Tetrahedron Letters No.38, pp. 3267-3268, 1969. Pergamon Press. Printed in Great Britain.

THE OXIDATIVE COUPLING REACTION OF VINYLIDINEBISDIALKYLAMINES

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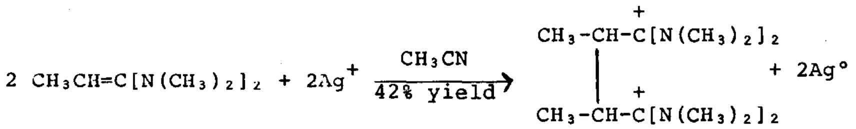
(Received in USA 5 June 1969; received in UK for publication 14 July 1969)

We wish to report a reaction in which vinylidinebisdialkylamines (1) (ketene-N,N-acetals) are oxidatively coupled to form diamidinium salts. Propenylidinebisdimethylamine, I, for example, reacts exothermically with silver nitrate in acetonitrile solvent to form a mixture of dl and meso-1,1,4,4-tetrakis(dimethylamino)-2,3-dimethylbutane-1,4-diylium nitrate, II. The diylium salt, II, isolated as a hexafluorophosphate, has the following



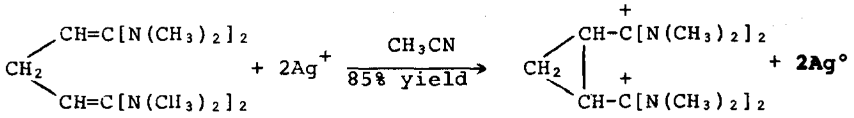
$$2\ CH_3CH{=}C[N(CH_3)_2]_2 + 2Ag^+ \xrightarrow[42\%\ yield]{CH_3CN} \begin{array}{l} CH_3\text{-}CH\text{-}\overset{+}{C}[N(CH_3)_2]_2 \\ \qquad | \\ CH_3\text{-}CH\text{-}\overset{+}{C}[N(CH_3)_2]_2 \end{array} + 2Ag^\circ$$

I II

properties: m.p. 245°d, nmr spectrum exhibits a multiplet centered at τ6.35, two singlets at τ6.75 and 6.81 (3:1 dl-meso ratio, not assigned) and two multiplets centered at τ8.54 and 8.66 in the ratio 1:12:3, (acetonitrile-d_3, TMS internal standard).

Anal. Calcd. for $C_{14}H_{32}N_4P_2F_{12}$: C, 30.8; H, 5.9; N, 10.3.
Found: C, 30.9; H, 6.0; N, 10.3

This method is also applicable to the synthesis of cyclic systems. An example is the oxidation, in good yield, of N,N,N',N',N'',N'',N''',N'''-octamethyl-1,4-pentadiene-1,5-tetramine, III, to a cis and trans mixture of



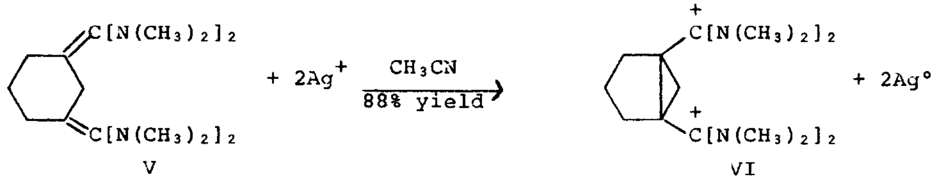
$$CH_2\left<\begin{array}{l} CH{=}C[N(CH_3)_2]_2 \\ CH{=}C[N(CH_3)_2]_2 \end{array}\right. + 2Ag^+ \xrightarrow[85\%\ yield]{CH_3CN} CH_2\left<\begin{array}{l} CH\text{-}\overset{+}{C}[N(CH_3)_2]_2 \\ \ | \\ CH\text{-}\overset{+}{C}[N(CH_3)_2]_2 \end{array}\right. + 2Ag^\circ$$

III IV

cyclopropylenebis(dimethylaminocarbonium) nitrate, IV. The product, IV, isolated as a hexafluorophosphate, has the following properties: nmr spectrum exhibits two sharp singlets at $\tau 6.68$ and 6.80 (cis:trans 2:3) and a poorly defined envelop of peaks between $\tau 7.17$ and 8.25 in a ratio 6:1 (acetonitrile-d_3, TMS internal standard),

Anal. Calcd. for $C_{13}H_{28}N_4P_2F_{12}$: C, 29.5; H, 5.3; 10.6.
Found: C, 29.7; H, 5.3; N, 10.3.

Furthermore, this method appears suitable for the synthesis of certain bicyclic systems. For example, 1,3-bis[bis(dimethylamino)methylene]cyclohexane, V, is converted to bicyclo[3.1.0]cyclohexan-1,5-ylenebis(dimethylaminocarbonium) nitrate, VI. The diamidinium salt, VI, isolated as a hexafluorophosphate, has the following properties: nmr spectrum exhibits a singlet at $\tau 6.74$ and a complex multiplet between $\tau 7.25$ and 8.06 in a ratio 3:1 (acetonitrile-d_3, TMS internal standard), *Anal.* Calcd. for $C_{16}H_{32}N_4P_2F_{12}$: C, 33.7; H, 5.7; N, 9.8 Found: C, 33.4; H, 5.4; N, 9.6.



The structural assignments of II, IV (2) and VI (3) were confirmed by hydrolysis to diamides and comparison to authentic diamides.

ESR and cyclic voltammetry suggest the reaction intermediates are radical cations.

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