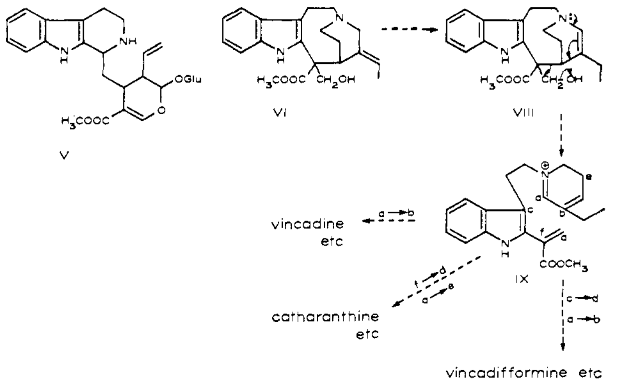
that the transannular cyclization process is not biosynthetically important is now strongly supported by the above results. Furthermore, the ring-opening process (II → I) as mentioned above is similarly unimportant in providing a pathway to the nine-membered ring alkaloids found in *V. minor* L. It is clear that such an interpretation of our results is valid only if we are able to exclude any equilibration in the plant between the two alkaloid groups. The rather constant *B*/*A* could be obtained if an equilibrium mixture were enriched with respect to the pentacyclic alkaloids vincadifformine (II) and minovine (IV) to the extent of approximately 20:1. An evaluation of this process was thereby in order. The incorporation of various nine-membered ring alkaloids into *V. minor* L. was studied, and some experiments in this direction have been already discussed.[1] An approach from the opposite direction was also studied more recently when the radioactive alkaloid minovine (IV) was incorporated into this plant. In a typical experiment, during which radioactive IV was administered over a 1-week period, the subsequent investigation of the isolated plant alkaloids showed essentially *no* activity in the nine-membered ring compounds ($B/A > 2500$). On this basis we must propose that the above equilibration process is not significant in *V. minor* L. In turn we must conclude that the above results strongly support the situation that the genesis of the quebrachamine–vincadine family is *independent* of the pathway leading to the rigid pentacyclic Aspidosperma series (II, IV, etc.).

The question as to how the present results fit into the biosynthetic pattern which is rapidly evolving from the combined data of other investigations is worthy of comment. Wenkert[6] suggested that "all indole alkaloids of the tryptamine + C_{10} structure type may be derived from corynantheinoid or closely related progenitors." Based on elegant experiments in his and other laboratories, Battersby[7] was able to postulate the possible role of structures such as V in the biosynthesis of corynantheinoid as well as Aspidosperma and Iboga bases. Strong support for this latter postulate is available from very recent reports.[8] The possible intermediacy of units similar in structure to the alkaloid stemmadenine (VI) was invoked in the sequence between the corynantheinoid and Aspidosperma bases,[2,6] and again recent work[9] on germinated *Vinca rosea* L. seeds supports its role in this regard. The conversion of the alkaloid tabersonine (VII) to vindoline and most interestingly to the Iboga alkaloid catharanthine has been demonstrated in *V. rosea* L. plants in our laboratories[1] and independently by Scott in germinated seeds.[9] This latter result suggests a possible relationship between the Aspidosperma and Iboga alkaloids. In summation, all of these results strongly suggest *but do not prove* that the sequential formation of the indole alkaloids may follow the order: Corynanthe → Aspidosperma → Iboga. The results of the present investigation relate to the possible structural units which bear on the Corynanthe → Aspidosperma pathway. An attractive sequence which is in accord with present findings may be postulated (VI → IX → vincadine, vincadifformine, etc.). The rearrangement of stemmadenine (VI) to an isomer (VIII) provides an attractive mechanistic rationale for bond fission to the intermediate IX.[10] This latter intermediate may then elaborate to the Aspidosperma and Iboga bases by the formal bond formations as indicated. The relative order of the latter processes relates directly to the results presented in this and the previous communication.[1] From the tryptophan incorporations discussed above, it is attractive to postulate that the independent biosynthetic pathways which lead to the vincadine and vincadifformine groups may initiate from a common intermediate such as IX. The eventual elaboration of the alkaloid systems depends merely on the relative order in which the bonds are formed. Thus the process a → b converts IX to vincadine, etc. The relative insignificance of the transannular cyclization process now suggests that the process c → d occurs *prior* to or *simultaneously* with a → b in the elaboration of IX to vincadifformine. In similar fashion, the conversion of unit IX to the alkaloid catharanthine is unlikely to proceed initially *via* the process a → e since this would lead to a carbomethoxycleavamine system. Previous results[1] have shown that we were unable to demonstrate the conversion of the latter to this Iboga alkaloid.



The relative importance of intermediates such as IX in the biosynthesis of indole alkaloids must await further investigations with appropriately designed experiments which will serve to test this postulate.

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(6) E. Wenkert and B. Wickberg, *J. Am. Chem. Soc.*, **87**, 1580 (1965).

(7) A. R. Battersby, *Pure Appl. Chem.*, **14**, 117 (1967).

(8) At the IUPAC Fifth International Symposium on the Chemistry of Natural Products, London, England, July 1968, two groups of workers (G. N. Smith and R. T. Brown, Manchester University, and A. R. Battersby and coworkers, University of Liverpool) reported the isolation of the alkaloidal glycoside V and mentioned its biosynthetic conversion to these various alkaloid families.

(9) A. A. Qureshi and A. I. Scott, *Chem. Commun.*, in press. We are very grateful to Professor A. I. Scott for providing us with results prior to publication.

(10) A similar postulate for the formation of IX has been advanced by A. I. Scott and coworkers.

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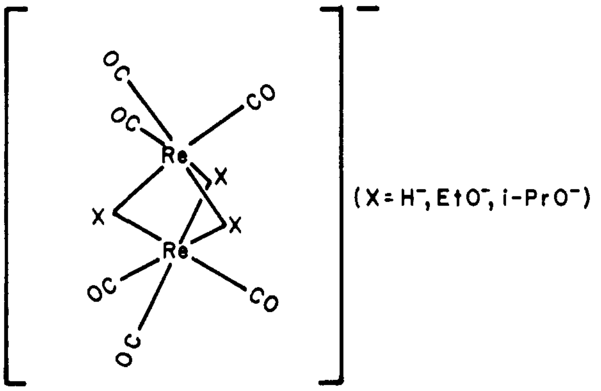
Received August 5, 1968

Tri-μ-hydrido- and Tri-μ-alkoxy-hexacarbonyldirhenate(I)

Sir:

The known carbonyl hydrides of rhenium are formed by reducing dirhenium decacarbonyl with sodium amalgam or sodium borohydride and acidifying the product.[1-3] An alternative approach to the formation of this type of compound is the reaction of the unsubstituted hydride species, ReH$_9^{2-}$,[4] with carbon monoxide. We have carried out this reaction in alkaline alcoholic medium and obtained a novel binuclear carbonyl hydride anion which, on the basis of ir and nmr spectra, we formulate as shown with three bridging hydrogen atoms (X$^-$ = H$^-$). This is the first example of a compound in which two transition metal atoms are linked by *three* hydride bridges. The same reaction affords the corresponding carbonyl alkoxide anion with three bridging alkoxide groups (X$^-$ = EtO$^-$, *i*-PrO$^-$). Three alkoxide bridges between two metal atoms have been proposed before for polynuclear alkoxides,[5] but carbonyl alkoxide species are not common. The only mention we have been able to find of compounds containing both CO and alkoxide groups bound to a metal atom are some trinuclear carbonyl methoxide complexes of tungsten,[6] the structures of which are not understood, and two trinuclear carbonyl methoxide complexes of osmium.[7]



A stream of carbon monoxide was passed into a refluxing solution[8] of (Et$_4$N)$_2$ReH$_9$ (1.8 g, 4.1 mmoles) in 2-propanol (300 ml) made alkaline with Et$_4$NOH (1 g, 6.7 mmoles). After about 20 hr the red precipitate (0.40 g) which had slowly formed was filtered off. Concentration of the yellow filtrate followed by addition of water gave an off-white precipitate (1.2 g) which on repeated recrystallization from 2-propanol afforded white crystals of the tetraethylammonium salt of tri-μ-isopropoxy-hexacarbonyldirhenate(I), Et$_4$N[Re$_2$(CO)$_6$(OCH(CH$_3$)$_2$)$_3$].[9] This air-stable compound decomposes at $\sim$200° on heating under vacuum. It is soluble in alcohols, acetone, and acetonitrile and insoluble in water and hydrocarbons. The carbonyl ethoxide Et$_4$N[Re$_2$(CO)$_6$(OC$_2$H$_5$)$_3$][9] results if the reaction is carried out in ethanol; it may also be obtained from the isopropoxide by interchange with ethanol.

The red precipitate from the reaction of CO with (Et$_4$N)$_2$ReH$_9$ in 2-propanol is a mixture of several rhenium carbonyl hydrides. Chromatography on alumina (Brockmann activity I) using ether–acetonitrile mixtures as the eluting agent separates it into three components: a purple compound (0.03 g), an orange compound (0.10 g), and a yellow compound (0.12 g). In this communication we discuss only the orange compound, which is the tetraethylammonium salt of tri-μ-hydrido-hexacarbonyldirhenate(I), Et$_4$N[Re$_2$(CO)$_6$H$_3$].[9] It is a moderately air-sensitive material (the solid is oxidized slowly, solutions rapidly) which decomposes at $\sim$190° on heating under vacuum and is soluble in acetone and acetonitrile but insoluble in water, alcohol, ether, and hydrocarbons.

Conductivity measurements on acetonitrile solutions of the hydride and alkoxides over the concentration range 10^{-2}–10^{-3} M confirm that they are correctly formulated as 1:1 electrolytes with a dimeric anion: for the hydride, Λ_0, 166; A, 447 (calcd, 353); for the isopropoxide, Λ_0, 148; A, 290 (calcd, 339).

Proton nmr spectra of the isopropoxide in CD$_3$CN solution (15%) show no absorptions on the high-field side of TMS (scanned to τ 60) and no resonance due to OH, confirming the absence of metal-bonded hydrogen and alcohol. In the low-field region, absorptions due to tetraethylammonium and isopropoxide are found with the expected intensity ratio. Ir spectra of the alkoxides in acetonitrile solution show only two bands, both strong, in the CO stretching region; the frequencies are 1995 and 1875 cm^{-1} for the isopropoxide and 1995 and 1880 cm^{-1} for the ethoxide. These are in the expected range for terminal CO stretching frequencies in an anionic complex. In view of this we conclude that the two Re atoms are most probably bridged by the three alkoxide groups and that all six CO groups are terminal. The proposed structure has local point group symmetry D$_{3h}$, so that two ir-active ν(CO) are expected, in agreement with what we observe. The inert gas formalism is obeyed and the observed diamagnetism is accounted for.

The proton resonance spectrum of the orange hydride complex in CD$_3$CN solution ($\sim$18%) shows a single high-field line at τ 27.49, demonstrating the presence of Re-bonded hydrogen. This τ value is considerably higher than what has been found for nonbridging Re-bonded hydrogen (*e.g.*, τ 15.7 for HRe(CO)$_5$,[10] τ 18.5 for ReH$_9^{2-}$,[4] and τ 18.2 for [ReH$_8${(C$_2$H$_5$)$_3$P}]$^-$ [11]), but it is in good agreement with the recently reported[3] τ 26.25 for the Re–H–Re bridge[12] in HRe$_3$(CO)$_{14}$. The intensity ratio of the high-field line to the low-field peaks due to Et$_4$N$^+$ leads to 2.8 hydridic protons per anion. Since the anion is dimeric, uninegative, and diamagnetic, the number of hydridic protons must be an odd integer. The nmr result therefore indicates the presence of three Re-bonded hydrogens per dimeric anion. To confirm this we studied the reaction of the orange compound with HCl (7 N) in 2-propanol; 2.8 moles of hydrogen was evolved[13] per mole of complex

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(1) W. Beck, W. Hieber, and G. Braun, *Z. Anorg. Allgem. Chem.*, **308**, 23 (1961).

(2) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4841 (1964).

(3) W. Fellmann and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **2**, 63 (1966).

(4) A. P. Ginsberg, *Transition Metal Chem.*, **1**, 111 (1965).

(5) D. C. Bradley, *Progr. Inorg. Chem.*, **2**, 303 (1960).

(6) W. Hieber and K. Englert, *Z. Anorg. Allgem. Chem.*, **300**, 311 (1959); W. Hieber, K. Englert, and K. Rieger, *ibid.*, **300**, 304 (1959).

(7) B. F. G. Johnson, J. Lewis, and P. A. Kilty, *Chem. Commun.*, 180 (1968).

(8) All solvents were dried and degassed, and manipulations were carried out under a nitrogen or argon atmosphere.

(9) Stoichiometry established by analysis for all elements except rhenium.

(10) A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).

(11) A. P. Ginsberg, *Chem. Commun.*, 857 (1968).

(12) H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Am. Chem. Soc.*, **89**, 2775 (1967).

(13) Mass spectrometric analysis showed the absence of CO and other impurities.

and the rhenium was recovered (95%) with its oxidation state unchanged in the new carbonyl chloride $(Et_4N)_2[Re_2(CO)_6Cl_4]$.[9]

$$[Re_2(CO_6)_3H_3]^- + 4HCl \longrightarrow 3H_2 + [Re_2(CO)_6Cl_4]^{2-} + H^+$$

The same carbonyl chloride complex may be obtained from the reaction of the carbonyl alkoxides with alcoholic HCl.

The ir spectrum in the CO stretching region of the orange hydride in acetonitrile solution is virtually identical with the carbonyl alkoxide spectra: there are just two bands, both strong, with frequencies of 1995 and 1905 cm^{-1}. We therefore assign both of these bands as terminal ν(CO). Since there are no other ir bands in the 1700–2200-cm^{-1} region, where terminal ν(Re–H) absorptions are expected,[4] the ir spectra support the indication of the nmr spectrum that the three hydridic protons bridge the two rhenium atoms. The six CO groups are all terminal giving a structure analogous to the alkoxides for which two ir-active ν(CO)'s are expected. $[Re_2(CO)_6H_3]^-$, as we have formulated it, is electron deficient; *i.e.*, more bonding orbitals are available than electrons to fill them. The hydrogen bridges may be regarded as bent two-electron, three-center bonds. The M–H–M bridges in $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$,[14] $[HFe_3(CO)_{11}]^-$,[15] and $[HMn_3(CO)_{10}(BH_3)_2]$[16] have been described previously as bent two-electron, three-center bonds.

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[14] R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965).

[15] L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

[16] H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965).

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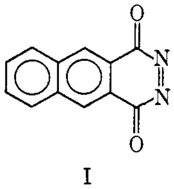
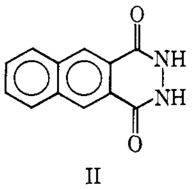
A Chemiluminescent Diazaquinone

Sir:

We have synthesized a relatively stable diazaquinone[1] (benzo[*g*]phthalazine-1,4-dione, I) which undergoes a chemiluminescent reaction relevant to the mechanism of the well-known chemiluminescence of cyclic aromatic hydrazides[2] such as 2,3-dihydrobenzo[*g*]phthalazine-1,4-dione (II)[3] and luminol (VII).


I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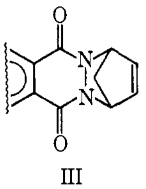
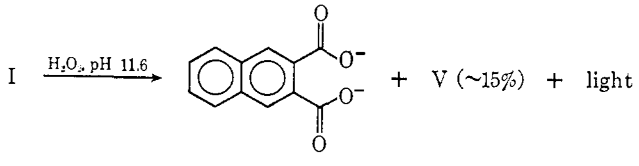

III

Addition of 0.5 equiv of chlorine to the monosodium salt of II suspended in 1,2-dimethoxyethane (glyme) at −50° yielded[4] a mixture from which maroon crystals of I were isolated after filtering and cooling at −80°: infrared (glyme) 1715 cm^{-1} (C=O);[1a] ultraviolet (glyme) 423 nm (log ϵ 3.5), 296 (4.0), 242 (4.8). *Anal.* Calcd for $C_{12}H_6N_2O_2$: C, 68.57; H, 2.88; N, 13.33. Found: C, 68.41; H, 2.92; N, 13.10. Structure I was corroborated by rapid formation of Diels–Alder adducts with butadiene or cyclopentadiene (*e.g.*, III).[1a] Unlike phthalazine-1,4-dione, which is a very unstable compound,[1a] crystalline I is stable for months at −20° and it persists for hours at room temperature in a dilute glyme solution.

Diazaquinone I reacts with alkaline hydrogen peroxide to give a bright violet chemiluminescence (eq 1). Chemiluminescence does not occur unless base and hydrogen peroxide are simultaneously present. The minor product V is apparently either hydrazide II or a labile dimer[1a] of II; addition of hemin to the reaction mixture converts V to IV with additional chemiluminescence.



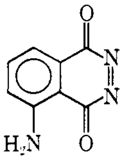
IV (~85%) (1)

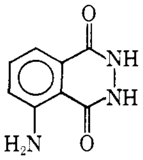
In contrast, the reaction of hydrazide II with alkaline peroxide does not yield appreciable chemiluminescence unless hemin[5] or other peroxide-decomposing catalysts (or oxidizing agents) are added (eq 2).

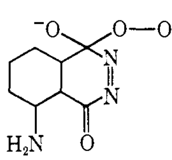
$$\mathrm{II} \xrightarrow[\text{pH 11.6}]{H_2O_2,\ \text{hemin}} \mathrm{IV}\ (>97\%) + \text{light} \tag{2}$$

The chemiluminescence emission spectra[6] of I and II are identical, λ_{max} 358 nm, and they coincide with the fluorescence of 2,3-naphthalenedicarboxylate ion, IV, which is presumably the light-emitting species. The ratio of chemiluminescence quantum yields of I to II is difficult to measure because the reaction of I is too fast to allow effective mixing. By comparing the emission from slowly dissolving *suspensions* of I to the emission of *solutions* of II, however, we estimate the ratio to be 0.25; the additional light available from V increases this ratio to 0.37. Under ideal conditions this ratio would certainly be closer to unity.

Diazaquinone VI has frequently been considered a critical intermediate in the chemiluminescence of luminol, but its lability has precluded a rigorous test of its role. Diazaquinone VI has been proposed to be: (1) the light emitter,[7] (2) a nonchemiluminescent by-product,[8] (3) the source of an intermediate diacyl


VI


VII


VIII

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[1] (a) T. J. Kealy, *J. Am. Chem. Soc.*, **84**, 966 (1962); (b) R. A. Clement, *J. Org. Chem.*, **25**, 1724 (1960); (c) E. Fahr and H. Lind, *Angew. Chem. Intern. Ed. Engl.*, **5**, 372 (1966).

[2] (a) E. H. White in "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961, p 183; (b) E. H. White, O. C. Zafiriou, H. M. Kägi, and J. H. M. Hill, *J. Am. Chem. Soc.*, **86**, 940 (1964); (c) E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964); (d) F. McCapra, *Quart. Rev.* (London), **26**, 485 (1966).

[3] H. D. K. Drew and R. F. Garwood, *J. Chem. Soc.*, 836 (1939).

[4] The method of Kealy[1a] was unsatisfactory in this application.

[5] R. Gatt and M. L. Kremer, *Trans. Faraday Soc.*, **64**, 721 (1968).

[6] Emission spectra of I and II were measured by scanning spectrographic plates with a microdensitometer; spectra of II and IV were measured with an Aminco-Bowman spectrophotofluorimeter. At high concentrations, I also yields a green emission similar to the fluorescence of II (sodium salt).

[7] A. Bernanose, T. Bremer, and P. Goldfinger, *Bull. Soc. Chim. Belges*, **56**, 269 (1947); *Chem. Abstr.*, **42**, 4855 (1948).

[8] F. H. Stross and G. E. Branch, *J. Org. Chem.*, **3**, 385 (1938).