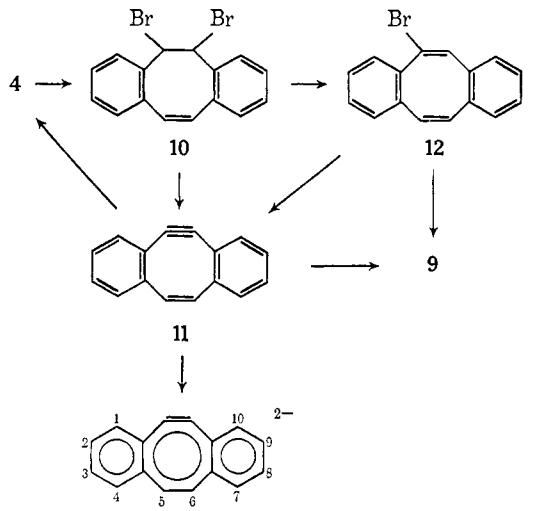

determination (rapid heating). The complex electronic spectrum resembled that of **6**, λ_{max} (hexane) 224 (ϵ 15,100), 228 (15,500), 233 sh (13,100), 240 (10,000), 252 sh (18,000), 260 (39,500), 265 (68,200), 275 (119,400), 296 (2500), 306 nm (1400), with a weak broad band between ~315 and 460 nm showing much fine structure (maximum ϵ 3100 at 365 nm).[9] The ^{1}H nmr spectrum ($CDCl_3$, 100 MHz) showed an 8 H multiplet at τ 3.0–3.5 (benzenoid) and a 2 H singlet at τ 4.50 (olefinic). The ir spectrum (KBr) did not exhibit a C≡C band at ~2200 cm^{-1}. The structure of **11** is based on the spectral data, the mass spectrum (Found: *m/e* 202.0796 (100%, M^+). Calcd: 202.0783), and the elemental analysis (Found: C, 94.67; H, 4.84. Calcd: C, 95.02; H, 4.98). Further structure proof of **11** was provided by catalytic hydrogenation in EtOAc over Pt, which led to **4** when 1 molar equiv of H_2 was absorbed and to **9** when allowed to proceed to completion. The monoacetylene **11** was very unstable, and the solid decomposed after a few minutes standing at room temperature.

Treatment of **11** in THF-d_8 with a K mirror[10] at −20° gave a deep green solution of the di-K salt of the dianion **13**.[11] The ^{1}H nmr spectrum (100 MHz, −40°) showed a 4 H multiplet centered at τ 2.25 (H^1, H^4, H^7, H^{10}), a 2 H singlet at τ 3.33 (H^5, H^6), and a 4 H multiplet centered at τ 3.8 (H^2, H^3, H^8, H^9). Attempts to prepare the corresponding dianion of **6** under the same conditions have so far been unsuccessful.

The acetylenes **6** and **11** presumably contain planar conjugated eight-membered rings.[12] Thus, the electronic spectra of **6** and **11** indicate them to be highly conjugated systems, unlike the nonplanar **4** (λ_{max} (hexane) 242 nm (ϵ 25,200)). The presence of a planar conjugated 4*n*-membered ring in **6** and **11**, as in biphenylene,[13] should be reflected in a paratropic contribution to the ring current. The high-field positions of both the benzenoid and olefinic proton resonances in the ^{1}H nmr spectra of both **6** and **11** as compared to **4**[14] support the presence of such a contribution. Further, reduction of **11** to **13**, involving the conversion of a 4*n* to a (4*n* + 2) π-electron system presumably without a change in geometry, leads to a downfield shift of the olefinic and part of the benzenoid resonances despite the introduction of two negative charges. The dianion **13** is clearly a diatropic system, and the ^{1}H nmr spectrum closely resembles that of the corresponding dianion of **4**.[10]

The interesting observation that the diacetylene **6** is much more stable than the monoacetylene **11** further supports our view that it might be possible to isolate the nonannelated diacetylene **2**. Experiments designed to prepare **2**, as well as to investigate the reactions of **6** and **11**, are now in progress.

Acknowledgments. H. N. C. W. acknowledges with thanks the award of a Shell Postgraduate Scholarship, administered by the Chinese University of Hong Kong.

(9) The ϵ values are minimum ones, due to the instability of **11**.

(10) See T. J. Katz, M. Yoshida, and L. C. Siew, *J. Amer. Chem. Soc.*, **87**, 4516 (1965).

(11) On brief treatment of **11** with K, the solution turned red, and the ^{1}H nmr spectrum of **11** disappeared, presumably due to the intervention of the radical anion.[10]

(12) An X-ray crystallographic analysis of **6** is in progress. For the only previously known presumably planar neutral cyclooctatetraene derivative, see C. F. Wilcox, J. P. Uetrecht, and K. K. Grohman, *J. Amer. Chem. Soc.*, **94**, 2532 (1972).

(13) See H. P. Figeys, *Chem. Commun.*, 495 (1967), and references cited there.

(14) **4**: ^{1}H nmr ($CDCl_3$, 100 MHz) τ 2.91 (8 H, AA'BB', benzenoid), 3.25 (4 H, s, olefinic); see also G. W. Buchanan and A. R. McCarville, *Can. J. Chem.*, **51**, 177 (1973).

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Electrophilic Substitution in Aromatic Systems by Coordinated Nitrosyl. Nitrosoarene Complexes of Ruthenium

Sir:

In an appropriate coordination environment, the nitrosyl group has been shown to react chemically as the nitrosonium ion, NO^+.[1-6] For example, nucleophiles such as N_3^- and OH^- add to suitably activated nitrosyls (those that have relatively high ν(NO) stretching frequencies in the infrared),[1-5] and recently we have shown that $Ru(bipy)_2(NO)Cl^{2+}$ (bipy is 2,2′-bipyridine) will diazotize primary aromatic amines within the coordination sphere of the metal ion.[6]

We now wish to report that the coordinated nitrosyl group in $Ru(bipy)_2(NO)X^{2+}$ can function as an electrophile in aromatic substitution reactions thus extending the parallelism in chemical behavior between NO^+ and coordinated NO to another class of reaction. The electrophilic substitution reactions occur under mild conditions with suitably activated arenes such as *N*-methylaniline and *N*,*N*-dimethylaniline which cannot be diazotized by NO^+. The products of the reactions are the para-substituted nitrosoarenes bound in the coordination sphere of the ruthenium ion.

Nitrosoarene complexes have been prepared previously by reaction of nitrosoarenes with metal com-

(1) T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Commun.*, 872 (1970); J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 2150 (1971).

(2) F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, **93**, 1294 (1971); S. A. Adeyemi, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, **11**, 994 (1972).

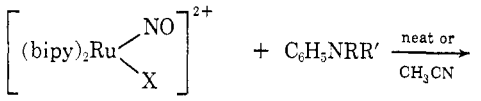
(3) J. H. Swinehart, *Coord. Chem. Rev.*, 2, 385 (1967).

(4) E. J. Barans and A. Muller, *Chem. Ber.*, **102**, 3915 (1969).

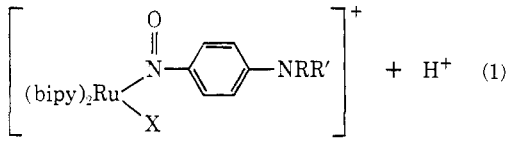
(5) P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, **93**, 84 (1971).

(6) W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, **95**, 5085 (1973).

plexes of palladium[7-9] and platinum[8]; an X-ray study has shown that the nitrosobenzene group is N bound in $Pd(C_6H_5NO)_2Cl_2$.[10] We find that both secondary and tertiary aromatic amines react with $Ru(bipy)_2(NO)X^{2+}$ (X is NO_2 or Cl) in aprotic solvents to give N-bound nitrosoarene complexes (eq 1). The nitroso-



Ia, X = Cl; R = R′ = CH_3
Ib, X = Cl; R = H; R′ = CH_3
Ia, X = NO_2; R = R′ = CH_3
Ib, X = NO_2; R = H; R′ = CH_3



(1)

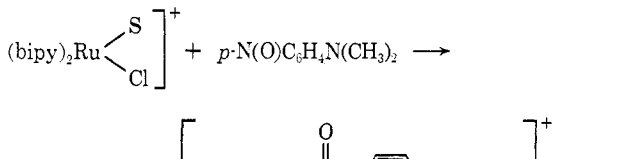
arene complexes have been isolated as hexafluorophosphate salts after chromatography on Kieselguhr.[11]

^{15}N labeled complexes have been prepared using $Ru(bipy)_2(^{15}NO)Cl^{2+}$. For the ^{15}N labeled ion, $Ru(bipy)_2[^{15}N(O)C_6H_4N(CH_3)_2]Cl^+$, a band in the infrared spectrum,[12] at 1286 cm^{-1} (in the unlabeled complex) shifts to 1261 cm^{-1} and a band at 875 cm^{-1} shifts to 866 cm^{-1} clearly showing that the nitrosyl group is retained in the product. The band at 1286 cm^{-1} is in the same region as the symmetric and asymmetric stretching bands for the coordinated nitro group, M–NO_2,[2,4,13] suggesting that the nitrosoarene ligands are N bound and that the band at 1286 cm^{-1} can be assigned to the ν(N–O) stretch. The band at 875 cm^{-1} may be a ν(N–C) rock.

Complex Ia was prepared by an independent route using the solvent complex $Ru(bipy)_2SCl^+$ (S is acetone)[2] as an intermediate.

$$S + Ru(bipy)_2(NO)Cl^{2+} + N_3^- \longrightarrow Ru(bipy)_2SCl^+ + N_2 + N_2O$$

(S is acetone)



Ia

The nitrosoarene complexes are intensely blue in color. In their uv-visible spectra in acetonitrile, strong bands appear with λ_{max} values in the region 566–600 nm (ϵ 2.0 × 10^4 to 3.2 × 10^4) and also in the region 417–428 nm (ϵ 1.2 × 10^4 to 1.8 × 10^4). On the basis of substituent effects the low energy bands can be assigned to a $d\pi \rightarrow \pi^*$ (nitrosoarene) charge transfer (CT) transition and the higher energy bands to an internal $\pi \rightarrow \pi^*$ nitrosoarene transition. The existence of intense, low energy $d\pi \rightarrow \pi^*$ CT transitions is a characteristic feature of complexes in which N-bonded heterocyclic ligands are bound to ruthenium(II).[14,15] $d\pi \rightarrow \pi^*$ (bipy) bands are also observed in the electronic spectra. From the positions of the $d\pi \rightarrow \pi^*$ (bipy) bands it is possible to estimate that the bound nitrosoarene groups are similar in back-bonding strength to pyridine and aceonitrile in *bis*-2,2′-bipyridine complexes of ruthenium(II).[14,16] There may, in fact, be an extensive, but as yet unexplored, coordination chemistry of the nitrosoarene group bound to spin-paired d^6 metal ions.

The nitrosoarene complexes where X = NO_2 (IIa and IIb) undergo a reversible reaction with acid in aqueous solution. The reaction involves the conversion of coordinated nitrite into nitrosyl[17]

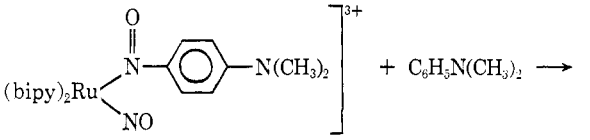
$$Ru(bipy)_2(NO_2)[N(O)C_6H_4NRR']^+ + 2H^+ \rightarrow Ru(bipy)_2(NO)[N(O)C_6H_4NRR']^{3+} + H_2O$$

which can be reversed by adding base

$$Ru(bipy)_2(NO)[N(O)C_6H_4NRR']^{3+} + 2OH^- \rightarrow Ru(bipy)_2(NO_2)[N(O)C_6H_4NRR']^+ + H_2O$$

The reactions are remarkable in that they indicate the stability of the ruthenium–nitrosoarene linkage in both acidic and basic aqueous solution.

The nitrosyl–nitrosoarene complex $Ru(bipy)_2(NO)[N(O)C_6H_4N(CH_3)_2]^{3+}$ has been isolated from acidic aqueous solution as its PF_6^- salt.[18] The nitrosyl group has a relatively high ν(NO) stretch (1931 cm^{-1})[12] and reacts with aromatic amines which has allowed us to introduce a second nitrosoarene group into the coordination sphere of the ruthenium ion.



$$(bipy)_2Ru[N(O)C_6H_4N(CH_3)_2]_2^{2+} + H^+$$

Reaction 1 was followed by uv-visible spectroscopy for the reactions between the nearly colorless ion $Ru(bipy)_2(NO)NO_2^{2+}$ and the two anilines in acetonitrile. In both cases products appear initially which absorb strongly at either 470 nm (R = R′ = CH_3) or 440 nm (R = H; R′ = CH_3) showing that reaction has occurred at the nitrosyl group. The nitrosoarene complexes are formed in a slower, subsequent step. The

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(9) C. J. Popp and R. O. Ragsdale, *Inorg. Chem.*, **7**, 1845 (1968).
(10) R. G. Little and R. J. Doedens, *Inorg. Chem.*, **12**, 537 (1973).
(11) Satisfactory analyses were obtained as PF_6^- salts, for Ib and IIa as monohydrates. Ia Calcd for $C_{28}H_{26}N_6RuClOPF_6$: C, 45.16; H, 3.49; N, 11.29. Found: C, 45.33; H, 3.52; N, 11.16. Ib·H_2O Calcd for $C_{27}H_{26}N_6RuClO_2PF_6$: C, 43.20; H, 3.47; N, 11.20. Found: C, 43.06; H, 3.32; N, 10.99. IIa·H_2O Calcd for $C_{28}H_{28}N_7RuO_4PF_6$: C, 43.52; H, 3.61; N, 12.59. Found: C, 43.57; H, 3.49; N, 12.41. IIb Calcd for $C_{27}H_{24}N_7RuO_3PF_6$: C, 43.78; H, 3.23; N, 13.23. Found: C, 43.60; H, 3.26; N, 13.08.
(12) Infrared spectra were obtained using KBr pellets, ±2 cm^{-1}.
(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., 1970.
(14) G. M. Bryant, J. E. Ferugsson, and H. K. J. Powell, *Aust. J. Chem.*, **24**, 257 (1971).
(15) P. Ford, DeF. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).
(16) R. W. Callahan, F. Dunn, T. R. Weaver, and T. J. Meyer, manuscript in preparation.
(17) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 2150 (1971).
(18) *Anal.* Calcd for $C_{28}H_{26}N_7RuO_2P_3F_{18}$: C, 32.68; H, 2.53; N, 9.53. Found: C, 32.45; H, 2.60; N, 9.46.

mechanistic details of the net reaction are currently under investigation.

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Novel Synthetic Route to Heterocycles *via* Intramolecular Cycloaddition of Azalogs of Hexatriene. New Syntheses of Purines and Pyrazolo[3,4-*d*]pyrimidines

Sir:

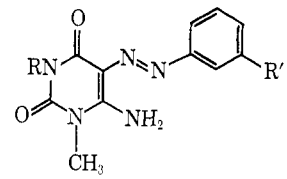
We would like to report a novel synthetic route to heterocycles which involves an intramolecular cycloaddition of azalogs of hexatriene and is of potential utility. This communication describes new syntheses of purines and pyrazolo[3,4-*d*]pyrimidines as typical examples of this route.

Refluxing 6-amino-1,3-dimethyl-5-phenylazouracil (Ia) in excess dimethylformamide dimethylacetal[1] for 5 hr gave 1,3-dimethyl-6-dimethylaminomethyleneamino-5-phenylazouracil (IIa) (mp 203°, 85%). Similarly, the 5-*m*-tolylazo analog (IIb) (mp 174°, 75%) was obtained from the condensation of 6-amino-1,3-dimethyl-5-*m*-tolylazouracil (Ib) (mp 257°) and dimethylformamide dimethylacetal. Fusion of IIa at 210–220° for 15 min under exclusion of moisture gave a mixture of 8-dimethylaminotheophylline (IIIa)[2] (mp >300°, 40%) and 1,3-dimethyl-7-dimethylamino-5-phenyl-5,6(or 5,8)-dihydro-6-azalumazine (IVa) (mp 251°, 42%) while releasing aniline (*ca.* 20%). Similarly, IIb gave a mixture of IIIa (45%) and the corresponding 5-*m*-tolyldihydro-6-azalumazine derivative (IVb) (mp 197°, 43%) together with *m*-toluidine (*ca.* 25%). In these reactions, lower melting 7-anilinotheophyllines (Va,b) (mp 170° dec) were isolated from the initial reaction mixtures. Although these compounds were isomeric with the starting materials (IIa,b) from their microanalyses and mass spectrometry, their ir spectra were quite different from those of IIa,b and showed similarity with the general pattern of ir spectra of 7-substituted theophyllines. Heating the isolated Va,b at 220° instantly gave IIIa and anilines. This conversion involves the thermal cleavage of the nitrogen–nitrogen bond of V to yield the theophylline and the respective nitrenes which abstract hydrogens probably from the substrate itself to give anilines. Therefore, Va and b are intermediates in the conversion of IIa and b to IIIa (Scheme I).

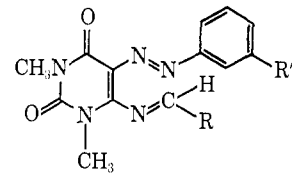
The structures of compounds IVa and b were ascertained by elemental analyses, molecular weight determination, and fragmentation study by mass spectrometry and from ir (the presence of NH absorption at 3270 cm^{-1}) and nmr spectra. Furthermore, the following transformation of IVa and b was carried out; reduction of IVa and b with sodium dithionite in formic acid gave 8-formylamino-7-phenyltheophylline (VIa) (mp 215°, 31%) and 8-formylamino-7-*m*-tolyltheophylline (VIb) (mp 208°, 32%).[3]

The heating of Ia with excess benzaldehyde at 220° for 3 hr, followed by cooling, caused to separate 8-phenyltheophylline (IIIc)[4] (mp >330°, 53%). From the filtrate, 1,3-dimethyl-5,7-diphenyl-5,6(or 5,8)-dihydro-6-azalumazine (IVc) (mp 248°, 25%) was isolated. Reduction of IVc with sodium dithionite in formic acid gave likewise 7,8-diphenyltheophylline (VIc)[5] (mp 223°, 25%). Similarly, the fusion of Ia with excess *p*-chlorobenzaldehyde gave 8-(*p*-chlorophenyl)-

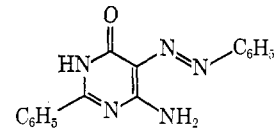
Scheme I



Ia, R = CH_3; R′ = H
b, R = CH_3; R′ = CH_3
c, R = H; R′ = H



IIa, R = $(CH_3)_2N$; R′ = H
b, R = $(CH_3)_2N$; R′ = CH_3



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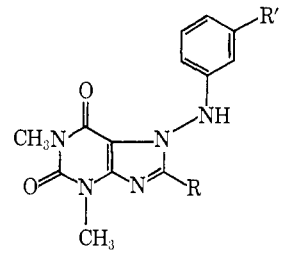
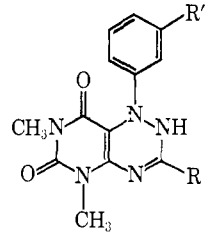
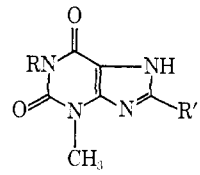


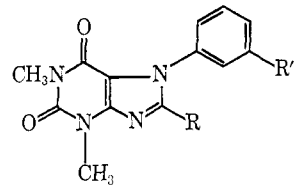
Va, R = $(CH_3)_2N$; R′ = H
b, R = $(CH_3)_2N$; R′ = CH_3



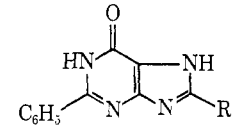
IVa, R = $(CH_3)_2N$; R′ = H
b, R = $(CH_3)_2N$; R′ = CH_3
c, R = C_6H_5; R′ = H
d, R = *p*-ClC_6H_4; R′ = H



IIIa, R = CH_3; R′ = $(CH_3)_2N$
c, R = CH_3; R′ = C_6H_5
d, R = CH_3; R′ = *p*-ClC_6H_4
e, R = H; R′ = C_6H_5
f, R = H; R′ = *p*-ClC_6H_4
g, R = H; R′ = 3,4-$Cl_2C_6H_3$
h, R = H; R′ = *p*-$CH_3OC_6H_4$
i, R = H; R′ = *p*-$(CH_3)_2NC_6H_4$



VIa, R = NHCHO; R′ = H
b, R = NHCHO; R′ = CH_3
c, R = C_6H_5; R′ = H



IIIj, R = C_6H_5
k, R = 3,4-$Cl_2C_6H_3$

(1) H. Bredereck, G. Simchen, S. Rebsdat, W. Kantlehner, P. Horn, R. Wahl, H. Hoffmann, and P. Grieshaber, *Chem. Ber.*, **101**, 41 (1968).
(2) (a) E. C. Taylor and F. Sowinski, *J. Amer. Chem. Soc.*, **90**, 1347 (1968); (b) F. Yoneda, M. Higuchi, T. Matsumura, and K. Senga, *Bull. Chem. Soc. Jap.*, **46**, 1836 (1973).
(3) This is best rationalized by assuming initial reductive nitrogen–nitrogen bond cleavage to a 5-anilino-6-amidinouracil derivative, followed by formylation and intramolecular cyclization with elimination of dimethylamine. An analogous ring contraction was observed by the reduction of other 6-azalumazine derivatives. F. Yoneda, Y. Sakuma, M. Ueno, and S. Nishigaki, *Chem. Pharm. Bull.*, **21**, 926 (1973).
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(5) E. C. Taylor and F. Yoneda, *J. Org. Chem.*, **37**, 4464 (1972).