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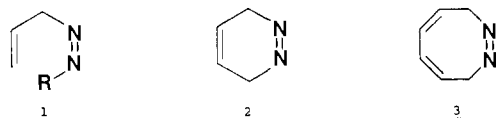
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Synthesis and Thermolysis of 7,8-Diazabicyclo[4.2.2]deca-2,4,7-triene

Sir:

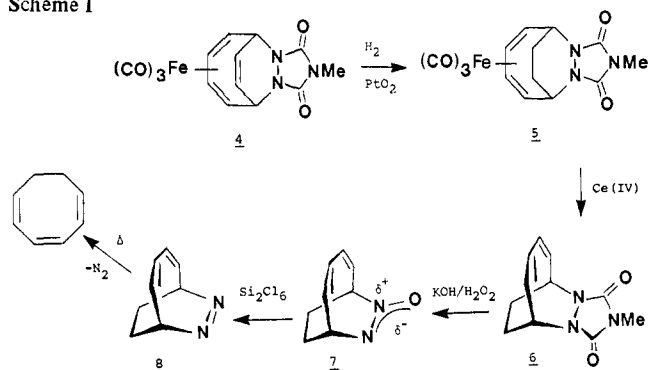
cis-Azoalkanes which possess vinyl substitution α to nitrogen, **1**, are isolable substances decomposing readily by loss of N₂ to give the corresponding allyl radical.¹ Cyclic analogues such as the diazacyclohexadiene **2** are represented by a number of species which have been generated in situ but rarely isolated or observed.² These extrude N₂ spontaneously by way of a



concerted retrocycloaddition. The latter can be attenuated, however, by replacing the carbon π unit with a three- or a four-membered ring.^{2c,3} We now wish to report the first synthesis of a stable, simple derivative of the diazacyclooctatriene system **3** and a preliminary account of its thermal cycloreversion.⁴

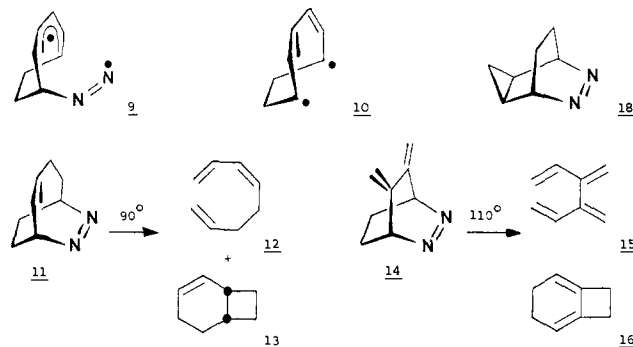
Scheme I outlines the synthetic sequence. Addition of *N*-methyltriazaolinedione to cyclooctatetraene iron tricarbonyl leads to cycloadduct **4**.⁶ Treatment of **4** with hydrogen in the presence of PtO₂ yields the dihydro derivative **5** quantitatively, which by ceric ammonium nitrate oxidation gives adduct **6** (99%).⁷ Oxidative hydrolysis with strongly basic hydrogen peroxide⁸ delivers azo-*N*-oxide **7** in low yield (13%). Deoxygenation of the latter with hexachlorodisilane results in pale yellow crystals of azobicyclo **8**: 46%; mp 46–48 °C (uncorr); IR ν_{max} (CHCl₃) 1542 cm⁻¹ (N=N); UV λ_{max} (CH₃CN) 238 nm (ϵ 2100), 306 (ϵ 520), and shoulder extending to 430; NMR τ (CCl₄/TMS) 4.22 (4 H, m), 5.17 (2 H, m), 7.78 (2 H, m), 8.24 (2 H, m). In solution in the absence of light azodiene **8**

Scheme I



dissociates quantitatively to 1,3,5-cyclooctatriene (COTr) at temperatures slightly above ambient. First-order rates of decomposition were determined by following the disappearance of the absorption at 340 nm ($k_{\text{isooctane}}$ (48.4 °C) = 1.0×10^{-4} s⁻¹; ΔG^\ddagger = 24.7 kcal/mol).

Several pathways connecting azocycle **8** and COTr/N₂ are conceivable. Of those likely to involve intervening energy minima, either the diazenyl diradical **9** or the hydrocarbon diradical **10** could follow the starting material directly or exist as successive intermediates, respectively. Single-step nitrogen



extrusion not involving radicaloid intermediates is possible by way of a least-motion forbidden route or a non-least-motion allowed path.⁹ Although not rigorously applicable, several criteria have evolved to distinguish radical from concerted reactions where direct observation cannot be accomplished. Product composition, in particular structural and stereoisomerism, is primary while relative reaction rates are often, but not always, supportive.^{2c,12}

In an attempt to shed some light on the thermolysis of **8**, the fragmentation of the model azobicyclo **11**^{7b} has likewise been investigated. It splits out nitrogen in a first-order process ($k_{\text{isooctane}}$ (90.4 °C) = 1.0×10^{-4} s⁻¹; ΔG^\ddagger = 28.1 kcal/mol) to give exclusively a mixture (25:75) of 1,3,7-octatriene (**12**) and bicyclo[4.2.0]oct-2-ene (**13**).^{13,14} The appearance of both acyclic and bicyclic products signals the intermediacy of a biradical of type **9** or **10**.

A bicyclic isomer of diazacyclooctatriene **8**, i.e., **14**, exhibits the same pattern, losing N₂ at 110 °C in solution to give a 65% mixture of dimers, 30% polymer, and a 5% mixture (33:67) of the acyclic and cyclic hydrocarbons **15** and **16**, respectively.¹⁵ The monomeric olefins **15** and **16** are produced exclusively in the same ratio in the gas phase (110 °C). Both a triplet and a singlet diradical have been inferred (CIDNP and ESR).¹⁵ Similarly all other reports of diradical species, allylic and otherwise, disclose the ultimate formation of acyclic and/or ring-closure products.^{1,2c,12,16} By comparison the butadiene-bridged azoalkane **8** in the condensed phase renders a single monocyclic hydrocarbon product (COTr) in quantitative yield. The formation of the COTr valence isomer, bicyclo[4.2.0]octa-2,4-diene (**17**), as a primary product was ruled out by

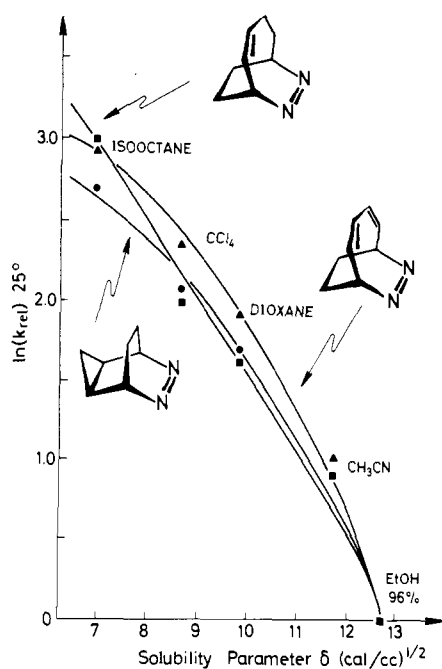


Figure 1. Plot of $\ln(k_{rel})$, 25 °C, for deazetation against the solubility parameter, δ , for azodiene **8**, azoene **11**, and the cyclopropyl derivative **18**. The individual points are the experimental values, while the curved lines represent the best parabolic fit to them. The plots have been scaled so that 96% EtOH arbitrarily is the common zero. In CH₃CN the plotted values for **11** and **18** are coincidentally superimposed.

monitoring the breakdown of **8** by NMR (60 °C, CCl₄). During the initial phase of the deazetation, COTr was the only product observed. However, toward the end of the thermolysis compound **17** was produced to the extent of only 5–10%. Since **17** has a half-life of 1–2 h at 60 °C,¹⁷ it is clearly being formed by leakage from COTr.

Relative rate comparisons have been pivotal in the interpretation of azo decomposition mechanisms.^{1–3} In the present case, however, ignorance of relative ground-state and transition-state strain energies, as well as possible differential conjugative effects, causes us to regard the relationship of these values with caution.¹⁸ More illuminating is the manner in which the rates change as a function of solvent. The first-order decomposition rates of **8** and **11** in five solvents²⁰ are compared with the results of an identical study for the cyclopropanated azo compound **18**¹⁹ (cf. Figure 1). The latter fragments quantitatively to 1,4-cycloheptadiene and N₂. Within the available mechanistic criteria, it has been established that tricycle **18** extrudes nitrogen by means of a pericyclic transition state.^{2c,3,19} Decreasing solvent polarity serves to accelerate the reaction slightly for all three substances. The plots of $\ln(k_{rel})$ vs. δ , the solubility parameter,^{21,22} have been constructed by fitting the points to a quadratic equation of the form $\ln(k_{rel}) = C_2\delta^2 + C_1\delta + C_0$. By taking advantage of the approximation $C_2 = -\Delta V^\ddagger/RT$,²¹ we obtain activation volumes ΔV^\ddagger (25 °C) = 27.3, 22.8, and 2.2 cm³/mol for **8**, **18**, and **11**, respectively.²³ The spread is in good qualitative agreement with the trend expected for a transition state experiencing simultaneous two-bond cleavage.²⁸ Significantly the pressure-dependent thermal decomposition of cyclic azo compounds via radical intermediates yields $\Delta V^\ddagger = 5\text{--}7$ cm³/mol.²⁹

In sum, the remarkable similarity of the response of azoalkanes **8** and **18** to media variation under conditions of deazetation is strongly suggestive of a persistence of mechanism. In agreement the deviant behavior of azobicyclic **11** both in its rate-solvent dependence and in its product delivery reduces considerably the likelihood of radical transients in the thermolysis of diazacyclooctatriene **8**. Further substantiation of

the apparently concerted loss of nitrogen from **8** and specification of its nature is under active investigation.

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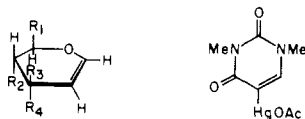
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Received September 22, 1976

Regiospecific Reaction of Enol Ethers with an Organopalladium Salt. Stereochemical and Conformational Effects on Product Formation

Sir:

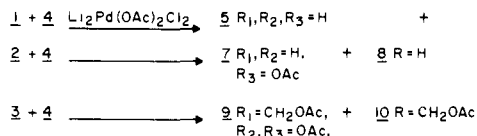
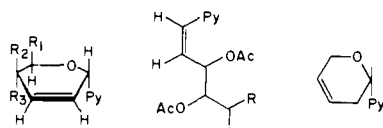
In connection with our interest in synthetic routes to C-nucleosides,¹⁻⁴ we have studied reactions of three cyclic enol ethers, 3,4-dihydro-2*H*-pyran (**1**), 3,4-di-*O*-acetyl-D-arabinal⁵ (**2**), and 3,4,6-tri-*O*-acetyl-D-glucal⁶ (**3**) with an organopalladium reagent generated in situ by treatment of 1,3-dimethyl-2,4-pyrimidinedion-5-ylmercuric acetate^{7,8} (**4**) with palladium salts.^{9,10} Each of the reactions exhibited complete



- 1** $R_1, R_2, R_3, R_4 = H$
2 $R_1, R_3 = H, R_2, R_4 = OAc$
3 $R_1 = CH_2OAc, R_2, R_3 = OAc, R_4 = H$

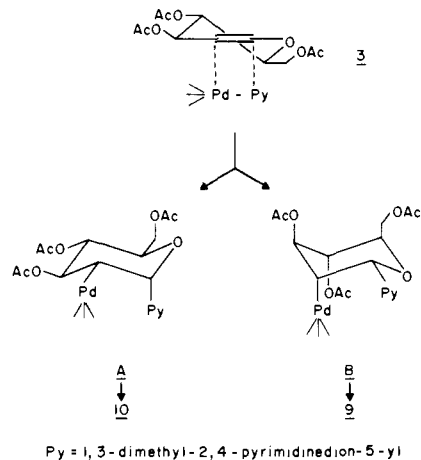
regiospecificity with carbon-carbon bond formation solely between C-5 of the pyrimidine and C-1 of the cyclic enol ether.⁹ Otherwise, the three reactions exhibited significant differences. Three distinct modes of decomposition of the intermediate enol ether-organopalladium salt adducts were observed. The various reaction pathways giving rise to the products isolated are a consequence of the respective stereochemical requirements of the addition and elimination reactions involved.

The preparation⁷ of 1,3-dimethyl-2,4-pyrimidinedion-5-ylmercuric acetate (**4**) was accomplished by addition of a stoichiometric amount of mercuric acetate to 1,3-dimethyl-2,4-pyrimidinedione¹¹ in methanol containing perchloric acid. When **4** (1 equiv), palladium acetate (1 equiv), lithium chloride (2 equiv), and 3,4-dihydro-2*H*-pyran (**1**, 1.5 equiv) in acetonitrile were stirred at 25 °C for 12 h, a precipitate of finely divided palladium was formed. Treatment of the reaction mixture with hydrogen sulfide to remove mercuric and residual palladium(II) ions followed by chromatography of the residue (after removal of solvent) on silica gel using dichloromethane yielded 1,3-dimethyl-5-(2',3'-dihydro-6'*H*-pyran-2'-yl)-



Py = 1,3-dimethyl-2,4-pyrimidinedion-5-yl

Scheme I. Stereochemistries of Organopalladium Salt Addition and Elimination Reactions



2,4-pyrimidinedione (**6**): 24%; mp 134–135 °C; λ_{max}^{MeOH} 270 nm; 1H NMR δ ($CDCl_3$) 1.8–2.8 (m, 3'- CH_2), 3.38, 3.43 (NMe), 4.35 (m, 6'- CH_2), 4.59 (d of d, $J = 10, 3.5$ Hz, 2'-CH), 5.6–6.1 (m, 4', 5'-CHs), 7.29 (s, 6-CH); mass spectrum, m/e 222 (M^+). Further elution produced 1,3-dimethyl-5-(5',6'-dihydro-2'*H*-pyran-2'-yl)-2,4-pyrimidinedione (**5**): 66%; mp 123–124 °C; λ_{max}^{MeOH} 270 nm; 1H NMR δ ($CDCl_3$) 1.8–2.5 (m, 5'- CH_2), 3.37, 3.41 (NMe), 3.6–4.2 (6'- CH_2), 5.25 (br, 2'-CH), 5.65–6.10 (m, 3', 4'-Hs), 7.27 (6-CH); mass spectrum m/e 222 (M^+).

In similar experiments,¹² reactions of the unsaturated pyran sugar derivatives **2** and **3** with **4** in the presence of palladium salts yielded products in which C-5 of the pyrimidine ring is bonded to a cyclic dihydropyran moiety (**7**¹³ and **9**¹³ respectively) or to an open-chain carbohydrate derivative (**8** and **10**, respectively). Thus, from reaction of **2** and **4** in the presence of $Li_2Pd(OAc)_2Cl_2$ was obtained 1,3-dimethyl-5-(5'-acetoxy-5',6'-dihydro-2'*H*-pyran-2'-yl)-2,4-pyrimidinedione (**7**):¹³ λ_{max}^{MeOH} 282, 235 nm; 1H NMR δ ($CDCl_3$) 2.11 (OAc), 3.37, 3.43 (NMe), 3.66 (d of d, $J = 12, 8$ Hz, 6'-CH), 4.17 (d of d, $J = 12, 6$ Hz, 6'-CH), 5.30 (br, 2', 5'-CHs), 6.02 (m, 3', 4'-CHs), 7.25 (6-CH); mass spectrum m/e 210 ($M - HOAc$) in 20% yield and 2,3-diacetoxy-5-(1',3'-dimethyl-2',4'-pyrimidinedion-5'-yl)pent-4-en-1-ol (**8**: mp 146–147 °C; λ_{max}^{MeOH} 270 nm; 1H NMR δ ($CDCl_3$) 2.08, 2.11 (OAc), 3.36, 3.50 (NMe), 3.81 (d, $J = 5$ Hz, 1-CH), 5.01 (d of t, $J = 5, 4$ Hz, 2-CH), 5.61 (d of d, $J = 12, 14$ Hz, 4-CH), 5.95 (d of d, $J = 10, 4$ Hz, 3-CH), 6.50 (d, $J = 12, 14$ Hz, 5-CH), 7.84 (s, 6'-CH); mass spectrum m/e 340 (M^+)) in 32% yield. From 3,4,6-tri-*O*-acetyl-D-glucal (**3**) and **4** were obtained the corresponding dihydropyran product **9**¹³ in ~20% yield¹⁵ and the acyclic carbohydrate product 6-(1',3'-dimethyl-2',4'-pyrimidinedion-5'-yl)-1,3,4-triacetoxyhex-5-en-2-ol (**10**: λ_{max}^{MeOH} 282, 236 nm; 1H NMR δ ($CDCl_3$) 2.05, 2.08, 2.10 (OAc), 3.35, 3.44 (NMe), 3.96 (m, 2-CH), 4.11 (d, $J = 5$ Hz, 1- CH_2), 5.14 (d of d, $J = 6, 5$ Hz, 3-CH), 5.59 (d of d, $J = 12, 12, 14$ Hz, 5-CH), 5.94 (d of d, $J = 10, 5$ Hz, 4-CH), 6.38 (d, $J = 12$ Hz, 6-CH), 7.66 (6'-CH); mass spectrum m/e 412 (M^+)) in 73% yield.

The general reaction of aryl (alkyl) palladium species with olefins is syn addition of the palladium derivative to the double bond followed by syn elimination of a hydridopalladium salt.^{10,16-18} The major product (**5**) resulting from reaction of 3,4-dihydro-2*H*-pyran (**1**) with the organopalladium reagent derived from **4** is that expected for this process. The minor product (**6**) arises by isomerization of **5**.¹⁰ It is noteworthy that the addition reaction is regiospecific owing to the strong polarization of the enol ether double bond; this electronic effect is largely lacking in reactions of aryl palladium salts with