Chemistry of 2-Carbenabicyclo[3.2.2]nona-3,6,8-triene[1]

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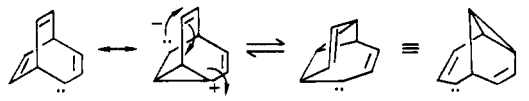
Received August 4, 1981

Pyrolysis of the lithium salt of the tosylhydrazone of bicyclo[3.2.2]nona-3,6,9-trien-2-one (**10**) produces indene and 7-ethynyl-1,3,5-cycloheptatriene. As an aid in analyzing likely carbene to carbene rearrangements, the pyrolytic decomposition of the lithium salt of tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-one tosylhydrazone was studied and found to result in the formation of indene as the sole volatile product. The decomposition of the lithium salt of tosylhydrazone **10** is discussed in terms of carbenes **13**, **15**, **16**, and **6a** and allene **14**.

Our interest in homoaromatic carbenes and in carbene intermediates with a potential for carbene to carbene rearrangements is the basis for our investigation of the nature of 2-carbenabicyclo[3.2.1]octa-3,6-diene (**1**, Chart I), which provided evidence for rearrangement of singlet **1** to bishomoaromatic carbene **2** (or alternatively rearrangment to allene **4**) and to bivalent **3**. In competition with these processes, singlet **1** apparently undergoes intersystem crossing to triplet **1**, which generates hydrogen abstraction products.[2]

If one introduces a third π ribbon by substituting a vinylene bridge for the methylene bridge of **1**, then carbenatricyclononatriene **5** is created, which might be expected to be a stabilized longicyclic carbene with π ribbons $2^{+}2^{+}3^{-}$ (not $2^{+}2^{+}3^{+}$)[3] and, thus, also potentially electrophilic in nature. In addition to the interesting prospects for transannular delocalization, carbene **5** might readily undergo a carbene to carbene rearrangement, generating bivalent **6a**, which can be viewed as a stabilized longicyclic carbene, a collapsed $1^{-}3^{+}3^{-}$ system (eq 1). Due to the



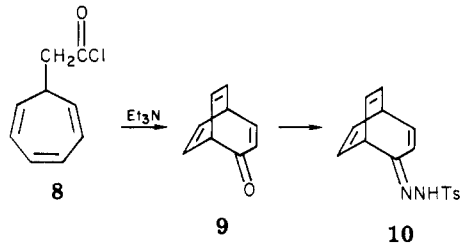
(1)

5 **6a**

symmetry of **5** a carbene rearrangement of this type would set up an equilibrium of enantiomeric carbenes **6a** and **6b**; in addition, the closely related interconversion of bivalent intermediates **7a** and **7b** seems equally plausible. Thus, a most interesting feature of this system is that two different degenerate rearrangements (**6a** ⇌ **6b**, **7a** ⇌ **7b**) and several carbene to carbene rearrangements may occur (Scheme I).

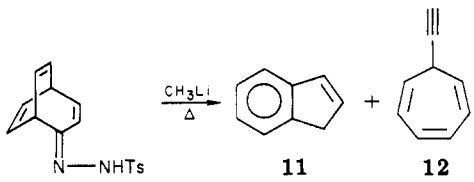
The key intermediate for the initiation of a study of carbene **5** is the related bicyclononatrienone **9** which was prepared by the method of Grutzner and Winstein from cycloheptatrienylacetyl chloride (**8**, eq 2).[4] The tosylhydrazone **10** was prepared by treating ketone **9** with tosylhydrazine in methanol with pyridine as a catalyst.

Tosylhydrazone **10** was converted to its lithium salt and the dry salt pyrolyzed by the static method at 130–185 °C. Two major volatile products were produced (eq 3), indene



(2)

8 **9** **10**



(3)

10 **11** **12**

11 (14%) and 7-ethynyl-1,3,5-cycloheptatriene **12** (8%), which were identified by NMR and infrared spectral comparison with the data of authentic samples. Two minor products were formed in 0.9% and 0.6% yields, but neither was identified.

Both major components **11** and **12** have the same molecular formula, C_9H_8, as parent carbene **5**, which provides an interesting contrast to the chemistry of 2-carbenabicyclo[3.2.1]octa-3,6-diene (**1**), in which abstraction of two hydrogen atoms is the major process. By analogy to the carbenabicyclooctadiene case it appears reasonable to suggest that a 1,2 hydrogen shift in carbene **5** generates **15** either via allene **14** or directly (Scheme II). Cyclopropylcarbene fragmentation[5] of bivalent **15** or cleavage directly from **14** leads to 7-ethynylnorcaradiene **17** which would undergo Cope rearrangement to monocyclic **12**.[6] A second option is available to carbene **15**, a cycloreversion ($_{\sigma}2_s + \sigma 2_s + {}_{\pi}2_s$) reaction producing carbenabicyclo[4.2.1]nonatriene **16**, which would be expected to rearrange to indene. Shechter and co-workers[7] have generated bivalent **16** from the corresponding tosylhydrazone and propose that it undergoes (a) valence isomerization to **15** and cleavage to **17**, with **17** forming **12**, and (b) a 1,2 vinyl shift (**16** ↔ **18** → **19**), followed by a [1,5] sigmatropic hydrogen shift to form indene **11** (Scheme III). The for-

(1) Reported in preliminary form: Freeman, P. K.; Swenson, K. E. 33rd Northwest Regional Meeting of the American Chemical Society, Seattle, WA, June 1978; American Chemical Society: Washington, DC, 1978; Abstract No. 198.

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(4) Grutzner, J. B.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2200.

(5) Freeman, P. K.; Balls, D. M. *J. Org. Chem.* **1967**, *32*, 2354. Freeman, P. K.; Kuper, D. G. *Ibid.* **1965**, *30*, 1047. Guarino, A.; Wolf, A. P. *Tetrahedron Lett.* **1969**, 655. Berson, J. A.; Bauer, W.; Campbell, M. M. *J. Am. Chem. Soc.* **1970**, *92*, 7515. Jones, M., Jr.; Reich, S. D. *Ibid.* **1967**, *89*, 3935. Kirmse, W.; Pook, K.-H. *Chem. Ber.* **1965**, *98*, 4022. Friedman, L.; Schechter, H. *J. Am. Chem Soc.* **1960**, *82*, 1002. Sauers, R. R.; Schlosberg, S. B.; Pfeffer, P. E. *J. Org. Chem.* **1968**, *33*, 2175. Lemal, D. M.; Fry, A. J. *Ibid.* **1964**, *29*, 1673. Cristol, S. J.; Harrington, J. K. *Ibid.* **1963**, *28*, 1413.

(6) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 402.

(7) Antowiak, T. A.; Sanders, D. C.; Trimitsis, G. B.; Press, J. B.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 5366. Babu, T. V. R.; Shechter, H. *Ibid.* **1976**, *98*, 8261.

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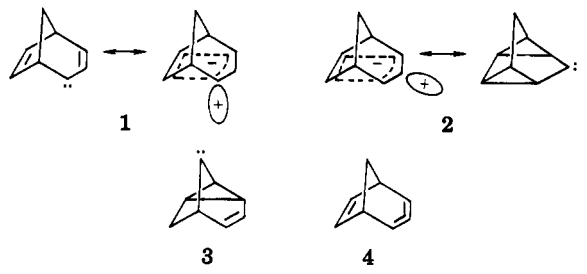
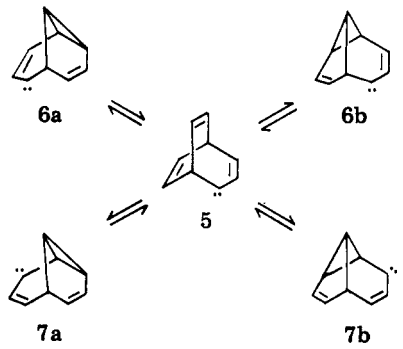
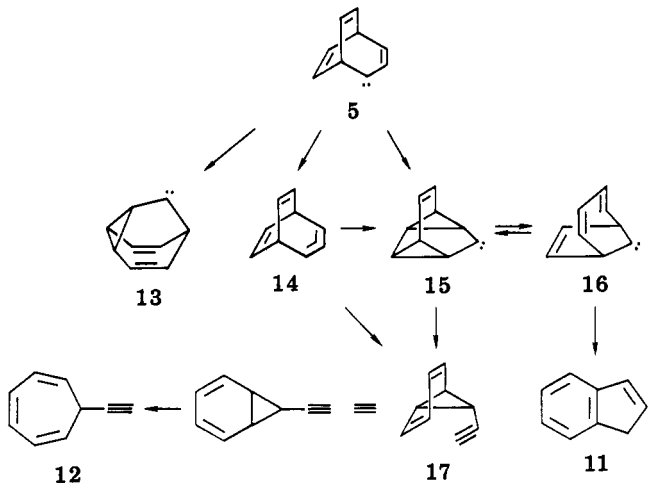
Chart I



Scheme I

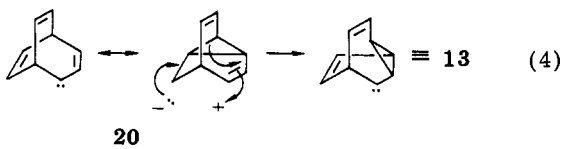


Scheme II



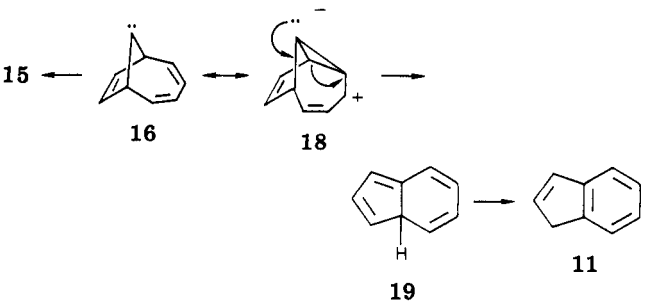
mation of **16** as the initial carbene species results in indene (**11**) and ethynylcycloheptatriene **12** in a ratio of 95:5, while generation of **5** directly from the corresponding tosylhydrazone salt produces **11** and **12** in a ratio of 64:36.

There is, however, an additional pathway for the formation of ethynylcycloheptatriene **12** suggested by analogy to the rearrangement of 2-carbenabicyclooctadiene **1** to bivalent **3**. A carbanionic cyclopropylcarbinyl to allylcarbinyl rearrangement[8] (**20** → **13**, eq 4) leads to barbaralylidene (**13**), which would be expected to undergo cyclopropylcarbene cleavage to ethynylcycloheptatriene **12**.

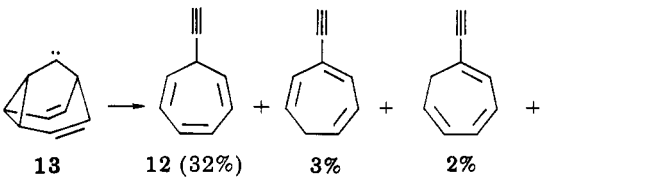


(4)

Scheme III



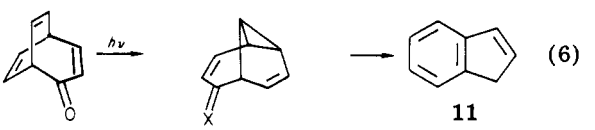
Barbaralylidene **13** has, in fact, been generated by pyrolysis of the corresponding sodium salt of the tosylhydrazone.[9] The products obtained were the three ethynylcycloheptatrienes and seven aromatic compounds (eq 5). It was assumed that **12** was the product formed from



seven aromatic compounds (5)

the carbene, and the two minor ethynylcycloheptatrienes were derived from it by thermal 1,5 hydrogen shifts. No yields for the aromatic compounds were given, but **12** was the major product. Of particular interest is the fact that indene is not one of the aromatic compounds found. Since indene is the major product of carbene **5** and a large array of aromatics is not formed, the mechanism involving the strained allene **14** and/or **15**, (Scheme II) remains more attractive.

Since, at the start we viewed the carbene to carbene rearrangement **5** → **6a** (Scheme I) as a reasonable expectation, we prepared the tosylhydrazone corresponding to **6a** (**22**) using the oxa-di-π-methane rearrangement of starting ketone **9**[10] (eq 6). Tricyclic ketone **21** was converted to tosylhydrazone **22** by reaction with tosylhydrazine in methanol with a pyridine catalyst. The tosylhydrazone was decomposed by treatment with potassium hydride and 18-crown-6 in diglyme. The only volatile product obtained was indene in 14% yield (a VPC peak for an additional component present to an extent of 3% of the indene component would have been detected). To rule out the possibility that the indene is derived from a possible indanone tosylhydrazone impurity in tosylhydrazone **22**, indanone tosylhydrazone was prepared and decomposed under similar conditions. Two volatile compounds, indene (6.9%) and an unknown (1.6%) were obtained. A reported photolysis of diazoindane is in harmony with these results. The products obtained were indene (10%), indanone (5%), and 1-indanone azine (50%).[11]



(6)

21, X = O
22, X = NNHTs

(8) Wilson, S. E. *Tetrahedron Lett.* **1975**, 4651. Maercker, A.; Geuss, R. *Chem. Ber.* **1973**, *106*, 773. Maercker, A.; Streit, W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 542. Moncar, M. V.; Grutzner, J. B.; Eisenstadt, A. *J. Org. Chem.* **1974**, *39*, 1604. Staley, S. W.; Reichard, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 3998. Grutzner, J. B.; Winstein, S. *Ibid.* **1968**, *90*, 6562.

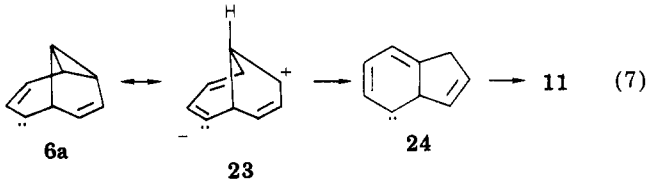
(9) Tsuruta, H.; Mori, S.; Nishizawa, Y.; Makai, T.; Murashashi, S.; Hino, K.; Bansho, K.; Moritani, I. *Chem. Lett.* **1974**, 1497.

(10) Paquette, L. A.; Broadhurst, M. J. *J. Org. Chem.* **1973**, *38*, 1893. Kende, A. S.; Goldschmidt, Z. *Tetrahedron Lett.* **1970**, 783.

(11) Moss, R. A.; Funk, J. D. *J. Chem. Soc. C* **1967**, 2026.

This low yield of indene from 1-indanylidene derived from precursor tosylhydrazone provides evidence that the indene obtained from the decomposition of **22** did not come from a possible 5% indanone tosylhydrazone impurity. NMR analysis of tosylhydrazone **22** revealed no indanone tosylhydrazone, but as much as 5% may have gone undetected.

Since ethynylcycloheptatriene **12** is not observed as a consequence of the generation of carbene **6a** from tosylhydrazone **22**, the rearrangement of **6a** to **5** is not important, but it is possible that **6a** is formed irreversibly from **5** and then proceeds along a reaction pathway leading to indene. Such a pathway might involve bishomoaromatic carbene (**6a** ↔ **23**) which could as a result of a 1,2 hydrogen shift undergo carbene to carbene rearrangement to **24** which would generate indene (eq 7).



(7)

In summary, it is conceivable that 2-carbenabicyclo[3.2.2]nona-3,6,9-triene (**5**) is exhibiting its great versatility by rearranging to carbenahomosemibullvalene **6a**, carbenes **15** and **16**, and barbaralylidene **13** as well as allene **14** on the way to products. However, the picture which seems most reasonable and economical and which fits the chemistry observed for the parent system **1** is the rearrangement via **15** ⇌ **16** or **14** → **15** ⇌ **16** as illustrated in Scheme II. There are, however, no hydrogen abstraction processes revealed for the chemistry of 2-carbenabicyclononatriene **5**, which provides the strongest point of contrast with the reactions of carbenabicyclooctadiene **1**. This may be ascribed to a competition between 1,2-hydrogen migration generating allene and intersystem crossing in the initially formed carbene. Allene formation from carbene **1** might be slower than that from **5** due to the enhanced strain in a six-membered relative to a seven-membered cyclic allene and thus allow intersystem crossing to be observed. An interesting alternative is based on the INDO MO calculations of Dillon and Underwood[12] which suggest that 1,2-cyclohexadiene has a triplet ground state and 1,2-cycloheptadiene a singlet ground state. Thus, intersystem crossing might be anticipated for **4** (**4** → **25**) but not for **14**, providing an appealing rationale for the formation of the observed hydrogen abstraction products (eq 8).

(8)

Experimental Section

Melting points were determined by using a Büchi melting point apparatus and are uncorrected. All boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 727B infrared spectrophotometer. Proton NMR spectra were recorded on a Varian Associates EM-360 (60 MHz) or HA-100 (100 MHz) spectrometer. Mass spectra were obtained on a Varian-MAT CH-7 mass spectrometer interfaced to a System 150 data system. High-resolution mass spectra were carried out by the University or Oregon Chemistry Department. VPC analyses were carried out on an Aerograph A-90-P2 chromatography equipped with a thermal-conductivity detector. The following columns were used: (A) 15 ft × 0.25 in., aluminum, containing 6% DC-200 on Anakrom AS, 60/80 mesh; (B) 9 ft × 0.25 in., aluminum, containing 10% SE-30 on Chromosorb P, 60/80 mesh; (C) 11 ft × 0.25 in., aluminum, containing 15% DC-710 on Chromosorb P, 60/80 mesh.

Preparation of Bicyclo[3.2.2]nona-3,6,8-trien-2-one Tosylhydrazone (10). A 100-mL flask fitted with a magnetic stirrer and a drying tube was charged with 2.990 g (22.7 mmol) of the title ketone dissolved in 20 mL of methanol. To this ketone solution was added 4.210 g (22.7 mmol) of tosylhydrazine dissolved in 40 mL of methanol. After the addition of 1 mL of pyridine, the reaction was allowed to stir at room temperature overnight. The solution, which had yellowed slightly, was concentrated on a rotary evaporator to about half of its original volume and was stored in a freezer. This yielded 5.60 g (18.7 mmol, 82%) of the tosylhydrazone **10**. Recrystallization from ethanol yielded tosylhydrazone **10** with a melting point of 191–193 °C dec and an NMR spectrum that suggests that the tosylhydrazone exists as a mixture of its syn and anti isomers: NMR (100 MHz, $CDCl_3$) δ 7.87 (d, J = 8 Hz, 2 H, aromatic protons), 7.32 (d, J = 8 Hz, 2 H, aromatic protons), 6.68 (broadened t, J = 8 Hz, 1 H, vinyl proton), 6.51–6.05 (m, 4 H, vinyl protons), 5.61 (dd, J = 11, 2 Hz, 0.5 H, vinyl H-3 proton), 5.38 (dd, J = 11, 2 Hz, 0.5 H, vinyl H-3 proton), 4.52 (m, 0.5 H, H-1 bridgehead proton), 4.00 (m, 0.5 H, H-1 bridgehead proton), 3.63 (m, 1 H, H-5 bridgehead proton), 2.46 (broadened s, 3 H, aromatic methyl protons); IR (Nujol mull), 3230 (m), 1618 (w), 1600 (w), 1340 (s), 1175 cm^{-1} (s); high-resolution mass spectra, calcd for $C_{16}H_{16}N_2O_2S$ m/e 300.093, found m/e 300.093.

Dry Salt Pyrolysis of the Lithium Salt of Bicyclo[3.2.2]nona-3,6,9-trien-2-one Tosylhydrazone (10). A 50-mL flask fitted with a magnetic stirrer, septum, and N_2 inlet was charged with 0.1264 g (0.421 mmol) of the title tosylhydrazone **10** dissolved in 10 mL of anhydrous THF. To this solution was added via syringe 0.29 mL (0.42 mmol) of 1.47 M methyllithium in ether. Gas was evolved, and the solution was stirred at room temperature for 15 min. The THF was removed by blowing dry nitrogen over the stirred solution. When most of the THF had been removed, the standard decomposition apparatus was set up and the salt dried further by pumping at 0.1 torr while warming to 40 °C. The salt was decomposed by heating the flask to 185 °C, and the volatile products were collected in two traps maintained at −78 °C. Nitrogen evolution began at about 130 °C, and heating at 185 °C was continued for 15 min after nitrogen evolution had ceased. The volatile material in the traps was washed out with pentane and the pentane removed by distillation through a 7-in. Vigreux column. The remaining oil was analyzed by VPC (column A, 115 °C, 70 mL/min). Four products, G–J, were found with the following retention times and percent compositions G (6.5 min, 3.6%), H (8.8 min, 34.6%), I (11.5 min, 2.5%), J (14.8 min, 59.3%). Compounds H–J were collected by preparative VPC (column A, 115 °C, 70 mL/min). Compound H was identified as 7-ethynyl-1,3,5-cycloheptatriene (**12**) by comparison of its NMR and IR spectra with those published.[13] Compound I remains unknown: NMR (100 MHz, $CDCl_3$) δ 7.30–6.87 (m, 1 H), 6.18 (m, 1 H), 5.47 (m, 1 H, 2.31 (m, 2 H). Compound J was identified as indene (**11**) by comparison of its NMR and IR spectra with those of an authentic sample. Undecane internal standard was added, and the yields were determined as follows: G, 0.9%; 7-ethynyl-1,3,5-cycloheptatriene (**12**), 8.3%; I, 0.6%; indene (**11**), 14.2%.

Preparation of Tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-one (21). The procedure of Paquette and Broadhurst[10] was adapted for use in this laboratory. A 500-mL Pyrex flask was charged with 0.4269 g (3.23 mmol) of bicyclo[3.2.2]octa-3,6,8-trien-2-one (**9**) and 0.2095 g (0.781 mmol) of Michler's ketone [4.4′-bis(dimethylamino)-benzophenone] dissolved in 400 mL of anhydrous benzene. This solution was deoxygenated by bubbling nitrogen through it for 45 min and was irradiated through Pyrex with a 450-W Hanovia high-pressure mercury lamp. The reaction was followed by VPC (column B, 150 °C, 70 mL/min) monitoring the disappearance of starting material. After 85 min the reaction had gone to completion. The benzene was removed on the rotary evaporator, and replaced with 100 mL of pentane–ether (1:1). This caused the Michler's ketone to precipitate, and it was removed by fil-

(12) Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1974**, *96*, 779.

(13) Hoskinson, R. M. *Aust. J. Chem.* **1970**, *23*, 399.

tration. The filtrate was washed with three 50-mL portions of water and dried over sodium sulfate. Four more batches similar to this were run, with a total of 2.1100 g (0.0160 mol) of bicyclic ketone **9**. These five batches were combined, and the ether was removed on the rotary evaporator to leave a yellow oil, which was distilled [45–47 °C (0.08 torr)] through a short-path column to yield 0.6237 g (4.720 mmol) of the title ketone **21** for a 30% yield. This ketone was slightly contaminated (about 10%) with another ketone identified as 1-indanone by comparison of its NMR spectrum with that of an authentic sample. The title ketone **21** has the following: NMR (100 MHz, $CDCl_3$) δ 6.53 (dd, J = 10, 5 Hz, 1 H, H-7), 6.00 (d, J = 10 Hz, 1 H, H-6), 5.84 (dddd, J = 5, 2, 1 Hz, 1 H, H-3), 5.54 (ddd, J = 5, 2, 1 Hz, 1 H, H-2), 3.38 (dd, J = 8, 2 Hz, 1 H, H-4), 2.90 (dt, J = 8, 2 Hz, 1 H, H-1), 2.61 (dq, J = 8, 1 Hz, 1 H, H-9), 2.03 (dt, J = 8, 5 Hz, 1 H, H-8).

Preparation of Tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-one Tosylhydrazone (22). A 10-mL flask was charged with 0.399 g (3.02 mmol) of tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-one (**21**) and 0.562 g (3.02 mmol) of tosylhydrazine dissolved in 6 mL of methanol. To this solution were added 2 drops of pyridine, and the solution was stirred at room temperature. The reaction was monitored by TLC (silica gel, chloroform). After 5 h, the starting ketone had reacted, and the reaction solution was placed in the freezer to induce crystallization. No crystallization had occurred after 24 h. The methanol was removed on the rotary evaporator and the resulting brown oil dissolved in warm ethanol. This was cooled in a freezer overnight to yield 0.0878 g (0.292 mmol, 10%) of tosylhydrazone: mp 141–143 °C dec; NMR (100 MHz, $CDCl_3$) δ 7.86 (d, J = 8 Hz, 2 H, aromatic protons), 7.60 (broadened s, 1 H, NH proton), 7.32 (d, J = 8 Hz, 2 H, aromatic protons), 6.38 (d, J = 9 Hz, 1 H, H-6 proton), 6.12 (m, 1 H, H-7), 5.77 (m, 1 H, vinyl proton), 5.47 (dd, J = 7, 2 Hz, 0.5 H, vinyl proton), 5.27 (dd, J = 7, 2 Hz, 0.5 H, vinyl proton), 4.20–3.50 (m, 1 H, H-4), 2.46 (s superimposed on m, 4 H, aromatic methyl and cyclopropyl protons), 2.22 (m, 1 H, cyclopropyl proton), 1.74 (m, 1 H, cyclopropyl proton); the product appears uncontaminated by 1-indanone tosylhydrazone as indicated by the absence of 1-indanone tosylhydrazone absorptions at δ 2.70 and 3.04; IR (Nujol mull), 3205 (m), 1642 (w), 1600 (m), 1350 (s), 1175 cm^{-1} (s); high-resolution mass spectrum, calcd for $C_{16}H_{16}N_2O_2S$ m/e 300.093, found m/e 300.093.

Decomposition of Tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-one Tosylhydrazone (22) with Potassium Hydride and 18-Crown-6 in Diglyme. A 100-mL flask fitted with a magnetic stirrer and gas inlet was charged with 62.7 mg (0.345 mmol) of 22% potassium hydride in mineral oil. The potassium hydride was washed with five 5-mL portions of dry hexane. After removal of the last hexane wash, 10 mL of anhydrous diglyme was added and the flask thoroughly flushed with nitrogen. A solution of 75.6 mg (0.252 mmol) of the title tosylhydrazone **22** in 5 mL of diglyme was added to the stirred potassium hydride suspension. After the gas evolution had subsided, 67.3 mg (0.255 mmol) of 18-crown-6 in 3 mL of diglyme was added. The flask was fitted with a reflux condenser, and the reaction mixture was heated to 140 °C for 2.5 h. Upon cooling, it was poured into 200 mL of cold water and extracted three times with 60 mL of pentane. The pentane extracts were combined, washed five times with 100 mL of water, and dried over sodium sulfate. The pentane was removed by distillation through a 7-in. Vigreux column to leave about 0.5 mL of yellow oil which was analyzed by VPC (column C, 131 °C, 70 mL/min). Two compounds were present; the first at 12 min was identified as residual diglyme by VPC retention time and comparison of the NMR spectrum of the sample collected by preparative VPC with the spectrum of an authentic sample. The second compound at 18.5 min was identified as indene by VPC retention time and comparison of the NMR spectrum of the isolated compound (preparative VPC) with that of an authentic sample. No other compounds more than 3% of indene) were present by VPC. Tridecane internal standard was added, and the yield of indene was found to be 14%.

Decomposition of 1-Indanone Tosylhydrazone with Potassium Hydride in Tetrahydrofuran/Diglyme. A 100-mL flask fitted with a magnetic stirrer, reflux condenser, and gas inlet was charged with 97.5 mg (0.536 mmol) of 22% potassium hydride in mineral oil. The potassium hydride was washed five times with 10 mL of dry hexane, and after removal of the last hexane wash, 10 mL of anhydrous THF was added. To the stirred potassium hydride suspension was added 130.5 mg (0.435 mmol) of 1-indanone tosylhydrazone in 5 mL of THF. After the gas evolution had subsided, 111.6 mg (0.422 mmol) of 18-crown-6 in 5 mL of THF was added, and the reaction mixture was heated at reflux (65 °C) for 20 min. No nitrogen was evolved, so 22 mL of anhydrous diglyme was added, which raised the reflux temperature to 95 °C. The solution turned a deep blue-green color and was heated at reflux for 80 min. After cooling, the reaction mixture was poured into 150 mL of water, which resulted in the immediate loss of the blue-green color. This aqueous solution was extracted with four 40-mL portions of pentane. The combined pentane extracts were washed with five 100-mL portions of water and dried over sodium sulfate. The pentane was removed by distillation through a 7-in. Vigreux column to leave a small amount of yellow oil which was analyzed by VPC (column A, 125 °C, 65 mL/min). In addition to diglyme (9 min) two other products were found: an unidentified compound appeared at 11 min, and a compound identified as indene by comparison of its retention time at 14.8 min. The indene identification was verified by comparison of the NMR spectrum of the VPC-collected compound with that of an authentic sample. Dodecane internal standard was added, and the yield of indene was found to be 6.9% and that of the unknown 1.6%.

Registry No. 9, 17684-75-2; **10** (isomer 1), 81044-30-6; **10** (isomer 2), 81044-31-7; **10** Li salt (isomer 1), 81044-32-8; **10** Li salt (isomer 2), 81044-33-9; **11**, 95-13-6; **12**, 25928-15-8; **21**, 38898-62-3; **22**, 81044-34-0; 1-indanone tosylhydrazone, 73424-46-1.

Nucleophilic Displacement of Primary Amino Groups via 1-Substituted 4-Tosylimidazoles[1]

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Received October 27, 1981

Two methods are described for the replacement of primary amino groups, situated either α or γ to a heterocyclic nitrogen atom, by ethoxy, alkylthio, and arylthio substituents, by Wittig reagents, and by hydrogen. Both methods involve transformation of the primary amino group into a nucleofugic pendant heterocycle. The first converts the primary amino group into a 5-phenyl-1-tetrazolyl substituent by benzoylation, formation of the imidoyl chloride, and reaction with sodium azide, while the second converts the primary amino group into a 1-(4-tosylimidazolyl) substituent by reaction with triethyl orthoformate and acid to give the (ethoxymethylene)amino derivative, which is then condensed with tosylmethyl isocyanide (TosMIC) anion. The 1-(4-tosylimidazolyl) substituent is shown to be more susceptible to nucleophilic displacement by a wider range of nucleophiles.

Primary amino groups α to a heteroatom are among the most accessible of functional groups in heterocyclic systems because of their genesis either from terminal ring closure reactions involving intramolecular addition of an appro-

0022-3263/82/1947-2043$01.25/0