Tetrahedron Letters, Vol.31, No.28, pp 4057-4060, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

SYNTHESES AND RACEMIZATION VIA INTERMOLECULAR PROTOTROPY OF OPTICALLY ACTIVE ALKYLTROPYLIUM IONS. A NOVEL SCALE FOR THE KINETIC BRØNSTED BASICITY OF ORGANIC SOLVENTS

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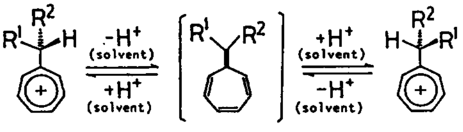
Abstract: Optically active (1-methylpropyl)tropylium ion (1) and (2-bicyclo[2.2.2]-octyl)tropylium ion (2) have been synthesized. The first-order rate constants of racemization via intermolecular prototropy of 1 provide a novel scale for the kinetic Brønsted basicity of organic solvents.

Although many scales have been proposed for the solvent basicity as Lewis[1] or Brønsted base,[2] none of them are correspondent to the kinetic Brønsted basicity which might be useful and practical in fundamental and applied chemistry.

Previously, we found the inversion of the tropylio-ring, i.e., the stereomutation (automerization), of alkyltropylium ions in acetonitrile,[3] which seemed to proceed through abstraction of the β-hydrogen by acetonitrile as a base followed by protonation of the heptafulvene intermediate from the opposite side, that is, "intermolecular prototropy" (Scheme 1).[4] Such a reaction rate would depend on the proton-abstraction ability of a solvent and could be anticipated to provide a novel measure for the kinetic Brønsted basicity of the solvent. In the case of optically active alkyltropylium ions, the stereomutation would cause the racemization of substrate and its rate constant might give a new scale for the solvent basicity.



Scheme 1

We now wish to report on the syntheses and the rates of racemization of optically active alkyltropylium ions to afford a practical measure for the kinetic Brønsted basicity of organic solvents.

Optically active alkyltropylium ion **1**, a slightly brownish white solid with mp 49.0-51.1°C (dec.), was prepared by four-step synthesis from (S)-(+)-2-

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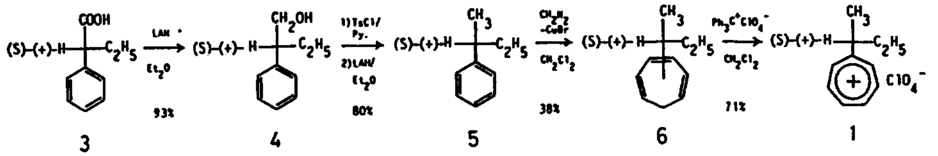
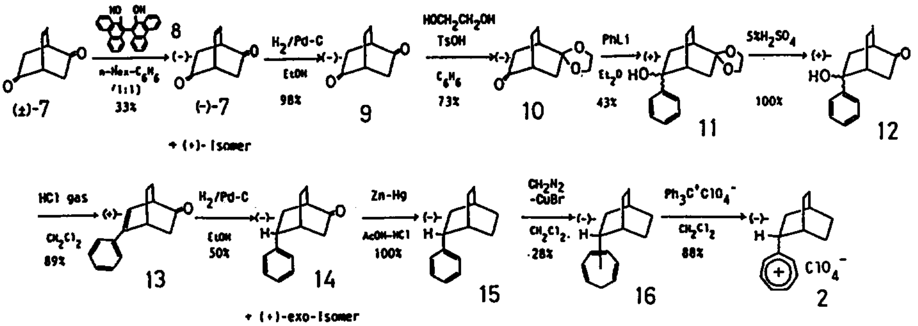


Scheme 2



Scheme 3

Table 1. Spectral Data for 1·ClO_4^- and 2·ClO_4^-[a]

Compd	^{13}C NMR (CD_2Cl_2)[b] δ/ppm	^1H NMR (CD_2Cl_2/TMS)[c] δ/ppm	IR (KBr) ν/cm^{-1}	UV (CH_3CN) λ/nm (ε)
1·ClO_4^-	12.2(q), 21.7(q), 32.0(t), 48.3(t), 153.6(d), 154.1(d), 154.6(d), 181.5(s)	0.93(t,3H), 1.49(d,3H), 1.88(m,2H), 3.35(m,1H), 9.25-9.28(m,6H)	750, 1060 1450, 2960	226(33300) 293(5400)
2·ClO_4^-	19.6(t), 25.1(d) 25.2(t), 25.4(t), 28.1(t), 33.0(t), 33.1(d), 49.4(d), 153.6(d),155.4(d), 181.2(s)	1.30-2.63(m,12H), 3.70(br. t,1H), 9.12(s,6H)	740, 750, 1080, 1435, 1480, 2850, 2900	315(3100)[d]

a) Both the new compounds gave satisfactory elemental analyses. b) 22.5 MHz; δ values based on δ = 53.60 ppm for CD_2Cl_2. c) 90 MHz. d) In CH_2Cl_2.

phenylbutanoic acid (3), α_D^{24} +81.9±0.3°C (neat, 1 dm),[5] in an overall 20.0 % yield (Scheme 2).[6] Another optically active alkyltropylium ion 2, a greenish yellow solid with mp 123-126°C, was synthesized via nine steps from (1S, 4S)-(-)-bicyclo[2.2.2]oct-7-ene-2,5-dione 7, $[\alpha]_D^{25}$ -1159±2° (c 0.109, CCl_4),[7] which was obtained by enantioselective host-guest complex formation using (S)-(-)-10,10'-dihydroxy-9,9'-biphenanthyl (8),[8] $[\alpha]_D^{27}$ -76.9±0.6° (c 0.247, $CHCl_3$), in an overall 3.37 % yield (Scheme 3).[6] The spectral data for 1 and 2 are listed in Table 1. The specific rotation of 2, $[\alpha]_D^{18}$ -4.4±1.6° (c 0.316, CH_2Cl_2), was too small to be used for the measurement of the racemization rate,[9] whereas that of 1, $[\alpha]_D^{25}$ +27.7±0.3° (c 0.770, CH_2Cl_2), was large enough to follow the reaction.

The rate of racemization via intermolecular prototropy of 1 (0.041-0.050 M) was measured at 25°C under vacuum or under nitrogen in nine kinds of organic solvent. The rate is first-order with regard to each of the substrate and the solvent, in 0.16-0.78 vol% (0.02-0.10 M) DMF-CH_2Cl_2 solutions, indicating that one solvent molecule should interact with one substrate ion. In DMF-CH_2Cl_2 solutions containing greater than 10 vol% DMF, the rate constant (k_1) is approximately constant. This fact suggests that the maximum number of solvent molecules which can participate in the reaction is limited.

The racemization rate (k_1) decreases in the sequence DMSO > DMF > Acetone[10] > Trimethylphosphate (TMP) ≥ THF > Dimethoxyethane (DME) > $CH_3CN \geq C_6H_5CH_2CN$ > CH_2Cl_2 (Table 2). The logarithms of k_1's can be correlated roughly with the known scales for Lewis basicity[1] (Fig. 1) and fairly with those for Brønsted basicity[2] of organic solvents (Fig. 2). The correlations confirm that the k_1 values reflect the Brønsted basicity and can provide a novel practical scale for the kinetic Brønsted basicity of organic solvents.

Table 2. The Racemization Rate Constants of $1 \cdot ClO_4^{-a}$

Solvent	k_1/sec^{-1}
Dimethylsulfoxide (DMSO)	> 0.06
Dimethylformamide (DMF)	0.05
Acetone	$5.4_6 \times 10^{-5}$
Trimethylphosphate (TMP)	$8.0_5 \times 10^{-6}$
Tetrahydrofurane (THF)	$7.1_6 \times 10^{-6}$
1,2-Dimethoxyethane	$4.8_0 \times 10^{-6}$
Acetonitrile	$2.0_4 \times 10^{-7}$
Benzonitrile	$1.8_4 \times 10^{-7}$
Dichloromethane	$< 2.3 \times 10^{-8}$

a) At 25°C, $[1 \cdot ClO_4^-]$ = 0.041 - 0.050 M.

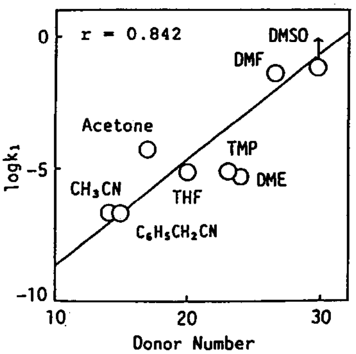


Fig. 1. log k_1 plotted against donor number (cited from ref. 1a,b)

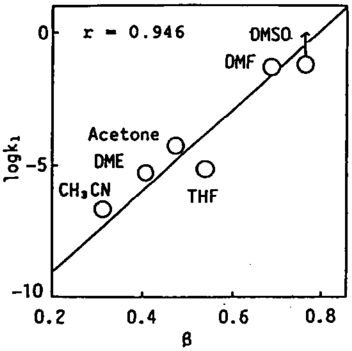


Fig. 2. log k_1 plotted against β (cited from ref. 2a)

Acknowledgements: This study was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan. We also thank Prof. F. Toda, Ehime Univ., Japan, for his technical information on the optical resolution of bicyclooctenedione.

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4. The intermediacy of the heptafulvene derivative in the stereomutation of **2** was proved by trapping with TCNE to afford the [8+2] cycloaddition product. Details will be reported elsewhere.
5. The racemic acid was optically resolved by the use of cinchonidine (J. S. Birtwistle, K. Lee, J. D. Morrison, W. A. Sanderson, and H. S. Mosher, J. Org. Chem., **29**, 37 (1964)); the absolute configuration and the maximum optical rotation of **3**: (S)-(+) (K. A. Petterson, Ark. Kemi., **10**, 283 (1956)) and $\alpha_D{}^{20}$ +105° (neat, 1 dm) (R. Weidmann and A. Horeau, Bull. Soc. chim. Fr., 117 (1967)).
6. The optical or specific rotations for compunds, **4** ~ **6** and **9** ~ **16**, are as follows; **4**: $\alpha_D{}^{23}$+16.7° (neat, 1 dm), **5**: $\alpha_D{}^{23}$ +24.7° (neat, 1 dm), **6**: $\alpha_D{}^{25}$ +28.0° (neat, 1 dm), **9**: $[\alpha]_D{}^{25}$ -48.3° (cyclohexane), **10**: $[\alpha]_D{}^{22}$ -22.6° ($CHCl_3$), **11**: $[\alpha]_D{}^{23}$ +46.4° ($CHCl_3$), **12**: $[\alpha]_D{}^{24}$ +11.0° ($CHCl_3$), **13**: $[\alpha]_D{}^{19}$ +447° ($CHCl_3$), **14**: $[\alpha]_D{}^{18}$ -13.3° ($CHCl_3$), **15**: $[\alpha]_D{}^{16}$ -51.4° ($CHCl_3$), and **16**: $[\alpha]_D{}^{18}$ -27.5° ($CHCl_3$).
7. For the absolute configuration and the maximum specific rotation ($[\alpha]_D{}^{29}$ -1235° (CCl_4)) of **7**, see R. K. Hill, G. H. Morton, J. R. Peterson, J. A. Walsh, and L. A. Paquette, J. Org. Chem., **50**, 5528 (1985).
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9. The precursor **16** which was reconverted by the reduction of **2** by $NaBH_4$ had almost the same value of specific rotation ($[\alpha]_D{}^{28}$ -26.8±0.7° (c 0.220, $CHCl_3$)) as that for **16** ($[\alpha]_D{}^{18}$ -27.5±1.0° (c 0.316, $CHCl_3$)) before the use for the synthesis of **2**.
10. In acetone, DMF, and DMSO, the intermolecular prototropy is accompanied in part by the formation of oligomers of the heptafulvene intermediates. However, the oligomerization after the racemization step should have no influence on the racemization rate.

(Received in Japan 19 April 1990)