concentrated to a yellow oil which was shown to be almost exclusively (97%) *cis*-2-cyclodecen-1-one (**16**) by glpc and nmr.

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# Structure and Thermal Isomerization Reactions of Protonated Cyclohepta-3,5-dienones in Superacids. A Convenient Preparation of Cyclohepta-2,4-dienone[1,2]

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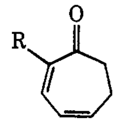
*Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.* *Received November 6, 1972*

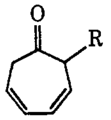
**Abstract:** An attractive synthetic route has been developed for the conversion of cyclohepta-3,5-dienone (**2a**) to cyclohepta-2,4-dienone (**1a**). The procedure is based upon the quantitative rearrangement of protonated **2a** to protonated **1a** in $FSO_3H$. Dependence of the rate of isomerization upon the acidity of the superacid medium suggests that the reaction proceeds through a dication intermediate. In more weakly acidic media, *e.g.*, 96% $H_2SO_4$, deuterium incorporation studies implicate a deprotonation–reprotonation mechanism. This change in mechanism is accompanied by the formation of some protonated cyclohepta-2,6-dienone (**3a**). The structures of these hydroxy cations, the mechanisms of the isomerizations, and extension of these reactions to 2-substituted systems are discussed.

In the course of our studies on the photochemistry of monocyclic dienones in acidic media[3] we had need of cyclohepta-2,4-dienone (**1a**) and its 2-methyl derivative **1b**. Although the preparation of **1a** has been described by van Tammelen and Hildahl,[4] their synthesis, albeit effective, is lengthy and not suited to the convenient preparation of large quantities. Moreover, the synthesis of 2-alkyl substituted derivatives by this route did not appear particularly attractive.

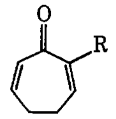
As cyclohepta-3,5-dienone (**2a**) and its 2-substituted derivatives can be readily obtained from tropone, it would seem with a suitable means of isomerization that these could serve as suitable precursors for **1**.[5] Furthermore, an alternative isomerization of **2a** would be to give the cross-conjugated dienone **3a** and cyclohepta-2,5-dienone. While **3a** can be obtained by the procedures of Garbisch,[6] or Birch,[7] this potential rearrangement could again provide access to the 2-substituted 2,6-dienones.



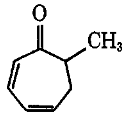
**1a**, R = H
**b**, R = Me



**2a**, R = H
**b**, R = Me



**3a**, R = H
**b**, R = Me



**4**

Thermal interconversion of **1a** with **2a**[8] and **1b** with **2b**[9] has been reported to take place in solution at temperatures greater than 60°. As the isomerization of **2a** proceeds by way of a 1,5-hydride shift, no cross-conjugated dienone, **3a**, was detected as a product. At 80° an equilibrium was reached which consisted of 35% **1a** and 65% **2a**. The thermal isomerization of **2b** produced not only **1b** in the equilibrium mixture but also **4**.[10]

Although the material balance in these isomerizations was good, the separation of the mixtures was found to be difficult. The most effective method, preparative glpc, was severely limited, not only in terms of the quantities obtainable, but by the extreme ease of the thermal interconversion of these compounds.

If the cyclohepta-3,5-dienones (**2**) are to be viable synthetic precursors of their 2,4 isomers, then the isomerization has to be made either essentially quantitative, or to give at least no other volatile products. Clearly, irrespective of the manner in which isomerization of **2** to **1** is accomplished, if thermodynamic equilibrium between the two ketones is reached, the separation problem will remain.

A possible solution to these problems, is to so structurally modify **1** and **2** that the equilibrium position

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[1] This work was supported by the National Research Council of Canada and the Research Board of the Science and Engineering Division, McMaster University.

[2] Part VI of a series entitled "The Chemistry of Cycloheptadienones."[3] Preliminary accounts of part of this work have been presented earlier.[3a]

[3] For earlier parts of this series, see (a) K. E. Hine and R. F. Childs, Abstracts, 55th Chemical Conference of the Chemical Institute of Canada, Quebec, June 1972, No. 63; K. E. Hine and R. F. Childs, *J. Chem. Soc., Chem. Commun.*, 144 (1972); (b) K. E. Hine and R. F. Childs, *ibid.*, 145 (1972); K. E. Hine and R. F. Childs, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. 120; K. E. Hine and R. F. Childs, *J. Amer. Chem. Soc.*, **93**, 2323 (1971).

[4] E. E. van Tammelen and G. T. Hildahl, *ibid.*, **78**, 4405 (1956).

[5] O. L. Chapman, D. J. Pasto, and A. A. Griswold, *ibid.*, **84**, 1213 (1962).

[6] E. Garbisch, *J. Org. Chem.*, **30**, 2109 (1965).

[7] A. J. Birch, G. M. Iskander, B. I. Magboul, and F. Stansfield, *J. Chem. Soc. C*, 358 (1967).

[8] A. P. ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 1189 (1963).

[9] (a) T. Nozoe, T. Mukai, and T. Tezuka, *Bull. Chem. Soc. Jap.*, **34**, 619 (1961); (b) *cf.* A. P. ter Borg, R. van Helden, and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **81**, 591 (1962).

[10] A systematic study of the thermal isomerizations of **2b** has not been reported. Preliminary results in our laboratory show that **2b** is converted to an equilibrium mixture of **1b**, **4**, and **2b** in solution at 80° or in the gas phase between 170 and 360°. In each case **1b** is the predominant isomer.

Table I. Pmr Spectra of Cycloheptadienones and Protonated Cycloheptadienones[a]

| Compd | Ring protons[b] |  |  |  |  |  | Methyls[c] | Coupling constants[d] |
|---|---|---|---|---|---|---|---|---|
|  | $H_2$ | $H_3$ | $H_4$ | $H_5$ | $H_6$ | $H_7$ |  |  |
| **1a** | 4.01 | 3.48 | 3.97 | 3.53 | 7.56 | 7.56 |  | $J_{2,3} = 12.8, J_{3,4} = 7.4, J_{4,5} = 11.4, J_{5,6} = 5.6$ |
| **1b** |  | 4.56 | 4.08 | 3.75 | 7.72 | 7.45 | 8.10 (s) | $J_{3,4} = 7.5, J_{4,5} = 11.6, J_{5,6} = 5.5$ |
| **2a** | 6.95 | 4.14 | 3.70 | 3.70 | 4.14 | 6.95 |  | $J_{2,3} = J_{6,7} = 5.5, J_{3,4} = J_{4,5} = 10.0$ |
| **2b** | 7.04 | 4.50 | 3.77 | 3.77 | 4.18 | 7.0 | 8.77 (d), $J = 6.7$ | $J_{2,3} = 4.8, J_{3,4} = 10.8, J_{4,5} = 8.5, J_{5,6} = 4.5$ |
| **3a** | 4.10 | 3.50 | 7.57 | 7.57 | 3.50 | 4.10 |  | $J_{2,3} = 12.0, J_{3,4} = 2.8$ |
| **3b** |  | 3.48 | 7.62 | 7.62 | 3.48 | 4.07 | 8.17 (s) | $J_{6,7} = 12.1, J_{3,4} = J_{5,6} = 3.0$ |
| **4** | 4.00 | 3.47 | 3.95 | 3.60 | 7.63 |  | 8.88 (d), $J = 6.8$ | $J_{2,3} = 12.7, J_{3,4} = 7.5, J_{4,5} = 11.3, J_{5,6} = 5.5$ |
| **5a**[e] | 6.10 | 4.25 | 3.16 | 3.16 | 4.25 | 6.10 |  | $J_{2,3} = J_{6,7} = 6.0, J_{3,4} = J_{5,6} = 10.0$ |
| **5b**[e] | 6.37 | 4.84 | 3.18 | 3.18 | 4.02 | 6.0 | 8.34 (d), $J = 6.9$ | $J_{3,4} = J_{5,6} = 10.3, J_{4,5} = 8.3, J_{6,7} = 5.5$ |
| **6a** | 3.09 | 2.02 | 3.19 | 2.72 | 7.18 | 6.76 |  | $J_{2,3} = 11.8, J_{3,4} = 7.9, J_{4,5} = 11.0, J_{5,6} = 5.9$ |
| **6b** |  | 2.05 | 3.27 | 2.75 | 7.30 | 6.73 | 7.74 (s) | $J_{3,4} = 8.3, J_{4,5} = 10.2, J_{5,6} = 5.5$ |
| **7a** | 3.26 | 2.05 | 7.16 | 7.16 | 2.05 | 3.26 |  | $J_{2,3} = 12.0, J_{3,4} = J_{4,5} = 3.3$ |
| **7b** |  | 2.05 | 7.17 | 7.17 | 2.05 | 3.21 | 7.80 (s) | $J_{3,4} = J_{5,6} = 3.3, J_{6,7} = 12.0$ |
| **8** | 3.10 | 2.05 | 3.20 | 2.70 | 7.2 | 6.8 | 8.59 (d), $J = 7.0$ | $J_{2,3} = 11.7, J_{3,4} = 8.0, J_{4,5} = 11.2, J_{5,6} = 6.0$ |

[a] Unless stated otherwise, all spectra taken at 100 MHz at +37°. Ketones in $CCl_4$ (TMS internal reference standard). Cations in $FSO_3H$ ($CH_2Cl_2$ internal standard taken as $\tau$ 4.70). [b] Assignments made with the aid of double or triple resonance experiments. [c] s = singlet, d = doublet. [d] ±0.3 Hz. [e] −30°.

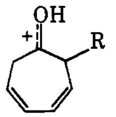
would now be in favor of modified **1**. For an effective synthetic procedure three conditions have to be met.

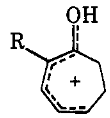
(a) The structural modification must be readily achieved and reversed in high yield.

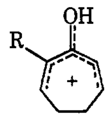
(b) The modified forms of **1** and **2** must be capable of interconversion.

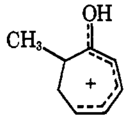
(c) The equilibrium position between modified **1** and **2** must lie greatly in favor of modified **1**.

One such modification that meets the above requirements is oxygen protonation of the ketones in strong acids. In this paper we report the results of an investigation of **5a** and show that **5a** can indeed isomerize to **6** or a mixture of **6** and **7** depending upon the acidity of the medium employed. Likewise, **5b** isomerizes to **6b** and **8** or **6b**, **7b**, and **8**. Since the equilibrium position is


**5a**, R = H
**b**, R = *Me*


**6a**, R = H
**b**, R = *Me*


**7a**, R = H
**b**, R = *Me*

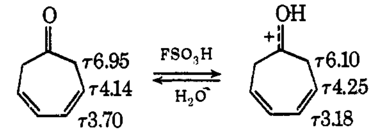

**8**

now greatly in favor of the conjugated and cross-conjugated cations, these reactions provide a viable synthetic route to both the cyclohepta-2,4- and -2,6-dienones.

## Results and Discussion

**Preparation of Cyclohepta-3,5-dienones.** Reduction of tropone[11] with sodium bis(2-methoxyethoxy)aluminum hydride followed by a work-up similar to that described by Schuster[12] gave **2a**. The methyl compound **2b** was obtained from reaction of tropone with methylmagnesium iodide.[9] Physical and spectral properties of **2a** and **2b** were in accord with those previously published.[5,9,12]

**Protonation of Cyclohepta-3,5-dienones.** The 3,5-dienones **2a** and **2b** dissolved in $FSO_3H$ or $FSO_3H$–$SbF_5$ at −78° to form solutions whose pmr spectra at −30° were consistent with the hydroxy cations **5a** and **5b**, respectively (Table I). The respective signals in



**2a** **5a**

these spectra were identified by double resonance and deuterium incorporation, *vide infra*. Apart from some viscosity broadening, identical spectra were obtained in 96% $H_2SO_4$ at −5°. Quenching these acid solutions of **5a** and **5b** at low temperatures regenerated **2a** and **2b**, respectively, in high yield.

One arresting feature of the changes accompanying the protonation of **2a** is the small, but definite, upfield movement of the $C_3$ and $C_6$ proton resonances. Thus, while the hydrogens on $C_2$, $C_7$ and $C_4$, $C_5$ are substantially deshielded, the $C_3$, $C_6$ protons move upfield from $\tau$ 4.14 in **2a**, to $\tau$ 4.25 in **5a**. It is clear, therefore, that the structure of **5a** is more complex than the noninteracting diene representation depicted, and that there must be some, through space, leakage of the positive charge at $C_1$ to the diene.

Symmetrical overlap of the electron deficient $C_1$ with $C_3$ and $C_6$ of the diene would result in a destabilized, 4

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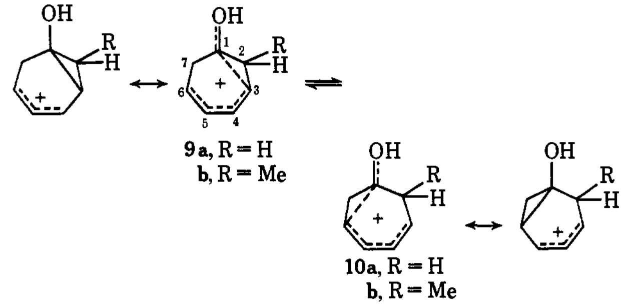
[11] P. Radlick, *J. Org. Chem.*, **29**, 960 (1964).

[12] D. I. Schuster, B. R. Sckolnick, and F. T. H. Lee, *J. Amer. Chem. Soc.*, **90**, 1300 (1968).

electron, "antibishomoaromatic" cation.[13,14] An alternative type of interaction is a nonsymmetrical overlap of the diene with $C_1$ to form the homopentadienylic cations **9a** and **10a**. Examination of molecular models



**9a**, R = H
**b**, R = Me

**10a**, R = H
**b**, R = Me

shows that not only is this type of interaction geometrically readily achieved but that interconversion of the two forms, which is necessary to account for the symmetry displayed by the pmr spectrum of **5a**, is facile.[16]

The observed pmr spectrum of **5a** is compatible with this protonated norcaradiene type structure.[17] The protons on $C_4$ and $C_5$ would be deshielded in both **9** and **10**. In contrast, the $C_3$ proton in **9** and $C_6$ proton in **10** would be expected to be shielded, similarly situated protons on cyclopropylallyl cations being reported in the $\tau$ 6.3–7.4 range.[18] This upfield movement has to be offset by the corresponding downfield position predicted for the $C_6$ and $C_3$ protons of **9** and **10**, respectively. Using the same cyclopropylallyl cation as a model, a resonance at $\tau$ 1.6 is likely, and averaging these expected positions puts the $C_3$ and $C_6$ protons into the $\tau$ 3.9–4.5 region. The agreement is surprisingly good considering the grossness of the model chosen. However, it does point out that overall little change might be expected in the resonance positions of the $C_3$ and $C_6$ protons in the cation as compared to the starting dienone. The small upfield shift observed is quite compatible with the suggested structure.

This "nonclassical" formulation of the structure of the protonated cyclohepta-3,5-dienones is strongly supported by their uv spectra (Table II). Thus **2a** in $FSO_3H$ at $-50°$ displayed a broad, reasonably intense absorption band at 318 nm. The identification of this band with **5a** was secured by the observation that it was replaced by the 375-nm absorption of **6a** on warming to 0° (*vide infra*). The position of this absorption at 318 nm is fully congruous with the homodienylic representations **9a** and **9b** and is, indeed, indicative of a substantial degree of delocalization. Some measure of this delocalization is provided by comparing this absorption at 318 nm with that of the fully conjugated cation **6a**, 375 nm, and contrasting it with the uv spectrum expected of the noninteracting diene, *ca.* 240 nm.[19] It is interesting that the absorption maximum for **5a** and **5b** correspond very closely to those reported for several cyclopropylallyl cations.[20]

**Table II.** Uv Spectra of the Cycloheptadienones and Protonated Cycloheptadienones

| Compd | Solvent | Temp, °C | $\lambda_{max}$, nm | Log $\epsilon$ |
|---|---|---|---|---|
| **2a**[a] | MeOH | 25 | 227 | 3.62 |
| **5a** | $FSO_3H$ | −50 | 318 | 3.0–3.3 |
| **2b** | MeOH | 25 | 228 | 3.64 |
| **5b** | $FSO_3H$ | −50 | 315 | 3.0–3.3 |
| **6a** | $FSO_3H$ | 25 | 375 | 3.89 |
| **6b** | $FSO_3H$ | 25 | 398 | 3.72 |

[a] Value quoted is this work, comparable figures have been obtained by other workers.[19b]

The pmr spectrum of **5b** (Table I) is also indicative of the same type of interaction although **9b** and **10b** are no longer of equal energy. The enhanced upfield shift of the $C_3$ proton as compared with that on $C_6$ would suggest that **9b** is the predominating form.[21]

A similar type of interaction of the double bonds and carbonyl group in the neutral ketone has been proposed by Chapman[23] to account for the anomalous photochemical reactions of **2a** and **2b**.[cf. 12] In charged species such as **5a** and **5b** the importance of this interaction should be enhanced.[15]

**Isomerization of Protonated Cyclohepta-3,5-dienones.** While $FSO_3H$ solutions of **5a** and **5b** were stable for long periods at low temperatures, when heated to 0° they underwent a clean rearrangement. This reaction proceeded until no ($\leq$0.5%) starting material could be detected by pmr. The isomerization of **5a**, which could conveniently be monitored by pmr, occurred at 0° with a pseudo-first-order rate constant of $8.5 \times 10^{-4}$ sec$^{-1}$ to give a new cation whose pmr showed the same ratio of olefin to aliphatic protons.[24] Quenching this rearranged cation in aqueous bicarbonate yielded, after a conventional work-up, an orange oil. Glpc analysis revealed that it consisted of just one product and no starting material, **2a** ($\leq$0.5%). The ir, uv, and pmr spectra of this oil were identical in all respects with those of cyclohepta-2,4-dienone (**1a**) prepared from the thermal isomerization of **2a** in $CCl_4$. The spectral properties of **1a** prepared by this strong acid route agreed with those previously reported for **1a**.[4,8,25] The product cation **6a** was stable for several days in $FSO_3H$ at room temperature.

Similarly, $FSO_3H$ solutions of **5b** rearranged at a somewhat slower rate at 0°, $k = 3.7 \times 10^{-4}$, to give a mixture of cations. After quenching, glpc analysis showed two products present but no starting ketone **2b**. The spectral properties of the pure products, obtained with repeated preparative glpc, were identical with those of authentic **1b** and **4**.

The product ketones **1a**, **1b**, and **4** and a mixture of **1b**

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(13) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(14) Alternatively, the symmetrical overlap of $C_1$ with $C_3$ and $C_6$ could be regarded as a suprafacial pericyclic combination with 4q electrons and is thus again unfavorable.[15]

(15) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

(16) The most favorable conformation would seem to be one in which $C_2$ is above and $C_7$ below the plane made by the dienyl carbons.

(17) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2280 (1972).

(18) T. S. Sorensen and K. Rajeswari, *ibid.*, **93**, 4222 (1971).

(19) *Cf.* (a) W. G. Dauben and R. L. Cargill, *Tetrahedron*, 12, 186 (1961); (b) J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *J. Amer. Chem. Soc.*, 77, 4401 (1955).

(20) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965).

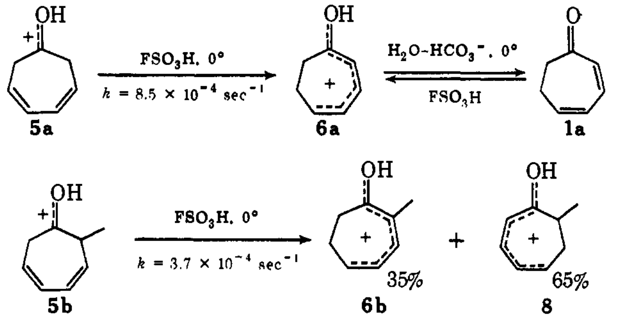
(21) This suggestion is consistent with the known preferences for the distribution of alkyl groups around an allyl system.[22]

(22) N. C. Deno in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 790–791.

(23) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962).

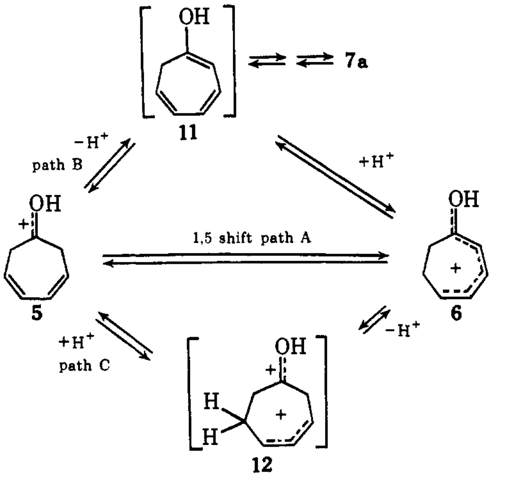
(24) The rate was dependent upon the concentration of ketone used and the purity of the acid.

(25) D. J. Bertelli, T. G. Andrews, and P. O. Crews, *J. Amer. Chem. Soc.*, **91**, 5286 (1969).



and **4** could be reprotonated with FSO$_3$H at −78° to give **6a**, **6b**, and **8** and a mixture of **6b** and **8**, respectively. In each case the pmr spectrum was identical with the spectrum of the cations obtained by the thermal rearrangement. No interconversion of **6b** and **8** in FSO$_3$H was observed, even when heated to +50° for 2 days, although extensive decomposition had occurred after 24 hr at this temperature.

**Mechanistic Studies.** There are only a limited number of ways in which it is possible to convert **5** to **6** in FSO$_3$H. The rearrangement, in simplest terms, involves the transfer of a hydrogen from C$_2$ to C$_6$. It is conceivable that this might proceed in a concerted fashion involving a suprafacial 1,5-hydride shift,[26] as has been proposed for the analogous reaction of the ketones, path A.[8,9] This isomerization of **5** to **6** could also occur in two steps, either by the initial loss of a proton to give the enol **11** followed by reprotonation, path B, or by further protonation of **5** to give the dication **12**, which then loses a proton to give **6**, path C.



Distinction between these three possibilities was made by examining the rearrangement in both FSO$_3$D and in media of differing acidity.

If the isomerization of **5** in FSO$_3$D were to proceed by path A, then, in the absence of exchange reactions, there would be no deuterium incorporated into **6**. However, if path C were operative, then deuterium would be incorporated at C$_6$ and possibly at C$_3$ depending upon the relative rates of the **12** → **6** and **12** → **5** deprotonation steps. Depending upon the site of protonation of the enol **11**, path B, deuterium exchange could occur not only at C$_6$ but also at C$_2$, C$_7$, C$_4$, and C$_5$ (*cf.* D$_2$SO$_4$ result).

In FSO$_3$D **5a**-*O*-*d* rearranged to **6a**-*O*-*d* with the incorporation of a single deuterium atom.[27] The reduction in the relative intensity of the τ 7.18 resonance in the nmr spectrum of **6a**-*O*-*d* to one proton and the changes in the multiplicity of the protons at C$_7$ and C$_5$ were completely consistent with the deuterium being at C$_6$. No exchange in **5a**-*O*-*d* could be detected during the course of the reaction nor did further exchange occur with **6a**-*O*-*d* on standing in FSO$_3$D.

These results are fully consonant with the diprotonation mechanism, path C, and further evidence to support this route can be found in the rate enhancement observed upon the addition of SbF$_5$ to the FSO$_3$H. As is shown in Table III, the rate of isomerization of **5b** to **6b** and **8** was increased by the addition of SbF$_5$ to the FSO$_3$H, the acceleration observed being proportional to the amount of SbF$_5$ added. The ratio of **1b** to **4** obtained remained independent of the SbF$_5$ concentration.

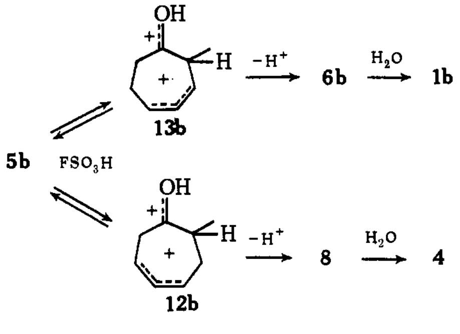
**Table III.** Rate of Isomerization of **5b** in FSO$_3$H and FSO$_3$H–SbF$_5$[a]

| $10^4k$, sec$^{-1}$ [b] | Mol % SbF$_5$ | Ratio **8**:**6b**[c] |
|---|---|---|
| 3.7 | 0 | 2.0 |
| 5.0 | 1.5 | 2.0 |
| 5.4 | 8.5 | 2.0 |

[a] 0 ∓ 1°. All isomerizations were carried out with the same batches of FSO$_3$H and SbF$_5$ using a constant ketone concentration, 4% wt/wt. [b] ±10%. [c] Measured by pmr.

This rate enhancement with increasing acidity[28] is in accord with the diprotonation mechanism, path C. The rate of reaction by path A should be independent of acid strength and path B would exhibit a rate attenuation with increased acidity.

The ratio of **1b** to **4** obtained in FSO$_3$H is also compatible with the dication mechanism. **1b** and **4** must arise from two different dications, **12b** and **13b**, respectively.



Of these **12b**, the precursor of **8**, and thence **4**, is expected to be the more stable.[22]

With regard to this dication mechanism, it is worth noting that Hogeveen[29] has suggested a dication intermediate to be involved in the rearrangement of protonated cyclohex-3-enone to protonated cyclohex-2-enone and protonated 3-methylcyclopent-2-enone. In FSO$_3$H–SbF$_5$ and HF–SbF$_5$ a very similar rate dependence upon SbF$_5$ concentration was found. Comparable mechanisms have been recently suggested by

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(26) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(27) The dependence of the rate of isomerization of these protonated ketones upon the purity of the acid used precludes an interpretation of the rate difference between FSO$_3$H and FSO$_3$D.

(28) R. J. Gillespie and T. E. Peel, *Advan. Phys. Org. Chem.*, **9**, 1 (1971).

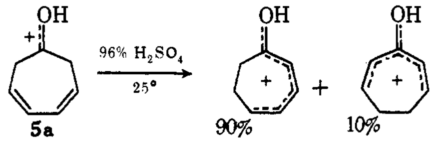
(29) H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **87**, 1299 (1968).

Olah[30] for the isomerization of a series of unsaturated ketones.

Thus, in contrast to the thermal isomerization of **2a** which produces an equilibrium mixture containing 35% **2a** and 65% **1a**, isomerization of the corresponding hydroxy cation results in an equilibrium consisting of greater than 99.5% **6a** and less than 0.5% **5a**. This substantial difference in equilibrium position between two protonated ketones compared with the ketones themselves must result from the greater need for delocalization within the charged species.

**Isomerization in Sulfuric Acid.** The use of $H_2SO_4$ as a solvent for these reactions was investigated, as it is not only a more generally available strong acid, but being a weaker acid than $FSO_3H$ it could provide additional mechanistic information.

The isomerization of **5a** in 96% $H_2SO_4$ proceeded smoothly at room temperature ($t_{1/2}$ *ca.* 5 min) to give a product whose pmr spectrum exhibited subtle differences to that of pure **6a** in the same acid. Glpc analysis of the quenched solution showed it to consist of two products, in a ratio of 9:1, and when separated these were identified as **1a**, 93%, and the cross-conjugated dienone **3a**, 7%.[6] Under the conditions of the isomerization no interconversion of **6a** and **7a** occurred.



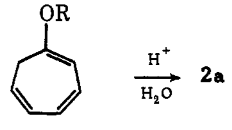
**5a** **6a** **11**

Similarly, rearrangement of **2b** in 96% $H_2SO_4$, followed by quenching, gave **3b** in addition to **1b** and **4** (Table V). The structure of **3b** was established from its spectral properties which closely resemble those of **3a**.

The appearance of **7a** as a rearrangement product of **5a** suggests the operation of a different mechanism in $H_2SO_4$ as compared with $FSO_3H$. As it is not possible to obtain **7a** by either path A or C, it seemed possible that in the weaker acid a deprotonation mechanism, path B, was occurring to some extent. Support for this proposal was found in examination of the isomerization of **5a** in $D_2SO_4$.

Solution of **5a** in 98% $D_2SO_4$ at 0° and examination of the pmr spectrum at the same temperature after *ca.* 4 min showed complete exchange of the 4 hydrogens on $C_2$ and $C_7$ had occurred without any rearrangement being detectable. Isomerization of the tetradeuterio **5a** in 98% $D_2SO_4$ took place at a much slower rate than with the perhydro cation in $H_2SO_4$. The products of rearrangement in the deuterated acid were **6a** and **7a** in the same ratio as observed before; however, both showed extensive deuterium incorporation.

These results clearly indicate that in 96 and 98% $H_2SO_4$ the enol intermediate **11** is in equilibrium with **5a** and it is preferentially reprotonated at $C_2$ to regenerate **5a**. Support for protonation at $C_2$ can be found in the acid hydrolysis of the enol ether **14**, which has been shown by Parham, *et al.*,[31] and Garbisch[6] to proceed with proton attack at $C_2$ to give **2a**.



**14**, R = Me or Et

The results of an investigation into the rearrangement of **2a** and **2b** in a series of $H_2SO_4$–$H_2O$ mixtures are given in Tables IV and V. It is worth noting that the ratio of protonated 2,6-dienone to protonated 2,4-dienone is dependent upon the acid concentration. Thus, for example, in 74% $H_2SO_4$ the initial rearrangement product of **5b** was almost entirely **7b**. The exact reason for this acid dependence is not clear at this stage. On prolonged standing at higher temperatures further isomerization of **7b** to **6b** was observed together with the formation of other minor, as yet unidentified products.[32]

Table IV. Product Distribution Resulting from the Isomerization of **5a**[a]

| | Product distribution | | | |
|---|---|---|---|---|
| | In acid[b] | | After quenching[c] | |
| Solvent | **6a** | **7a** | **1a** | **3a** |
| 96% $H_2SO_4$ | 90 | 10 | 93 | 7 |
| 86% $H_2SO_4$ | 80 | 20 | 78 | 22 |
| 74% $H_2SO_4$ | 70 | 30 | 70 | 30 |

[a] At 23°. [b] Relative percentage of product cations measured by pmr. [c] Glpc and pmr analysis.

Table V. Product Distribution Resulting from the Isomerization of **5b**[a]

| | Product distribution | | | | |
|---|---|---|---|---|---|
| | In acid[b] | | | After quenching[c] | |
| Solvent | **1b** | **4** | **3b** | **1b** + **4** | **3b** |
| 96% $H_2SO_4$ | 36 | 15 | 49 | 50 | 50 |
| 86% $H_2SO_4$ | 25 | 11 | 64 | 35 | 65 |
| 74% $H_2SO_4$ | 15 | 8 | 77 | 20 | 80 |
| $FSO_3H$ | 35 | 65 | 0 | 100 | 0 |
| $FSO_3H$–$SbF_5$ | 35 | 65 | 0 | 100 | 0 |

[a] At 23°. [b] Relative percentage of product cations measured by pmr. [c] Glpc analysis. **1b** and **4** were not well separated under the conditions employed and are reported together.

The acid-catalyzed isomerization of cyclohex-3-enone to cyclohex-2-enone in aqueous $H_2SO_4$ (*ca.* 10–35%) has been shown to proceed *via* an enol intermediate which is preferentially reprotonated to $C_2$.[33] It is interesting that the mechanism proposed here for the isomerization in concentrated $H_2SO_4$ differs from this more normal mode only in the position of the various equilibria between protonated and unprotonated forms.[34]

**Synthetic Utility.** For these procedures to become synthetically attractive, it is required that they be capable of being scaled up beyond the amounts used in these pmr experiments. When the protonation and thermal rearrangement of 1 g of **2a** was attempted,

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(30) G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *J. Amer. Chem. Soc.*, **94**, 3554 (1972).

(31) W. E. Parham, R. W. Soeder, and R. M. Dodson, *ibid.*, **84**, 1755 (1962).

(32) In more dilute sulfuric acid systems (60 and 74%) there was pmr evidence for incomplete protonation of the dienones.

(33) D. S. Noyce and M. Evett, *J. Org. Chem.*, 37, 394 (1972).

(34) No mention has been made in this paper of the role of the base $HSO_4^-$, $H_2O$, $FSO_3^-$ present in the acid media. The base present will be important in determining the rate of the deprotonation step leading to the enol 11.[cf. 35]

(35) T. S. Sorensen, I. J. Miller, and C. M. Viness, *Can. J. Chem.*, **48**, 3374 (1970).

after vacuum transfer, 0.800 g of **1a** was obtained in greater than 99.5% purity. No difficulties were encountered in this "large" scale reaction and further scale up should present few problems. As the product cation **6a** is stable in $FSO_3H$ at room temperature for several days, the reaction time is critical only in the sense that one must be certain all starting material has reacted. The progress of the reaction can be conveniently monitored by pmr. It should be emphasized that for the reactions to be clean and recoveries high the $FSO_3H$ used must not contain an excess of $SO_3$.

While the extension of this reaction to the selective synthesis of 2-alkyl- or 7-alkylcyclohepta-2,4-dienones is not so straightforward, the $H_2SO_4$ reactions described do provide simple access to the 2-alkylcyclohepta-2,6-dienones.[36]

The reactions described in this work are capable of being extended to the isomerization of other unsaturated carbonyl compounds and could provide a generally useful synthetic route to compounds where the more normal isomerization procedures fall short of the ideal.

## Experimental Section

**General.** Pmr spectra were obtained on Varian HA 100, A60, and T60 spectrometers, the former two being equipped with variable-temperature probes. Probe temperature was measured with a methanol sample or a thermocouple inserted into a nonspinning nmr tube containing an inert liquid. Ir spectra were recorded on a Perkin-Elmer Model 521 grating spectrophotometer using NaCl disks. Uv spectra were obtained with a Cary 14 spectrometer and mass spectra from a Hitachi Perkin-Elmer RMU-6A mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Varian Aerograph 204 (analytical) and Aerograph A 90-P3 (preparative) gas chromatographs were used: column A, 5 ft × $^1/_8$ in. 5% QF-1 on Chromosorb 60–80; column B, 10 ft × 0.25 in. 5% SE-30 on Chromosorb 60–80; column C, 13 ft. × 0.25 in. 20% Carbowax 2000 M on Chromosorb 60–80.

**Reagents.** $FSO_3H$ (Allied Chemical) was distilled from NaF (1 g/400 ml of acid) and stored in glass ampoules. $SbF_5$ was distilled before use. 96% $H_2SO_4$ (C. I. L.) and 98% $D_2SO_4$ (Merck, Sharp and Dohme) were used as supplied. Carbon tetrachloride and methylene chloride were distilled from $K_2CO_3$. Pentane was purified by treatment with fuming $H_2SO_4$. Dioxane was distilled from lithium aluminum hydride before use.

**Cyclohepta-3,5-dienone (2a).** A benzene solution of sodium bis(2-methoxyethoxy)aluminum hydride (0.17 mol) was added over 1 hr to a rapidly stirred solution of tropone[11] (9.0 g, 0.085 mol) in anhydrous ether (400 ml) at 0°. The mixture was stirred for 1 hr at room temperature, cooled to 0°, and worked up by the procedure described by Schuster, *et al.*,[12] to give **2a** as a colorless liquid, 1.5 g, bp 22–24° (0.5 mm). Analysis by glpc, column A, ir, and nmr showed no other isomer to be present. Ir (thin film) 3030, 2970, 2860, 1710, 1380, 1043, 892, 833 $cm^{-1}$; uv max (MeOH) 227 nm (log $\epsilon$ 3.62).

**2-Methylcyclohepta-3,5-dienone (2b)** was prepared in 72% yield by the method of Nozoe and coworkers.[9a] Distillation of the crude oil at low temperatures gave **2b**, a pale yellow oil: bp 23° (0.7 mm); ir (thin film) 3020, 2965, 2860, 1712, 1375, 1050, 927, 840 $cm^{-1}$; uv max (MeOH) 228 nm (log $\epsilon$ 3.64).

**Cyclohepta-2,6-dienone (3a)** was prepared by the procedure of Garbisch.[6]

**Thermal Isomerization. General.** Gas-phase isomerization was accomplished by distilling the appropriate ketone under vacuum through a 40-cm glass tube kept at a temperature greater than 200° with a Haskins Electric Furnace. The product was collected in a trap kept at −78°. Pure samples of the appropriate ketones were obtained by glpc, column B. Alternatively, degassed solutions of **2a** or **2b** (0.1 g) in $CCl_4$ (0.5 ml) were heated in sealed nmr tubes in an oil bath at 80–100° for 18 hr. The product mixture was analyzed by nmr and the ketones were separated as above. Obtained as such from **2a**, **1a** had spectra identical with those previously reported.[4,8,25]

**2-Methylcyclohepta-2,4-dienone (1b)** was obtained from **2b**; ir (thin film) 3040, 2980, 1653, 1435, 1360, 1228, 705 $cm^{-1}$; uv max (MeOH) 300 nm (log $\epsilon$ 3.95).

**7-Methylcyclohepta-2,4-dienone (4)** was obtained from **2b**; ir (thin film) 3035, 2980, 1655, 1435, 1360, 675 $cm^{-1}$; uv max (MeOH) 295 nm (log $\epsilon$ 3.8).

**Preparation of Cations. (a) $FSO_3H$.** Distilled $FSO_3H$ (*ca.* 0.5 ml) was added to the ketone (*ca.* 35 mg) at −78° contained in a nmr tube. The mixture was stirred at −78° until complete solution was achieved.

**(b) $H_2SO_4$.** To the acid (0.5 ml) cooled to −8° in a nmr tube was added the ketone (35 mg). The mixture was again stirred to achieve solution. $CH_2Cl_2$ was used as an internal standard in both media, taken as $\tau$ 4.70.

**Isomerization of the Cations.** All isomerizations were followed by monitoring the appropriate changes in the nmr spectra at the temperatures indicated. Thermal stabilities of **6a**, **6b**, **7a**, **7b**, and **8** were investigated by heating the acid solutions sealed in nmr tubes at 50° for several hours. Isomerization products were characterized by their nmr spectra in acid and by quenching with aqueous $NaHCO_3$ at 0° followed by glpc analysis of the recovered ketones, column C. In aqueous sulfuric acid the isomerizations were complete in *ca.* 20 min and quenching at this stage gave good material recovery, on standing in the $H_2SO_4$–$H_2O$ mixtures decomposition of the products occurred (50% loss in 24 hr).

Kinetic studies were performed on 4% solutions (wt/wt) of the ketones in $FSO_3H$ using dioxane as an internal standard. Solutions of the cations were kept in an ice-water bath at 0° and removed at the appropriate time intervals. The isomerization was stopped by cooling to −78° and the extent of reaction determined by nmr at −35°. Reactions were followed to 90% completion and the rates evaluated in the normal manner.

**Cyclohepta-2,4-dienone (1a). Preparative Scale.** Cyclohepta-3,5-dienone (**2a**) (1 g) was added dropwise as a 90% solution in $CH_2Cl_2$ to rapidly stirred $FSO_3H$ (10 ml) at −78°. After addition was completed, 15 min, the solution was warmed at 25° and stirred for 4 hr. After complete isomerization had been checked by running a nmr spectrum, the acid solution was added dropwise to a rapidly stirred suspension of $NaHCO_3$ (20 g) in water (50 ml) kept at −5 to 0°. The resultant mixture was extracted with ether (3 × 50 ml) (it was sometimes necessary to filter off the inorganic precipitate under vacuum to facilitate this extraction), and the solid collected was washed well with ether. The combined ether extracts were washed with water until neutral and dried over $MgSO_4$. Careful removal of the ether *in vacuo* gave an orange oil which was distilled through a short column to give **1a**: 0.8 g (80%); bp 30° (0.5 mm); purity $\geq$99.5% (pmr); ir (thin film) 3050, 2960, 2900, 1660, 1410, 1270, 685 $cm^{-1}$; uv max (MeOH) 294 nm (log $\epsilon$ 3.8).

**2-Methylcyclohepta-2,4-dienone (1b) and 7-Methylcyclohepta-2,4-dienone (4).** 2-Methylcyclohepta-3,5-dienone (**2b**) (1.9 g) dissolved in purified pentane (2 ml) was added over 30 min to rapidly stirred $FSO_3H$ (25 ml) at −78°. The solution was stirred at 25° for 3 hr, complete isomerization checked for by pmr, and quenched by adding dropwise to a rapidly stirred suspension of $NaHCO_3$ (100 g) in water (400 ml) at −5 to 0°. The organic material was extracted into pentane (3 × 30 ml), washed rapidly with 0.2% aqueous HCl (10 ml) and with saturated NaCl solution (2 × 10 ml), and then dried ($MgSO_4$). Careful removal of the pentane under vacuum gave an orange oil (1.7 g) which was vacuum transferred to give 1.5 g of a mixture of **1b** (35%) and **4** (65%). Separation was difficult, repeated glpc on column B at 70° gave small amounts of pure **1b** and **4** (physical data given earlier).

**2-Methylcyclohepta-2,6-dienone (3b).** 2-Methylcyclohepta-3,5-dienone (**2b**) (1.0 g) dissolved in $CH_2Cl_2$ (1 ml) was added dropwise to rapidly stirred 96% $H_2SO_4$ (8 ml) at 0°. The solution was stirred for 1 hr at 25°, completion of isomerization checked for by pmr and worked up by adding to excess $NaHCO_3$–$H_2O$ at 0° as previously described. Distillation of the yellow oil obtained gave 0.92 g (bp 34° (0.6 mm)) of a mixture of **3b** (45–50%) and **1b** and **4** (50–55%). Preparative glpc, column C, readily gave **3b**: 0.4 g (40%), >99% purity; ir (thin film) 3035, 2930, 1650, 1615, 1435, 1405, 1378, 1280, 1220, 1080, 865, 792 $cm^{-1}$; uv max (EtOH) 240 nm (log $\epsilon$ 3.89), 275 (3.40); mass spectrum (70 eV) *m/e* (rel intensity) 122 (90), 107 (25), and 79 (100).

*Anal.* Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.60; H, 7.99.

**Acknowledgment.** We thank Mr. B. G. Sayer of this department for running the 100-MHz pmr spectra.

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[36] Both the 2-ethyl and 2-isopropyl derivatives can be obtained in greater than 60% yield by this route as well.