1.2-1.75 (several m), 1.93 (m, 1 H), 3.20 (dd, 1 H, J = 1, 9 Hz), 3.34 (m, 1 H), 4.02 (m, 1 H), 4.55 (br d, 1 H, J = 9 Hz); mass spectrum, $(M + 1)^+$ 304. Anal. Calcd for $C_{16}H_{33}NO_4$: C, 63.33; H, 10.96; N, 4.62. Found: C, 63.47; H, 11.04; N, 4.72.

Registry No. **1**, 104882-10-2; **6a**, 98105-42-1; **6b**, 58521-45-2; **10a**, 103322-56-1; **10b**, 82010-31-9; (2*R*,3*S*)-**11a** (R′ = TMS), 117499-02-2; (2*S*,3*S*)-**11a** (R′ = TMS), 117499-03-3; (2*R*,3*S*)-**11a** (R′ = H), 117499-04-4; (2*S*,3*S*)-**11a** (R′ = H), 117499-05-5; (2*R*,3*S*)-**11b** (R′ = TMS), 117499-06-6; (2*S*,3*S*)-**11b** (R′ = TMS), 117499-07-7; **13a**, 114457-87-3; **13b**, 117499-08-8; **14a**, 117499-09-9; **14b**, 117678-48-5; **15**, 117161-46-3.

Reactivity of Azaannulenones

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We recently demonstrated the free existence in solution of 2-aza-2,4-cyclopentadienone, **1**.[1] Compound **1** was able to act either as a diene or as a dienophile in Diels-Alder reactions. It was of interest to study how the presence of another nitrogen in the ring might affect the reactivity and the stability of these reactive intermediates. We now describe the generation of 2,3-diaza-2,4-cyclopentadienone, **2** (Chart I).

Several 4,5-substituted 2,3-diaza-2,4-cyclopentadienones have been proposed as intermediates in a number of reactions.[2,3] However, the parent compound **2** has received less attention although its existence has been proposed in the oxidation of 3-pyrazolin-5-one with lead tetraacetate.[4] In order to study the free existence, reactivity, and stability of this intermediate we used the three-phase test as we did with **1**.[1] In such a test, a reagent solution liberates the suspected intermediate from a polymeric precursor, and a second solid phase suspended in the same solution is used to trap the intermediate. As polymeric precursor for **2** we prepared the 2-polymeric sulfamide of the 3-pyrazolin-5-one, **3**.

Results and Discussion

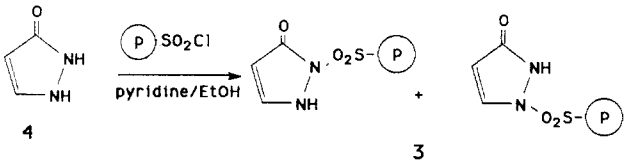
Synthesis of Precursor 3. The polymeric precursor **3** was synthesized as shown in Scheme I. Reaction of **4**[4] with chlorosulfonated macroreticular resin[5] gave **3** (IR: 3010, 2410, 1617, 1478, 1440, 1151, 1017 cm^{-1}). This resin acts as the nonpolymeric postulated precursors of **2**. Thus, when **3** reacted with 2,3-dimethyl-1,3-butadiene in the presence of a base, the product isolated, **7**, was the one previously described[4] (Scheme III).

Free Existence of 2 and Dienophilic Character. Polymeric 2-(carboxymethyl)-3-methyl-1,3-butadiene **5** was used as the trapping dienic polymer for **2**. Compound **5** was prepared in the way indicated in Scheme II. Treatment of 2,3-dimethyl-1,3-butadiene with NBS gave 2-(bromomethyl)-3-methyl-1,3-butadiene, **6**. This bromo compound was stirred with the silver salt of the polymeric carboxylic acid[6] to give **5**. A suspension of **3** and **5** in HMPT was stirred at 30 °C in the presence of $LiNH_2$ (Scheme III). The resins were separated in the usual way, and the Diels-Alder adduct, **7**, was obtained from polymer **8** via dealkylation[7] with trimethylsilyl chloride and sodium iodide followed by reduction with $NaBH_4$.[8] The formation of this adduct supports the free existence of 2,3-diaza-2,4-cyclopentadienone since direct reaction between solid phases **3** and **5** is physically precluded.

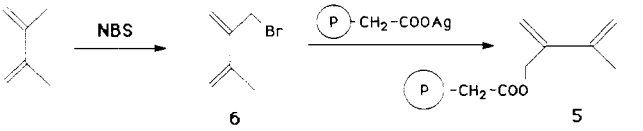
2,3-Diaza-2,4-cyclopentadienone as a Diene. Trapping of the intermediate **2** as a diene was attempted by some polymers functionalized with dienophilic groups such as the polymeric monoester of acetylenedicarboxylic acid[9] and the polymeric benzylmaleimide.[10] Under more drastic experimental conditions for which the trapping of **2** by **5** was done, both dienophilic polymers were recovered unchanged. The polymer precursor was converted into polymeric sulfonic acid, and CO release was observed.

Chart I

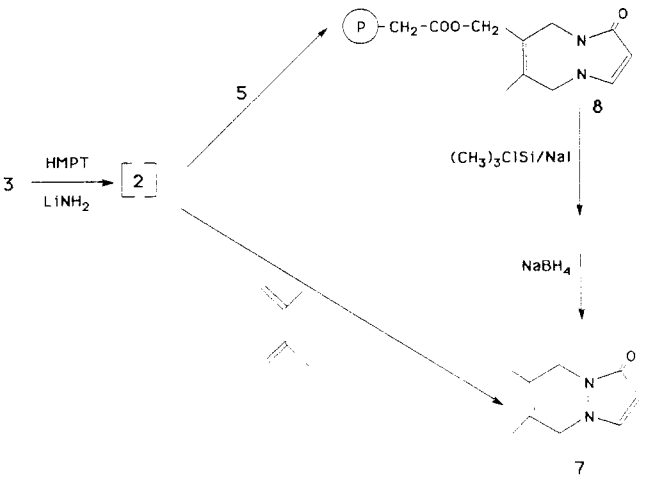
Scheme I



Scheme II



Scheme III



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Lifetime Determinations. The three-phase test modified by using the "Poliphasic Dynamic Reactor" (PDR)[9] has been applied to determine the lifetime of 1 and 2. In PDR, resins are separated to a constant distance and a variable flow of the liquid phase is introduced. The intermediate is generated from a polymeric precursor in a vessel of PDR and trapped in another vessel. The reagent solution flows inside the PDR from precursor to trap through a conduit of known volume and outside the PDR from trap to precursor through an adjustable peristaltic pump. We found, in the same experimental conditions, the value of 2.0 ± 0.5 s for 2-aza-2,4-cyclopentadienone and 63.5 ± 0.5 s for 2,3-diaza-2,4-cyclopentadienone.

Conclusions

2,3-Diaza-2,4-cyclopentadienone, 2, is able to act as an azadienophile, but seems not be able to act as an azadiene. Thus, its reactivity differs from that of 2-aza-2,4-cyclopentadienone, 1, which behaves as a diene or as a dienophile in Diels–Alder reactions.

Lifetime values show that 1 is a very unstable intermediate compared to homocyclic 2,4-cyclopentadienone (lifetime 13.0 s).[9] This fact seems likely to depend on the high reactivity of the C=N bond. 2,3-Diaza-2,4-cyclopentadienone, 2, has also a very reactive bond (N=N); still, it is more stable than homocyclic annulenone. Probably, 2 does not dimerize, since its behavior as a diene has never been detected. Thus, the disappearance of this intermediate might follow a different pathway, and this fact could explain its larger lifetime.

Further theoretical and experimental studies on these and related azaannulenones will show us the relationship between number and positions of ring nitrogens and reactivity of these species. Such studies are under way.

Experimental Section

Preparation of the Polymeric Sulfonate of 3-Pyrazolin-5-one (3). Polymeric tosyl chloride[5] (2.0 g), 3-pyrazolin-5-one (5.1 g, 0.061 mol), and pyridine (24 mL) were stirred in 200 mL of ethanol for 3 days at room temperature. After the reaction, the resin was filtered and washed with aqueous 10% HCl, dioxane, acetone, and ether to obtain 3: IR (KBr) 3010, 2910, 1617, 1478, 1440, 1151, 1017 cm^{-1}. Analysis indicated 1.70 mequiv/g (1.95% N).

Preparation of the Bromo Compound 6. A mixture of 2,3-dimethyl-1,3-butadiene (3.86 g), NBS (4.88 g), and benzoyl chloride (0.12 g) in 34 mL of CCl_4 was heated in a steam bath for 1 h, and then the solution was chilled and filtered. The organic phase was washed with saturated sodium thiosulfate solution/iced water (1:1), dried, and evaporated to give 6: IR 2910, 1690, 1600, 1450, 1225, 1180, 1030, 1000, 705 cm^{-1}; ^1H NMR (CCl_4) δ 5.00 (m, 4 H), 4.90 (s, 2 H), 1.90 (s, 3 H); MS 162, 160, 135, 133, 97, 95, 81, 79, 67, 53, 41; bp 50 °C/30 Torr. Anal. Calcd: C, 44.72; H, 5.59. Found: C, 44.70; H, 5.60.

Preparation of Trapping Polymer 5. The polymeric acid (2 g) was added to a solution of 0.36 g of KOH in 40 mL of water. After 10 min, $AgNO_3$ (1.12 g) was added and the solution stirred at room temperature for 30 min. The silver salt of polymeric acid was separated by filtration and washed with ether: IR (KBr) 3015, 2910, 1580–1560, 1450, 1380 cm^{-1}; 2.04 mequiv/g (21.99% Ag).

Compound 6 (0.37 g) and 1.0 g of the so obtained polymer in 20 mL of dioxane were heated in a steam bath for 24 h. After filtration, the solid AgBr was removed with a solution of KCN and the resin 5 washed with dioxane, acetone, and ether: IR (KBr) 3010, 2917, 1600–1560, 1450, 1390–1370, 1020 cm^{-1}. Titration indicated 2.15 mequiv of ester/g.

Reaction of 2 as a Dienophile. Compound 3 (1.0 g) and 1.02 g of 5 were suspended in 7 mL of HMPT. Lithium amide (0.6 g in 10 mL of HMPT) was added dropwise at 30 °C, and then the mixture was stirred for an additional 24 h at room temperature. Washing and separation of the resin gave 8 (2.00 mequiv/g): IR (KBr) 3015, 2905, 1703, 1490, 1445, 1020 cm^{-1}. Compound 8 (0.83 g) was stirred in 200 mL of acetonitrile with 0.51 g of NaI, then 0.27 g of trimethylsilyl chloride was added slowly, and the reaction mixture was kept for 3 h in a steam bath. The polymer was separated by filtration, and the solution was diluted in 100 mL of HMPT and treated with $NaBH_4$, 64.4 mg, in a steam bath for 1 h. Then 200 mL of water was added and the solution extracted with CH_2Cl_2. From the evaporated mixture, 7 could be separated by TLC (silica gel as stationary phase and benzene/ethanol, 1:1, as eluent): IR (KBr) 2915, 2850, 1615, 1450, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35 (d, 1 H), 5.55 (d, 1 H), 4.15 (s, 2 H), 4.00 (s, 2 H), 1.80 (ds, 6 H); mp 115–117 °C. It was identical with an authentic sample.[4]

Behavior of 2 as a Diene. As an example, 0.1 g of 3 and 0.43 g of polymeric monoester of acetylenedicarboxylic acid were suspended in 7 mL of HMPT, and then 0.6 g of lithium amide in 10 mL of HMPT was added dropwise. The solution was allowed to stand at 40 °C for 24 h. Unchanged polymeric trapping agent was then isolated.

Lifetime Determinations. Lifetime determinations were made as described.[9] In a series of experiments, a suspension of 6.5 mequiv of polymeric precursor (3 or 5-polymeric sulfonate of the 3-pyrrolin-2-one[1]) with 1.5 g of lithium amide in HMPT was heated and stirred at 30 °C in a vessel of PDR. Trapping agent 5 (4.5 mequiv) was stirred in the other vessel. Reagent solution flowed from precursor to trapping agent through a conduit of known volume. The run time through this conduit was adjusted by the peristaltic pump. After each experiment, the polymeric trapping agent was tested for the presence of the azaannulenone moiety. This presence showed the transfer of azaannulenone and a lifetime for the intermediate higher than the run time. The lifetime values so obtained were 2.0 ± 0.5 s for 1 and 63.5 ± 0.5 s for 2.

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Registry No. 1, 54036-77-0; 2, 56240-95-0; 4, 137-45-1; 6, 74793-41-2; 7, 73977-45-4; 2,3-dimethyl-1,3-butadiene, 513-81-5.

Determination of a New Tetracyclic Diterpene Skeleton through Selective INEPT Spectroscopy

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Salvia prionitis Hance (Labiateae) is native to the Southern Provinces of the People's Republic of China and is used as an antibacterial, antitubercular and antiphlogistic drug in traditional Chinese medicine. Previous phytochemical studies on this plant have described the isolation of several abietane and 4,5-seco-5,10-*friedo*-abietane diterpenoids.[3,4]

We report here on the isolation and structure elucidation of a new type of tetracyclic diterpene, prionitin (1), obtained by chromatographic separation of the chloroform-soluble part of the crude ethanolic extract of the roots of

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