

Structures and Isomerism of the Hydrofluoroborate Salts of Reissert Compounds

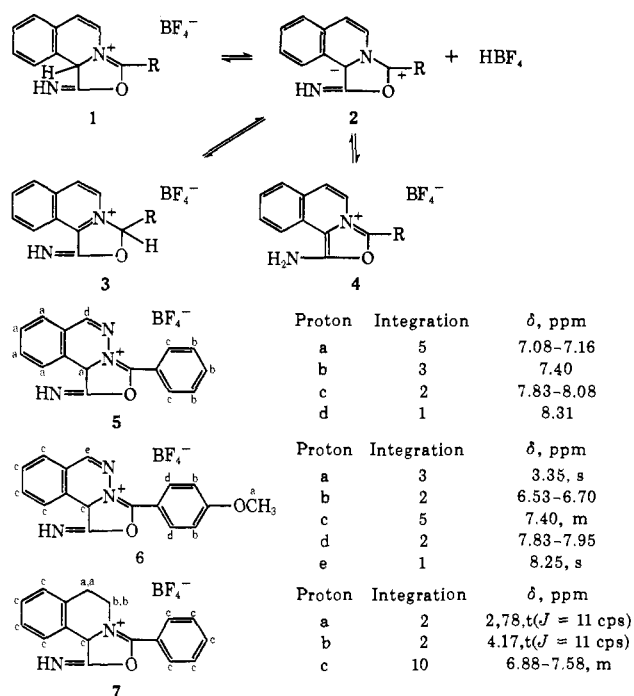
Sir:

The hydrofluoroborate salts of 2-acyl-1,2-dihydroisoquinaldonitriles, also known as Reissert compounds,¹ are useful reagents in synthesis. They undergo 1,3-dipolar addition reactions with alkynes² and complex condensation-rearrangement reactions with alkenes,³ the initial step of which is thought to be a Diels-Alder type of condensation.⁴ The reactive intermediate in the 1,3-dipolar addition reaction is the conjugate base, **2**, of the Reissert salt, while that of the Diels-Alder reaction has the structure **4**.

The detailed structures of several hydrofluoroborate salts of Reissert compounds have now been investigated by means of pmr spectroscopy and by hydrolysis experiments. 2-Benzoyl-1-cyano-1,2-dihydrophthalazine⁵ hydrofluoroborate (**5**), mp 225–227° dec, was prepared by the addition of 48% fluoroboric acid to an acetic acid solution of the Reissert compound, and the salt was recrystallized from absolute ethanol. The pmr spectrum, taken in a fresh trifluoroacetic acid solution, was clearly consistent with structure **5**, the assumption being made that the proton of the =NH group exchanges rapidly with the acidic protons of the solvent and consequently does not appear in the spectrum. Also consistent with this structure is the fact that treatment with sodium bicarbonate solution leads to recovery of the original Reissert compound in 96% yield; rearranged salts of types **3** or **4** are known⁶ to give aldehydes plus heterocyclic amides on treatment with an alkaline aqueous solution. Of course, treatment of **5** or the parent Reissert compound with an aqueous acid solution gives benzaldehyde in high yield.^{5,6}

Similar conclusions with regard to the structures of the salts were reached by examination of the pmr spectra and hydrolysis behavior of 2-*p*-anisoyl-1-cyano-1,2-dihydrophthalazine hydrofluoroborate (**6**), mp 234–235° dec, and 2-benzoyl-1,2,3,4-tetrahydroisoquinaldonitrile⁷ hydrofluoroborate (**7**), mp 197–199° dec, both of which gave back the unchanged Reissert compound on treatment with cold sodium bicarbonate solution. In agreement with the observations of Elliott and Leflore,⁸ we found that direct acid-catalyzed hydrolysis of the latter compound gave only benzoic acid. However, when the salt was first stirred in dimethylformamide solution for 5 hr and then subjected to hydrolysis, benzaldehyde was obtained. Thus, isomerization of the initially prepared salt of type **1** structure to one of type **3** or type **4** structure (or both) had occurred during the period of digestion in DMF.

More direct information about the isomerization of Reissert salts was obtained by pmr spectral examina-



tion of 2-acetyl-1,2-dihydroisoquinaldonitrile hydrofluoroborate (**1**, R = CH₃). This salt, mp 169–170° dec, was prepared in the usual manner,² and the pmr spectrum of a fresh solution in DMSO-*d*₆ showed a singlet at δ 2.88 (3 H) and a multiplet at δ 7.2–7.8 (7 H). Treatment of this salt with 5% sodium hydroxide solution led to the recovery of 2-acetyl-1,2-dihydroisoquinaldonitrile in 100% yield. The hydrofluoroborate salt (6.0 g) of mp 169–170° dec was suspended in 150 ml of chloroform and 30 ml of trifluoroacetic acid was added; the solution was stirred for 75 min at room temperature. The clear solution was filtered and the filtrate added to 1200 ml of anhydrous ether. A yellow solid was collected, allowed to dry with the aspirator on until it became granular, and then it was washed with a small amount of anhydrous acetone. There was obtained 1.30 g of a new salt, mp 232–233° dec. The pmr spectrum of this salt was taken in pure trifluoroacetic acid solution, TMS being used as an external standard, and showed a 3 H doublet at δ 1.68 ($J = 6$ cps), a 1 H quartet at δ 6.54 ($J = 6$ cps), and a series of multiplets at δ 7.6–8.9 (6 H). This is clearly consistent with structure **3** (R = CH₃). Furthermore, acetaldehyde was obtained on treatment of the new salt with 5% sodium bicarbonate solution. The mechanism of the latter type of hydrolysis reaction has been given elsewhere.⁶ Finally, the salt **1** (R = CH₃) was allowed to equilibrate in deuteriochloroform containing sufficient trifluoroacetic acid to provide a homogeneous solution. The original methyl singlet at δ 2.85 was rapidly transformed at room temperature to a doublet at δ 2.13 ($J = 6$ cps), characteristic of **3** (R = CH₃), and singlets at δ 2.91 and 3.09, respectively. Equilibrium was obtained in about 70 min, and **3** was the predominant (at least 75%) component of the equilibrium mixture.

Finally, 2-*p*-anisoyl-1,2-dihydroisoquinaldonitrile hydrofluoroborate^{2,9} was dissolved in trifluoroacetic acid, and its pmr spectrum was taken after an equilib-

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rium among the various salts had been achieved. The average of 13 integrations gave the ratio of 3.5 to 1 of aromatic protons to methoxyl protons. For structure **1** or **3** ($R = p$ -anisyl) the ratio would be 3.7 to 1. For structure **4** ($R = p$ -anisyl), the ratio would be 3.3 to 1. Thus, the tentative conclusion was reached that the equilibrium mixture in solution contained about 50% of **4** ($R = p$ -anisyl) in this system.

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William E. McEwen,* Michael A. Calabro
Isidore C. Mineo, Irene C. Wang

Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01002

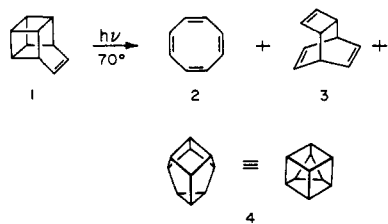
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Concurrent Thermolysis and Photolysis of Basketene. Formation and the Interrelation of Some New $(CH)_{10}$ Isomers

Sir:

The part of organic chemistry dealing with the $(CH)_{10}$ hydrocarbons continues to be of interest to many people.¹ Currently a large effort is being directed toward mapping of the energy surfaces and understanding what factors influence the relative positions of the minima. In this regard, we wish to report that basketene (**1**) can be converted to a new $(CH)_{10}$ isomer **4**.² We also describe the interrelation of some of the isomers in this new facet of $(CH)_{10}$ chemistry.

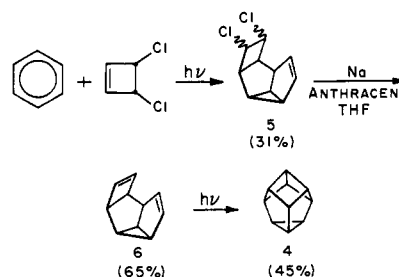
Irradiation of a 1% solution of **1**³ in cyclohexane (Vycor tube) with 2537-Å light for 10 days at 70° produced **2** (ca. 2%), **3** (30–35%), and **4** (10–15%) as the



major products. Compounds **2** and **3** were isolated by glpc and were identified as cyclooctatetraene and Nenitzescu's hydrocarbon,⁴ respectively, by nmr spectral comparisons with authentic samples. Preparative glpc afforded a pure sample of **4**, mp 101–102° (sealed capillary). The structure assigned to **4** follows directly from the spectral data. A high-resolution mass spectrum establishes the molecular formula as $C_{10}H_{10}$ (calcd, m/e 130.0783; obsd, m/e 130.0786). The proton nmr spectrum ($CDCl_3$), which exhibits only two complex multiplets centered at τ 6.5 (6 H) and 7.4 (4 H), eliminates structures with vinyl hydrogens. The proton noise-decoupled carbon-13 nmr spectrum (C_6H_6) shows signals as singlets at 70.70 (3 C), 78.08 (3 C),

78.22 (3 C), and 96.64 (1 C) ppm upfield from benzene.⁵ Off-resonance decoupling displays each signal as a doublet.⁶ These data exclude all structures with trigonal carbons⁷ and clearly establish that each carbon is tetrahedral and bears a single hydrogen substituent. The ir spectrum (CCl_4) is quite simple and is characterized by a 3040-cm^{-1} absorption which is diagnostic of a cyclopropane moiety.⁸ Reference to Balaban's⁹ and Lederberg's¹⁰ complete lists of all the $(CH)_{10}$ isomers and examination of models singles out **4** as the only structure which fits the special requirement of four different types of carbon atoms in the ratio of 3:3:3:1 and which is consistent with all of the other observations.¹¹

The structure assigned to **4** has been confirmed by independent synthesis. Photochemical addition of benzene to 3,4-dichlorocyclobutene¹² produced **5**,¹³ which on treatment with sodium anthracene in tetrahydrofuran¹⁴ gave the tetracyclodecadiene **6**.¹⁵ Intra-



molecular photochemical closure of **6** led directly to **4**.

The question of the nature of the reaction pathway which leads from **1** to **4** is of special interest because of the intrinsic need of other $(CH)_{10}$ isomers in effecting the conversion. Control experiments with **1** show that thermolysis in the absence of light yields only **3** and that photolysis at 0° does not produce **4**. Photolysis of **3** at 70° also does not produce **4**. These results clearly indicate the involvement of a thermally generated intermediate which undergoes photochemical transformation. A likely candidate for this intermediate is tricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene (**7**), the known intermediate in the thermal isomerization of **1**

(5) Measured with a Varian XL-100-15 Fourier transform nmr spectrometer.

(6) W. O. Crain, W. C. Wildman, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 990 (1971).

(7) Carbon-13 signals for vinyl carbon atoms appear some 70 ppm downfield from any of the carbons in **4**. For example, the vinyl carbons of norbornene appear 6.61 ppm downfield from benzene (unpublished work in our laboratory). See also D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).

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(11) The occurrence of the cyclopropyl proton nmr absorption below τ 8 has precedent. For example, see A. Meijere, D. Kaufmann, and O. Schallner, *Angew. Chem., Int. Ed. Engl.*, **10**, 417 (1971); L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 6366 (1970).

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(15) Compound **6** had the correct mass and nmr spectra. Its structure was established unequivocally by partial hydrogenation (Pd/C) to tetracyclo[5.3.0.0^{2,10}.0^{8,9}]dec-8-ene of known 3,6-endo configuration.¹³

(1) For an extensive review and list of references see L. T. Scott and M. Jones, *Chem. Rev.*, **72**, 181 (1972).

(2) The systematic name assigned to **4** by Dr. K. L. Loening, Chemical Abstracts Service, is hexacyclo[4.4.0.0^{2,4}.0^{3,9}.0^{5,8}.0^{7,10}]decane.

(3) S. Masamune, H. Cuts, and M. Hogben, *Tetrahedron Lett.*, 1017 (1966); W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966).

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