13a/13c pair; ^{1}H NMR δ 5.83 (q, 2 H, C_5H and C_7H), 5.07 (m, 2 H, C_4H and C_8H), 2.7 and 2.1 (m, 9 H overall, bis-allylic, allylic, and methyne H), 0.99 (d, 3 H, CH_3) (irradiation at δ 2.8 and 2.4 decouples the low- and high-field part, respectively, of an AB quartet with J = 16 Hz (E double bonds)); ^{13}C NMR (at ambient temperature) δ 139.7 (C_7), 135.9 and 135.4 (C_4 and C_5, interchangeable), 128.4 (C_8), 45.6 (C_2), 39.1 (C_3), 38.8 (C_{10}), 35.9 and 34.2 (C_6 and C_9, interchangeable), 18.8 (CH_3). At -90 °C in $CHFCl_2$ two sets of signals obtain having the same line width (intensity ratio ~4:1). By variable-temperature ^{13}C NMR (-90 to -30 °C) the resonances of corresponding carbons have been identified as follows (minor conformer in parentheses): 140.7 (142.0), C_7; 138.1 (135.0), C_5; 135.6 (137.4), C_4; 129.3 (128.1), C_8; 45.7 (45.7), C_2; 42.0 (36.1), C_3; 39.3 (39.1), C_{10}; 37.4 (37.0), 35.4 (35.1), C_6 and C_9, interchangeable; 21.2 (15.7), CH_3.

The kinetic parameters of the exchange process (ΔG^*) = 11.0 ± 0.2 kcal/mol) were evaluated by computer simulation of the line shapes in the -32 to -60 °C range. The pair of lines having the largest chemical shift difference was selected (the CH_3 lines), which also are unencumbered by overlapping signals.

Unsuccessful Ring Expansion of 4-Ethyl-9-phenyl-3-vinyl-8,10-dioxa-4-thioniabicyclo[5.3.0]decane Tetrafluoroborate. Sulfide **6** (1.31 g, 5 mmol) in 40 mL of CH_2Cl_2 was reacted with triethyloxonium tetrafluoroborate (1.04 g, 5.5 mmol), as described for the preparation of the methyl derivative (**7**), to give 1.78 g of crude sulfonium salt. This was immediately treated with t-BuOK as described for the preparation of **8**, to give 1.12 g of a mixture of several products (TLC and GLC). Partial chromatographic separation (15% ether/light petroleum ether) showed the material to be largely made up (^{13}C NMR) of the four isomers of **6**, i.e., the products of β elimination of ethylene from **9**. Two minor products were also partially separated, each characterized in the ^{1}H NMR spectra by a quartet, δ 2.54 and 2.52, and a triplet, δ 1.22 and 1.24, respectively, indicative of the presence of a SCH_2CH_3 grouping. Both were tentatively assigned structure **10**, arising from a 2,3-sigmatropic shift of the endocyclic ylide from **9**. Since none of the chromatographic fraction showed any evidence in the ^{1}H NMR of the methyl doublet expected in the product of three-carbon ring expansion (5-methyl-12-phenyl-11,13-dioxa-4-thiabicyclo[8.3.0]tridec-7-ene), the separation of the reaction products was not pursued further.

Registry No. **1**, 82134-56-3; **2**, 82188-38-3; **3**, 82188-39-4; **4**, 82134-50-7; **5**, 82134-51-8; **6**, 82134-52-9; **7**, 82134-54-1; **8** (isomer 1), 82134-55-2; **8** (isomer 2), 82188-40-7; **11**, 82134-57-4; **12**, 82134-59-6; **13** (isomer 1), 82134-60-9; **13** (isomer 2), 82188-41-8; **13** (isomer 3), 82188-42-9; **13** (isomer 4), 82188-43-0; (+)-**14**, 82149-52-8; (-)-**14**, 82149-53-9; (1*R*,4*S*,5*R*,8*S*)-4,8-dichloro-2,6-dioxobicyclo[3.3.0]octane, 82188-37-2; D-mannitol, 69-65-8.

Notes

Tropone Revisited

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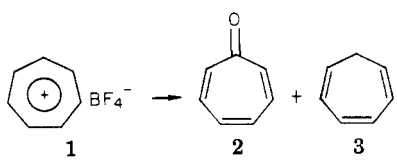
We recently reported a new synthesis of tropone (**2**) which involved heating tropylium fluoborate (**1**) in dimethyl sulfoxide (Me_2SO).[1] Soon after publication we received word that the reaction did not work well for some people;[2] and, indeed, on moving from Pennsylvania to Vermont, we ourselves occasionally had some difficulty reproducing our yields.[3] On the other hand, others reported no problems.[4] Faced with these conflicting results, we have embarked on a reinvestigation of the reaction and report our results herein.

When tropylium fluoborate is heated in Me_2SO, a 1:1 mixture of tropone (**2**) and cycloheptatriene (**3**) is produced over the course of several hours (eq 1). There is no intermediate detectable by NMR spectroscopy, and the reaction appears to be quantitative. Addition of solid anhydrous sodium carbonate to the reaction mixture markedly accelerates the reaction and causes the vigorous evolution of carbon dioxide. Thus, a mixture of tropylium fluoborate and Me_2SO is converted quickly to tropone and cycloheptatriene on addition of solid sodium carbonate at room temperature. After workup the yield of tropone (corrected for Me_2SO contamination) is consistently 45-49% based on tropylium salt, which is 90-98% of expected tropone.



1 2 3 (1)

The mechanism of the reaction and the source of the oxygen that ends up on the tropone remain unknown, but it is clear that the mechanism proposed by us[1] and others,[5] which involves a dimethyl sulfoxonium salt in a process related to the Corey-Kim oxidation,[6] is not correct, for this does not account for the generation of cycloheptatriene along with the tropone. Furthermore, on the analytical scale, the sodium carbonate catalyzed reaction works equally well in dimethylformamide and, with heating, in acetone, tetraglyme, and acetonitrile. On a preparative scale, tropone can be generated in acetonitrile without distillation, as all the byproducts can be removed by filtration or evaporation.[7] Ditropyl ether is a tempting intermediate to propose for this transformation, because it is known to disproportionate slowly into tropone and

(1) Garfunkel, E.; Reingold, I. D. *J. Org. Chem.* **1979**, *44*, 3725.
(2) Ledlie, D., personal communication; Gribble, G. W., personal communication.
(3) Reingold, I. D.; Halsey, D., unpublished results.
(4) Thummel, R. P., personal communication.
(5) Kitahara, Y.; Funamizu, M. Japanese Patent 11 122; *Chem. Abstr.* **1963**, *59*, 10012b.
(6) Corey, E. J.; Kim, C. U. *J. Am. Chem. Soc.* **1972**, *94*, 7586; *J. Org. Chem.* **1973**, *38*, 1233.
(7) Despite efforts to exclude moisture, some ditropyl ether was produced when this was done in the summer; winter reactions gave clean tropone. Ditropyl ether was not a problem in the summer when Me_2SO was the solvent, but then a distillation is necessary to remove the Me_2SO. If time is not of the essence, ditropyl ether presents no problem, as it disproportionates to tropone and cycloheptatriene within a few days (see note 8).

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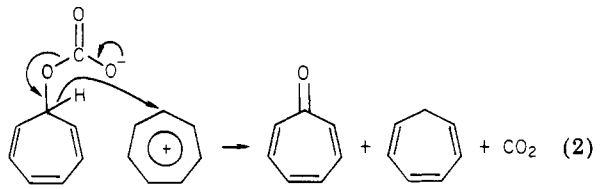
cycloheptatriene,[8] but it is inert to the reaction conditions on our time scale. It may also be relevant that in addition to sodium carbonate, sodium bicarbonate and to a lesser extent sodium acetate[9] and tribasic potassium phosphate also speed the reaction. Monobasic sodium phosphate has no effect.

A possible mechanism for the reaction in the presence of sodium carbonate or bicarbonate is shown in eq 2. It



(2)

accounts for the known facts about the reaction but does not explain why the process should occur. It also leaves open the question of the mechanism in the absence of added carbonate. The answers to these questions await further experimentation.

Since cycloheptatriene is a product of this reaction, the yield of tropone from tropylium salt is limited to 50%. However, tropylium fluoborate can be made from cycloheptatriene by treatment with trityl fluoborate.[10] Thus, treatment of the reaction mixture containing tropone and cycloheptatriene with trityl fluoborate should regenerate tropylium salt and eventually provide more tropone.[11] Indeed, one should be able to start with cycloheptatriene, treat with an excess of trityl fluoborate and sodium carbonate in acetonitrile, and obtain tropone in high yield. We have been able to produce tropone by this method (30–40% yield), but even a large excess of trityl fluoborate does not remove all of the cycloheptatriene; furthermore, the large amount of triphenylmethane generated in the reaction makes isolation of the tropone difficult. Since tropylium fluoborate[12] is as easy to prepare as trityl fluoborate,[10] we prefer the former intermediate.

Finally, we have noticed that tropyl methyl ether, like ditropyl ether, slowly decomposes to tropone on standing.[13] If this could be made to happen quantitatively and on a reasonable time scale, it would represent the first method for converting tropylium salts into tropone in greater than 50% yield. We have not yet found the appropriate conditions to do this, but we are continuing our search.

Experimental Section

Tropone (2). A mixture of 25 g (0.14 mol) of tropylium fluoborate, 10 g (0.095 mol) of anhydrous sodium carbonate, and 250 mL of acetonitrile was heated to reflux under nitrogen for 30 min, cooled, and stripped of solvent. The residue was swirled with 150 mL of dichloromethane, filtered, washed with water and saturated sodium chloride solution, dried, and concentrated to give 7.14 g (48%) of tropone. The product is light brown in color but pure by NMR and IR spectroscopy.[7]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(8) Harmon, K. M.; Harmon, A. B.; Coburn, T. T.; Fisk, J. M. *J. Org. Chem.* **1968**, *33*, 2567.
(9) Surprisingly, no ditropyl ether was formed even though the trihydrate was used.
(10) Dauben, H. J.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.
(11) We thank Dr. R. P. Thummel for this suggestion.
(12) Conrow, K. "Organic Syntheses"; Wiley: New York, 1973; Collected Vol. V, p 1138.
(13) Harmon et al.[8] have also noticed this in passing.

The α Effect: On the Origin of Transition-State Stabilization

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One of the most intriguing problems in the field of nucleophilic substitution reactions is no doubt the α effect. This effect is expressed as a positive deviation of an α nucleophile (a nucleophile possessing a nonbonding pair of electrons on an atom α to the nucleophilic site) from a Brønsted-type plot of log k vs. the pK_a of the nucleophile.[1] Although the α effect has received much attention, the consensus of opinion is that its origin is still rather unclear.[2] This is well manifested by the multitude of explanations given to this effect.[3] However, it is generally accepted that in many cases, the enhanced nucleophilic reactivity of α nucleophiles results from extra stabilization of the transition state.[2f,3f,i,j,4] In an attempt to characterize the origin of this extra stabilization we must first examine the nature of the transition state in nucleophilic reactions. Regarding bond scission, Salem has stated that a molecule with a broken bond can be partly diradical–partly zwitterionic.[5a] Similar diradical–zwitterionic resonance structures were postulated by Walling[5b] and subsequent workers[5c,d] for intermediates in the decomposition reactions of certain peroxides. Since this should hold for a nucleophilic bonding process as well, it implies that one of the canonical structures describing the transition state will be diradicaloid (eq 1)

$$N^- C\text{–}X \leftrightarrow N\text{–}C\ X^- \leftrightarrow N\cdot\ {}^-C\text{–}X \leftrightarrow \ldots \qquad (1)$$

Further support for this conclusion is obtained from several recent reports of nucleophilic reactions in which a seemingly simple bond formation is found to proceed by an electron transfer to form a radical pair which subsequently collapses to yield a covalent bond (eq 2; charges omitted for clarity). The reactions of Grignard reagents

$$N: + S \rightarrow [N\cdot + S\cdot] \rightarrow N\text{–}S \qquad (2)$$

with benzophenone,[6] the coupling of cyclopropenyl cation

(1) Edwards, J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 16.
(2) (a) Oae, S.; Kadoma, Y.; Yano, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1110. (b) Pratt, R. F.; Bruice, T. C. *J. org. Chem.* **1972**, *37*, 3563. (c) Fina, N. J.; Edwards, J. O. *Int. J. Chem. Kinet.* **1973**, *5*, 1. (d) Kice, J. L; Puls, A. R. *J. Am. Chem. Soc.* **1977**, *99*, 3455. (e) Grekov, A. P.; Veselov, V. Ya. *Russ. Chem. Rev.* **1978**, *47*, 1200. (f) Buncel, E.; Chuagui, C.; Wilson, H. *J. Org. Chem.* **1980**, *45*, 3621.
(3) (a) Epstein, J.; Demek, M. M.; Rosenblatt, D. H. *J. Org. Chem.* **1956**, *21*, 796. (b) Jencks, W. P. *J. Am. Chem. Soc.* **1958**, *80*, 4585. (c) Bunton, C. A. In "Peroxide Reaction Mechanism"; Edwards, J. O., Ed.; Interscience: New York, 1962; p 25. (d) Ibne-Rasa, K. M.; Edwards, J. O. *J. Am. Chem. Soc.* **1962**, *84*, 763. (e) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithica, NY, 1969; p 452. (f) Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969; p 107. (g) Aubort, J. D.; Hudson, R. F. *J. Chem. Soc., Chem. Commun.* **1970**, 937, 938. (h) Klopman, G.; Tsuda, K.; Louis, J. B.; Davis, R. E. *Tetrahedron* **1970**, *26*, 4549. (i) Dixon, J. E.; Bruice, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 2052. (j) Liebman, J. F.; Pollack, R. M. *J. Org. Chem.* **1973**, *38*, 3444. (k) Ritchie, C. D.; Minasz, J. R.; Kamego, A. A.; Sawada, M. J. *J. Am. Chem. Soc.* **1976**, *99*, 3747. (l) Heaton, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 2004. (m) England, W. B.; Kovacic, P.; Hanrahan, S. M.; Jones, M. B. *J. Org. Chem.* **1980**, *45*, 2057.
(4) Fersht, A. R.; Requena, Y. *J. Am. Chem. Soc.* **1971**, *93*, 3499.
(5) (a) Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486. (b) Walling, C.; Waits, H. P.; Milovanovic, J.; Pappiaonou, C. G. *Ibid.* **1970**, *92*, 4927. (c) Taylor, K. G.; Govindan, C. K.; Kaelin, M. S. *Ibid.* **1979**, *101*, 2091. (d) Pomerantz, M.; Dassanayake, N. L. *J. Am. Chem. Soc.* **1980**, *102*, 678.
(6) Ashby, E. C.; Bowers, J. S., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 8504.

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