using oxygen-17. When helium is bubbled through the solution for 15 sec immediately after the oxygenation, no signal is detected, indicating the reversibility of the oxygen addition process.

The esr signal of the freshly oxygenated solution decays with time, accompanied by an increase in optical density in the region 300–400 mμ. This optical absorption corresponds to the binuclear complexes where oxygen is bridging two cobalt complexes.[8] The disappearance of the esr signal is attributed to bimolecular termination between the peroxy cobalt radical and the paramagnetic chelated cobalt atom.

The esr signal for the peroxy cobalt radical with polyethylenimine as the ligand decays with first-order kinetics with a half-life of 3 min, whereas with other low-molecular-weight ligands the decay was much more rapid. Since the cobalt atom and the peroxy radical are attached to the polymer, the likelihood of their encounters is thereby reduced. Decreasing the pH stabilizes the radical due to electrostatic repulsion arising from protonation of the amine groups. Below pH 5.6, however, the metal complexation is reduced, hence the esr signal is decreased. The esr signal is also suppressed when salt is added to the solutions. Thus addition of KCl to the concentration of 0.3 *M* wipes out the signal, apparently due to suppression of the electrostatic repulsion between these polyelectrolyte ligands.

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(7) B. R. McGarvey and E. L. Tepper, *Inorg. Chem.*, **8**, 498 (1969).

(8) S. Yamada, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Jap.*, **26**, 72 (1953).

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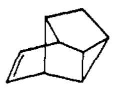
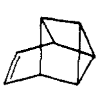
Methyl Tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene-4-carboxylate

Sir:

General interest in valence isomers $(CH)_{2p}$[1,2] and our own interests in tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-enes (I)[3] have caused us to attempt the conversion of a derivative of I into a structure containing the closely related (CH) skeleton of the as yet unsynthesized $(CH)_8$ isomer tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene (II).[4] To

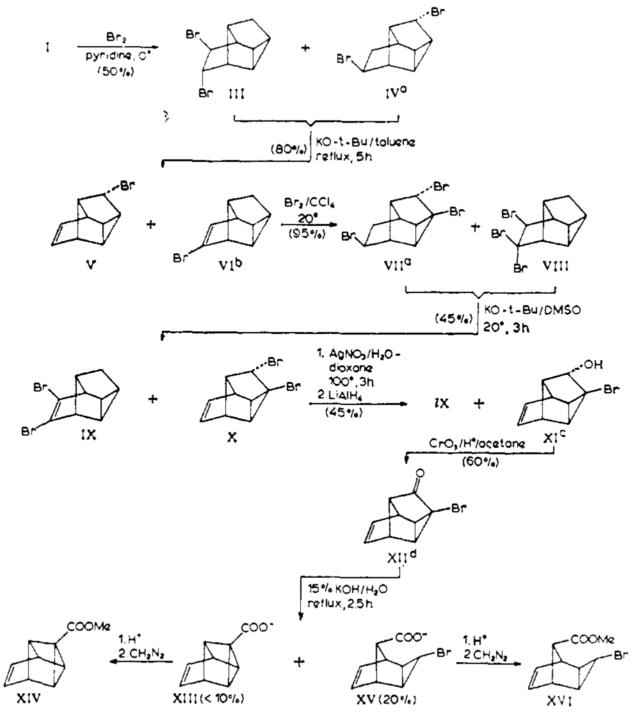

I


II

achieve this goal we chose the pseudo-Favorskii reaction of bridgehead α-bromo ketones, which has served so well in the synthesis of cubane and other cage compounds.[9]

Bromo ketone XII was prepared by a series of addition–elimination reactions starting with I[10] (Chart 1).

Chart I



[a] Configuration at C-5 assigned on mechanistic grounds only. [b] Purified by fractional distillation: bp 80–83° (18 mm); nmr (τ, CCl_4) 4.03 (d,d, 3 and 1 cps), 7.38, 7.87, 8.15–8.68. [c] Separated from IX by chromatography on alumina: nmr (τ, CCl_4) 3.95, 5.97 (d, 2 cps), 6.60, 7.10, 7.65 (OH), 8.15, 8.25. [d] Though isolated as a single peak on vpc, ir and nmr indicated that an unknown contamination was present (±25%): ir (cm^{-1}, CCl_4) 1775 and 1757; nmr (τ, CCl_4) 3.80, 6.58, 6.78, 7.62–8.20; mass: 212/210, 211/209, 184/182, 131, 103, 102, 77.

Important steps were: (1) bromination of I in pyridine, which gave predominantly unrearranged dibromide III;[11] (2) introduction of the bridgehead bromine *via*

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(1) Compilation of possible structures $(CH)_{2p}$: A. T. Balaban, *Rev. Roum. Chim.*, **11**, 1097 (1966).

(2) Whereas $(CH)_{10}$ isomers and their interconversions have received much attention, similar activities in the $(CH)_8$ field have only recently been reported: (a) J. Meinwald and H. Tsuruta, *J. Amer. Chem. Soc.*, **91**, 5877 (1969), and references given therein; (b) H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

(3) G. W. Klumpp, *Recl. Trav. Chim. Pays-Bas*, **87**, 1053 (1968).

(4) So far, 4,5-diphenylbenzotetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene, obtained by photoreaction between naphthalene and tolane, appears to be the only derivative of II that has been prepared.[5,6]

(5) W. H. F. Sasse, *Austr. J. Chem.*, **22**, 1257 (1969), and earlier papers by the same author.

(6) Other attempts to synthesize the carbon skeleton of II have failed: 8-carbenatricyclo[3.2.1.0^{2,4}]octane gave bicyclo[3.3.0]octa-1,6-diene as the main product;[7] 3-carbenatricyclo[3.2.1.0^{2,4}]oct-6-ene, supposed to be an intermediate in the gas-phase irradiation of norbornadiene and carbon suboxide, produced C_8H_8, which most probably is *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene.[8] After this communication had been submitted for publication, the report of R. G. Bergman and V. J. Rajadhyaksha on *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene (*J. Amer. Chem. Soc.*, **92**, 2163 (1970)) became available to us. Since then comparison of ir spectra has established the identity of the compounds from both laboratories. We are grateful to Professor Bergman for sending us copies of the spectra of *exo*- and *endo*-6-ethynylbicyclo[3.1.0]hex-2-ene.

(7) P. K. Freeman and D. G. Kuper, *Diss. Abstr. B*, **28**, 109 (1967).

(8) G. W. Klumpp and P. M. van Dijk, unpublished results.

(9) *Cf.* references given by K. V. Scherer, Jr., *Tetrahedron Lett.*, 5685 (1966).

(10) Prepared by the method of T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, *J. Org. Chem.*, 32, 1301 (1967).

(11) Bromination of I in all other solvents studied gives largely rearranged dibromide IV. It is interesting to note that amine or ammonium perbromides, which are probably the active species on bromination in pyridine, have found wide application in selective bromination of ketones,[12] but have seldom been used with olefins,[12,13] despite several promising reports.[14] We are currently studying the nature of this reaction.

(12) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, pp 855, 966 ff.

(13) P. B. D. De La Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, Amsterdam, 1966; however, see also L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **82**, 2341 (1960).