

hexane under ice cooling.⁸ When the reaction was complete water was added and the methylenecyclohexane formed was analyzed by vpc using ethylbenzene as internal reference. The yield was 71% (based on 3-pyrroline perchlorate). In another experiment, decomposition of pure spiro salt **3** with *n*-BuLi gave a quantitative yield of methylenecyclohexane. Other examples tried are summarized in the Table I.

(8) *Ca.* 1.5 or 2.0 mol of *n*-BuLi-hexane was used. A few minutes after the crystals of **3** had disappeared and the reaction finished, the reaction mixture became thick by the deposition of LiClO₄.

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1,3-Dipolar and Diels-Alder Reactions of Reissert Salts with Stilbenes and Tolans

Sir:

Although freshly prepared hydrofluoroborate salts of 2-acyl-1,2-dihydroisoquinaldonitriles (Reissert compounds¹) usually have the structure **1**, they readily isomerize to **3** and **4** in solution by way of the mesoionic intermediate **2**.² 1,3-Dipolar addition reactions of these salts with reactive acetylenic 1,3-dipolarophiles, such as dimethyl acetylenedicarboxylate, ethyl phenylpropionate, and ethyl tetrolate, have been shown to take place in high yields.³⁻⁵ Also, complex condensation-rearrangement reactions of these salts, the initial step of which is thought to be a Diels-Alder reaction involving **4**,⁶ have been shown to occur with reactive olefinic dienophiles, such as ethyl cinnamate, dimethyl maleate, and ethyl acrylate.^{7,8}

In all of the reactions studied up to the present time, the Reissert salts have given only 1,3-dipolar addition products with alkynes and only the complex condensation-rearrangement products with alkenes. We considered this to be somewhat unusual, inasmuch as both 1,3-dipolar addition reactions and Diels-Alder reactions are known to occur with either alkenes or alkynes. Furthermore, the rates of 1,3-dipolar addition reactions of sydnone and murchonone with structurally similar alkenes and alkynes are not greatly different.⁹

We have now carried out reactions of 2-benzoyl-1,2-dihydroisoquinaldonitrile hydrofluoroborate (**1**, R = C₆H₅) with stilbene and tolan. The reaction of **1** (R = C₆H₅) with stilbene was carried out in DMF solution at 100° for 18 hr, and there was obtained the known^{10,11}

(1) A. Reissert, *Ber.*, **38**, 1603, 3415 (1905).

(2) W. E. McEwen, M. A. Calabro, I. C. Mineo, and I. C. Wang, *J. Amer. Chem. Soc.*, **95**, 2392 (1973).

(3) W. E. McEwen, I. C. Mineo, Y. H. Shen, and G. Y. Han, *Tetrahedron Lett.*, 5157 (1968).

(4) W. E. McEwen, I. C. Mineo, and Y. H. Shen, *J. Amer. Chem. Soc.*, **93**, 4479 (1971).

(5) W. E. McEwen, K. B. Kanitkar, and W. M. Hung, *J. Amer. Chem. Soc.*, **93**, 4484 (1971).

(6) E. K. Evangelidou and W. E. McEwen, *J. Org. Chem.*, **31**, 4110 (1966).

(7) Y. F. Hua, Doctoral Dissertation, University of Massachusetts, Amherst, 1968.

(8) R. M. Padronaggio, M.S. Thesis, University of Massachusetts, Amherst, 1971.

(9) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).

(10) W. E. McEwen, T. T. Yee, T. K. Liao, and A. P. Wolf, *J. Org. Chem.*, **32**, 1947 (1967).

(11) W. E. McEwen, D. H. Berkebile, T. K. Liao, and Y. S. Lin, *J. Org. Chem.*, **36**, 1459 (1971).

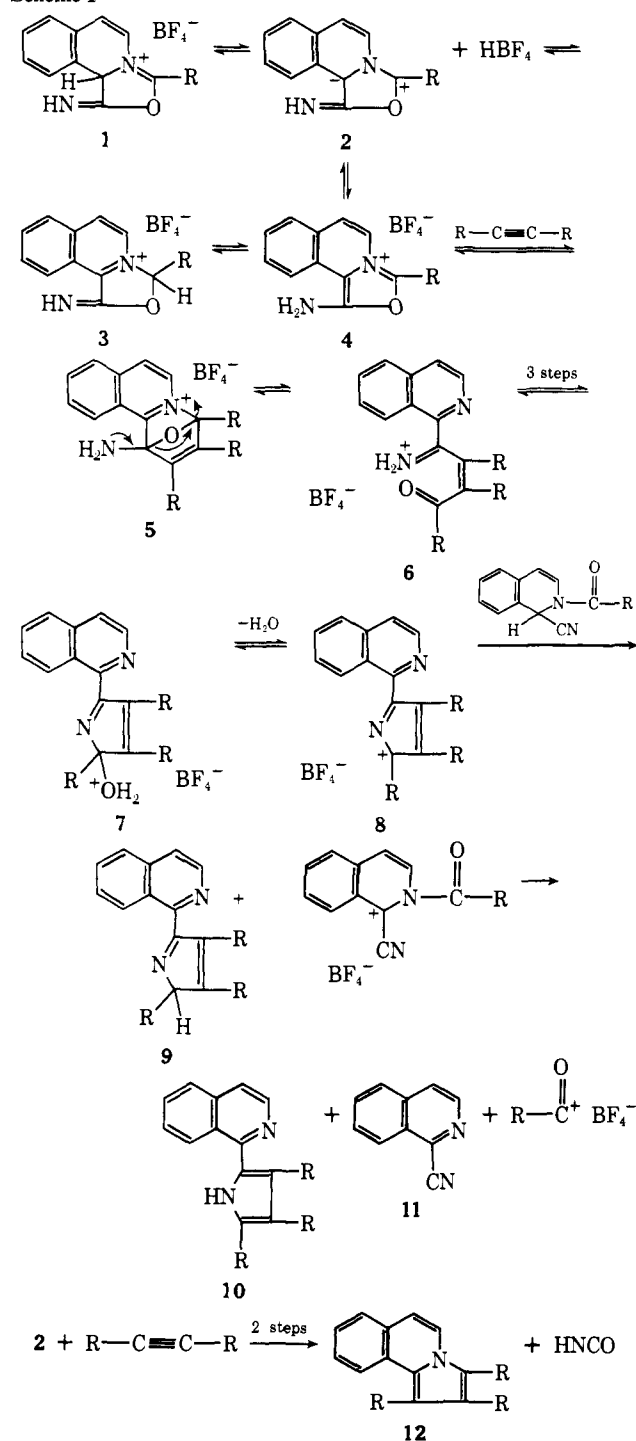
2-(1-isoquinolyl)-3,4,5-triphenylpyrrole (**10**, R = C₆H₅) in 34% yield, but no trace of a product of a 1,3-dipolar addition reaction could be found. The reaction of **1** (R = C₆H₅) with tolan was carried out in refluxing DMF solution (*ca.* 153°) for 24 hr, and there was obtained a mixture of products, which included 1,2,3-triphenylpyrrolo[2,1-*a*]isoquinoline (**12**, R = C₆H₅), mp 178-179°, 2-(1-isoquinolyl)-3,4,5-triphenylpyrrole (**10**, R = C₆H₅), and isoquinaldonitrile (**11**). Unreacted tolan, which had been used in threefold excess, was recovered in 82% yield, and the yields of **12**, **10**, and **11**, based on the amount of **1** (R = C₆H₅) used, were 28, 6.4, and *ca.* 1%, respectively. We were able to show conclusively, by means of control experiments, that **10** (R = C₆H₅) arose from the reaction of **1** (R = C₆H₅) with tolan, and that its formation was not attributable to the presence of a small amount of stilbene, as an impurity, in the tolan. Thus, for the first time, we have found evidence for competing 1,3-dipolar addition and Diels-Alder condensation reactions of a Reissert salt.

In order to obtain an estimate of the relative rates of the competing 1,3-dipolar and condensation-rearrangement sequences, a mixture of 8.64 × 10⁻² mol of *trans*-stilbene, 8.64 × 10⁻² mol of tolan, and 2.88 × 10⁻³ mol of **1** (R = C₆H₅) was heated in DMF solution at 100° for 24 hr. There was obtained 0.73 g (60%) of **10** (R = C₆H₅) and 0.16 g (14%) of **12** (R = C₆H₅). Thus, the approximate rate ratio of the Diels-Alder condensation-rearrangement sequence to the 1,3-dipolar addition sequence was about 4, this value being corrected for the relatively small amount of **10** (R = C₆H₅) formed in the reaction of **1** (R = C₆H₅) with tolan.

The mechanisms of the 1,3-dipolar addition reactions³⁻⁵ and of the complex condensation-rearrangement reactions^{6,10} have been depicted elsewhere. We tentatively suggest that the mechanism of the reaction by which **10** (R = C₆H₅) and **11** are obtained from **1** (R = C₆H₅) and tolan is that shown in Scheme I. A key step in this overall transformation is the transfer of a hydride ion from 2-benzoyl-1,2-dihydroisoquinaldonitrile, which is present in equilibrium with **1** (R = C₆H₅), to the intermediate carbonium ion **8**, a precursor of **10**.

In the light of these results, we are now able to provide an explanation for the fact that alkenes ordinarily give complex condensation-rearrangement products which arise from Diels-Alder adducts in reactions with **1**, while alkynes ordinarily give 1,3-dipolar addition products, or compounds derived from them. We have already demonstrated⁵ that the reaction between **1** (R = C₆H₅) and ethyl phenylpropionate in DMF-ethanol solution at 41° is a second- and first-order reversible one, and it is well known that Diels-Alder reactions are reversible. Thus, it is reasonable to assume that the equilibrium mixture of **1**, **2**, **3**, and **4** undergoes the initial steps of both types of reaction with both alkenes and alkynes. With alkynes, however, the subsequent pathway to form a fully aromatic heterocyclic product *via* the 1,3-dipolar addition intermediate (which involves merely loss of isocyanic acid from a bridged adduct^{3,4}) has a smaller overall free energy of activation than the conversion of the Diels-Alder adduct of type **5** to the final, fully aromatic product of type **10** *via* **6-9**. The reverse relative con-

Scheme I



figurations of the respective energy profiles hold true when an alkene is used as the substrate. Thus, under conditions whereby the reactions are forced to completion, alkynes mainly form products of type 12, and alkenes form products of type 10.

An independent and unambiguous synthesis of 12 ($\text{R} = \text{C}_6\text{H}_5$) has been achieved. The lithium salt of 1-benzylisoquinoline was caused to react with 2-(α -bromobenzyl)-2-phenyl-1,3-dioxolane (the ethylene glycol ketal of desyl bromide), and the mixture of reaction products was treated with polyphosphoric acid. A small quantity (ca. 2%) of 10 ($\text{R} = \text{C}_6\text{H}_5$) was isolated from the reaction mixture. Its ir and nmr spectra were identical with those of the product obtained by the

reaction of 1 ($\text{R} = \text{C}_6\text{H}_5$) with tolan, and a mixture melting point test of the two samples showed no depression.

p-Nitrostilbene has been caused to react with 1 ($\text{R} = \text{C}_6\text{H}_5$) in DMF solution for 18 hr at 100° , and 2-(1-isoquinolyl)-3-*p*-nitrophenyl-4,5-diphenylpyrrole was isolated in 45% yield. The structure of the product was proved by its conversion *via* the amino derivative and its diazonium salt to be the known¹¹ 2-(1-isoquinolyl)-3-*p*-anisyl-4,5-diphenylpyrrole. The reaction of *p*-methoxystilbene with 1 ($\text{R} = \text{C}_6\text{H}_5$) under the same conditions as specified for the corresponding reaction of *p*-nitrostilbene gave 2-(isoquinolyl)-3-*p*-anisyl-4,5-diphenylpyrrole in 18% yield and 2-(1-isoquinolyl)-4-*p*-anisyl-3,5-diphenylpyrrole in 9% yield. The reaction of 1 ($\text{R} = \text{C}_6\text{H}_5$) with *p*-methoxytolan in refluxing DMF solution for 24 hr gave, in 12% yield, a mixture of 1,3-diphenyl-2-*p*-anisylpyrrolo[2,1-*a*]isoquinoline and 2,3-diphenyl-1-*p*-anisylpyrrolo[2,1-*a*]isoquinoline in a ratio of 1:2. There was also obtained, in 5.4% yield, a mixture of 2-(1-isoquinolyl)-3,5-diphenyl-4-*p*-anisylpyrrole and 2-(isoquinolyl)-3-*p*-anisyl-4,5-diphenylpyrrole in a ratio of about 35:65. Under the same reaction conditions, 1 ($\text{R} = \text{C}_6\text{H}_5$) and *p*-nitrotolan gave, in 31% yield, a mixture of 2,3-diphenyl-1-*p*-nitrophenylpyrrolo[2,1-*a*]isoquinoline and 1,3-diphenyl-2-*p*-nitrophenylpyrrolo[2,1-*a*]isoquinoline in a ratio of about 2:1. Also, there was obtained, in 7.3% yield, a mixture of 2-(1-isoquinolyl)-4-*p*-nitrophenyl-3,5-diphenylpyrrole and 2-(1-isoquinolyl)-3-*p*-nitrophenyl-4,5-diphenylpyrrole in approximately a 1:1 ratio. The formation of mixtures of isomers in most of these reactions indicates that the initial condensation reactions involve essentially synchronous formation of two new covalent bonds in each ring closure, as indicated in previous publications.⁴⁻⁶ The structures of all of the products cited above were proved by unambiguous methods.

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Correlation between Deuterium and Carbon-13 Relaxation Times. A Convenient Means to Determine the Mechanism of ^{13}C Relaxation and ^2H Quadrupole Coupling Constants

Sir:

The dominant contribution to ^{13}C magnetic relaxation comes from the $^{13}\text{C}-^1\text{H}$ dipole-dipole interaction, except for very small molecules or rapidly rotating methyl groups where spin-rotation interaction has also to be considered. Scalar interaction and chemical shift anisotropy usually do not contribute significantly to the ^{13}C relaxation of protonated carbons.^{1,2} If

(1) (a) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N. Y., 1971; (b) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972.

(2) (a) G. C. Levy and G. L. Nelson, *J. Amer. Chem. Soc.*, **94**, 4897 (1972); (b) G. C. Levy, J. D. Cargioli, and F. A. L. Anet, *ibid.*, **95**, 1527 (1973).