Acknowledgment.—The mass spectrometer used in this work was purchased with funds granted to the Department of Chemistry by the National Science Foundation. We are indebted to Dr. William B. Budde of Midwest Research Institute for determination of the nmr spectrum of **2** and **3** at 100 Mc.

2-Thiaazulen-6-one and the 2-Thiaazulenium Cation. New 10-π-Electron Aromatic Systems

MARTIN WINN[1] AND F. G. BORDWELL

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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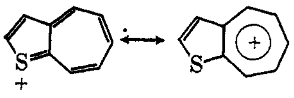
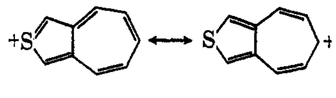
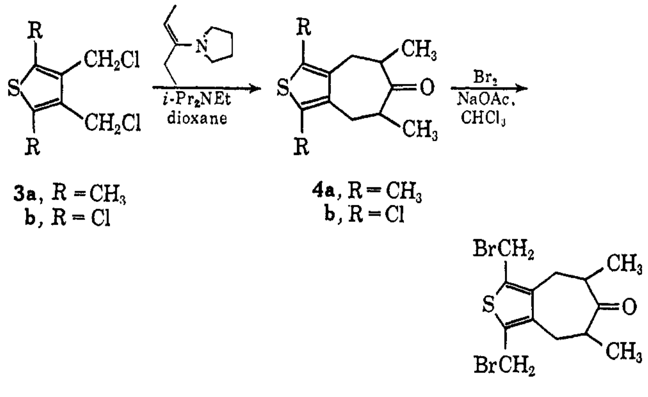
The observation that the 1-thiaazulenium cation (**1**) is relatively stable (pK_R = +6 in water)[2] prompted us to attempt the synthesis of 2-thiaazulenium cation (**2**) in order to determine its stability, relative to **1**, by pK measurements. It would be interesting to compare the relative stability of these cations with the relative stability of their neutral analogs, benzo[*b*]thiopene (stable) and benzo[*c*]thiophene (very reactive).[3] Although synthesis of the parent cation (**2**) was not achieved, we were successful in preparing several derivative of **2** and of the analogous 2-thiaazulen-6-ones.


1


2

The readily accessible 2,5-dimethyl-3,4-bis(chloromethyl)thiophene[4] underwent cyclization[5] with the pyrrolidine enamine of 3-pentanone in good yield to give the fused thiophene–cycloheptanone system (**4a**), but this could not be aromatized to **6a** by bromination followed by dehydrobromination. The bromination of the methyl groups on the thiophene ring competed successfully with the introduction of the second bromine on the seven-membered ring. Under certain conditions, methyl bromination was the exclusive result (giving **5**).



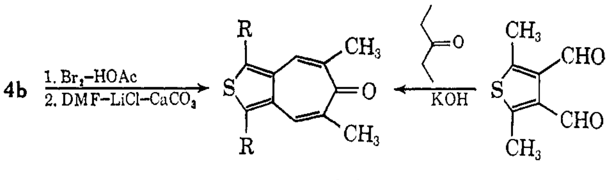
3a, R = CH_3
b, R = Cl

4a, R = CH_3
b, R = Cl

5

The enamine cyclization failed with 2,5-di-*t*-butyl-3,4-bis(chloromethyl)thiophene, presumably because of steric hindrance.

Cyclization of 3,4-bis(chloromethyl)-2,5-dichlorothiophene (**3b**) (prepared by chloromethylation of 2,5-dichlorothiophene) with the pyrrolidine enamine of 3-pentanone gave **4b** in fair yield. In contrast to **4a**, this compound was easily converted to the thiaazulenone (**6b**) by bromination–dehydrobromination.

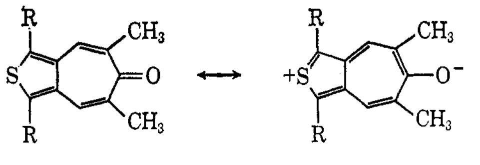


6a, R = CH_3
b, R = Cl

7

The tetramethyl compound (**6a**) was synthesized from the aldehyde (**7**) and 3-pentanone by the method of Theile.[6] Dialdehyde **7** was prepared from 2,5-dimethyl-3,4-diiodothiophene[7] by treating with butyllithium followed by dimethylformamide as described by Robba, *et al.*;[8] **7** has been recently synthesized from **3a** by another method.[9]

Thiaazulenone **6a** is deep yellow; **6b** is pale yellow. In contrast to benzo[*c*]thiophene, they are unreactive to maleic anhydride. The carbonyl bands in the infrared are at 6.36 and 6.21 μ, respectively. This shows that there is electron delocalization in the molecule and that the electronegative chlorine atoms in **6b** hinder delocalization of electrons from sulfur to oxygen relative to the effect of the methyl groups in **6a**. A similar effect is noted in the ultraviolet spectrum. The dichlorodimethyl compound (**6b**) has a lower λ_{max} in the ultraviolet than the tetramethyl compound **6a** (2680 *vs.* 2740 A). This is the opposite of the effect of substituting a chlorine for a methyl on a benzene ring.



In trifluoroacetic acid (TFA), the tetramethyl compound (**6a**) forms a purple solution. The color change is accompanied by a change in the nmr spectrum; the singlet at 2.60, doublet at 2.22, and quartet at 7.45 observed in chloroform all become singlets in TFA (at 2.71, 3.02, 8.68).[10] This is consistent with the formation of cation **8a**. Although the dichlorodimethyl

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[1] National Science Foundation Predoctoral Fellow, 1962–1963; Texaco Fellow, 1963–1964; Ethyl Corp. Fellow, 1964–1965. Abstracted in part from the Ph.D. Dissertation of M. Winn, Northwestern University, Aug 1965.

[2] K_R = $[ROH][H^+]/[R^+][H_2O]$: R. Turnbo, D. L. Sullivan, and R. Pettit, *J. Am. Chem. Soc.*, **86**, 5630 (1964).

[3] R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *Angew. Chem. Intern. Ed. Engl.*, **1**, 115 (1962); *J. Prakt. Chem.*, **20**, 244 (1963); M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **88**, 4112 (1966); B. D. Tilak, H. S. Desai, and S. S. Gupte, *Tetrahedron Letters*, 1953 (1966).

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[5] F. G. Bordwell and M. Winn, *J. Org. Chem.*, **32**, 42 (1967).

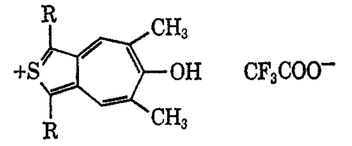
[6] J. Theile and E. Weitz, *Ann.*, **377**, 1 (1911).

[7] S. Gronowitz and R. Beselin, *Arkiv Kemi*, **21**, 349 (1963).

[8] M. Robba, R. C. Moreau, and B. Roques, *Compt. Rend.*, **259**, 3568 (1964).

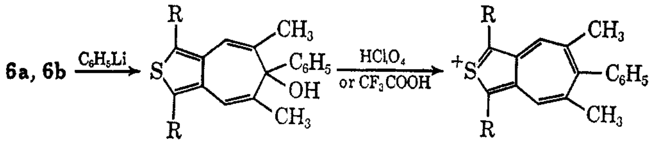
[9] K. Dimroth, G. Pohl, and H. Follmann, *Ber.*, **99**, 634 (1966).

[10] The numbers are parts per million (ppm) downfield from tetramethylsilane.



8a, R = CH_3
b, R = Cl

compound (**6b**) gives a red color in TFA, its nmr spectrum does not change as much in going from chloroform to TFA as does **6a** (the doublet at 2.22 and quartet at 2.51 change to a doublet at 240 and a quartet at 7.82). This and the fact that **6b** does not dissolve in concentrated hydrochloric acid, while **6a** does, shows **6b** to be much less basic than **6a**. The thiaazulenium ions were prepared in the following sequence.



9a, 9b   10a, 10b

a, R = CH_3
b, R = Cl

The nmr spectra of alcohol **9b** in TFA (green color, singlets at 2.62 and 9.42 beside phenyl peaks) showed the presence of **10b**. No crystalline salt of **10b** could be isolated, however. The nmr spectrum of alcohol **9a** in TFA (green color, singlets at 2.52, 3.23, and 9.28 beside phenyl peaks) also showed the presence of **10a**. In this case the perchlorate could be isolated. Its nmr spectrum in deuteriochloroform matched that of **9a** in TFA. The green, crystalline salt was stable in air.

Ultraviolet data for these ions (in TFA) are presented in Table I.

TABLE I

ULTRAVIOLET MAXIMA FOR 2-THIAAZULENIUM CATIONS

Compd	λ_{max}, A	Log ϵ
10a	2800 (3210)	4.09 (3.99)
10b	2890 (3310)	4.54 (4.38)
6a $\rightleftharpoons$ **8a**	2620 (3090)	4.26 (4.74)
6b $\rightleftharpoons$ **8b**	2750 (2840, 3120)	4.40 (4.52, 4.68)

The ease of formation and stability of these 2-thiaazulenium cations and of the analogous 2-thiaazulen-6-ones suggests that these systems are more stable relative to the corresponding 1-thiaazulene system, than is benzo[*c*]thiophene relative to benzo[*b*]thiophene.

Experimental Section

1,3,5,7-Tetramethyl-5,6,7,8-tetrahydro-4H-cyclohepta[*c*]thiophen-6-one (4a).—To 3,4-bis(chloromethyl)-2,5-dimethylthiophene[4] (33.10 g, 0.158 mole) and 61.2 g (0.475 mole) of diisopropylethylamine in 300 ml of dioxane, under nitrogen at 40–50°, was added, over a period of 1 hr, a solution of 21.98 g (0.158 mole) of 3-(N-pyrrolidino)-2-pentene in 60 ml of dioxane. The temperature was then raised to 95° (white solid formed) and kept for 4 hr at 95°. Then 100 ml water was added slowly and the solution was kept at 95° for an additional 45 min. The solvents were removed under reduced pressure and the residue was treated with ether and dilute hydrochloric acid giving 21.30 g (0.0961 mole, 60.8%) of colorless crystals, mp 114–115° (ether–hexane).

Anal. Calcd for $C_{13}H_{18}OS$: C, 70.24; H, 8.16. Found: C, 70.09; H, 8.18.

1,3-Bis(bromomethyl)-5,7-dimethyl-5,6,7,8-tetrahydro-4H-cyclohepta[*c*]thiophen-6-one (5).—To the above ketone (965 mg, 4.34 mmoles) with 1.00 g of sodium acetate in 5 ml of chloroform over a 30-min period was added a solution of 1.44 g (9.00 mmoles) of bromine in 10 ml of chloroform. The mixture was stirred for an additional 30 min and treated with sodium bisulfite solution to give 707 mg (43%) of colorless crystals, mp 131–132° (chloroform–hexane).

Anal. Calcd for $C_{13}H_{16}Br_2OS$: C, 41.05; H, 4.21. Found: C, 40.90; H, 4.21.

2,5-Dimethylthiophene-3,4-dicarboxaldehyde (7).—About half the volume of a solution of butyllithium in hexane (194.0 ml, 300.9 mmoles) was evaporated in a dry, 1-l. flask, and dry ether was added to give a 200-ml volume. Then, under nitrogen, at −65° while stirring, a solution of 50.0 g (137.5 mmoles) of 3,4-diiodo-2,5-dimethylthiophene[7] in 350 ml of ether was added over a 30-min period. After stirring at −65° for 1 hr, 33 ml (426.0 mmoles) of dimethylformamide was added over a 10-min period. After stirring for 3 hr the mixture was allowed to warm to −20° and treated with dilute hydrochloric acid and ether giving 7.22 g (43.1 mmoles, 31.5%) of light yellow crystals, mp 95–96° (hexane) (lit.[9] mp 92–93°).

1,3,5,7-Tetramethyl-6H-cyclohepta[*c*]thiophen-6-one (6a) (Tetramethyl-2-thiaazulen-6-one).—The above dialdehyde (5.00 g, 29.8 mmoles) 3-pentanone (4.25 g, 50.6 mmoles), and 9.0 ml of 2.50 *N* potassium hydroxide solution in methanol (22.5 mmoles) were added to 180 ml of methanol and refluxed for 20 min. The methanol was evaporated under vacuum and the residue was treated with ether and water giving 2.73 g (12.5 mmoles, 43.1%) of bright yellow crystals, mp 153–154° (methanol).

Anal. Calcd for $C_{13}H_{14}OS$: C, 71.54; H, 6.47. Found: C, 71.43; H, 6.60.

6-Phenyl-1,3,5,7-tetramethyl-6H-cyclohepta[*c*]thiophen-6-ol (9a).—To 1.09 g of tetramethyl-2-thiaazulen-6-one (5.00 mmoles) in 10 ml of benzene under nitrogen, 3.0 ml (6.41 mmoles) of a solution of phenyllithium in benzene–ether was added. The solution was kept at room temperature for 20 min and then water was added to give 0.974 g (3.29 mmoles, 65.8%) of colorless crystals, mp 141–142° (benzene–ether), which tend to turn yellow in air.

Anal. Calcd for $C_{19}H_{20}OS$: C, 77.00; H, 6.80. Found: C, 77.16; H, 6.64.

6-Phenyl-1,3,5,7-tetramethylcyclohepta[*c*]thiophenium Perchlorate (10a) (Tetramethylphenyl-2-thiaazulenium Perchlorate).—The above alcohol (400 mg, 1.35 mmoles) was dissolved in 8.0 ml of ether; then 0.5 ml of 70% perchloric acid was added slowly, giving a dark green solution. Slow addition of water and cooling gave dark green crystals (421 mg, 1.11 mmoles, 82.3%), mp 155–157°.

Anal. Calcd for $C_{19}H_{19}ClO_4S$: C, 60.23; H, 5.05. Found: C, 60.08; H, 5.06.

3,4-Bis(chloromethyl)-2,5-dichlorothiophene (3b).—A solution of 60.0 g (230 mmoles) of tin tetrachloride in 10 ml of carbon disulfide, was added over a period of 1 hr to a stirred solution of 30.6 g (200 mmoles) of 2,5-dichlorothiophene and 55.0 g (603 mmoles) of chloromethyl methyl ether in 150 ml of carbon disulfide at 0°. When the red solution was kept at 0° for 1 hr and at 30° for 2 hr, a red oil separated. After treatment with ice water and distillation, 5.10 g of 3-chloromethyl-2,5-dichlorothiophene [bp 100–125° (2.0 mm)] and 37.05 g of the desired product [148.0 mmoles, 73.8%, bp 137–145° (2.0 mm)] which solidified on standing was obtained. The latter was used directly in the next step; purification by chromatography on silica gel (hexane) gave colorless crystals, mp 41–42°.

Anal. Calcd for $C_6H_4Cl_4S$: C, 28.84; H, 1.61. Found: C, 28.85; H, 1.81.

1,3-Dichloro-5,7-dimethyl-5,6,7,8-tetrahydro-4H-cyclohepta[*c*]thiophen-6-one (4b).—The reaction of the above tetrachloro compound (22.3 g, 89.2 mmoles) and 13.05 g (94 mmoles) of 3-(N-pyrrolidino)-2-pentene was carried out as was with **3a**, except the reaction time was increased to 12 hr. There was obtained 9.60 g (35.7 mmoles, 39.9%) of colorless crystals, mp 113–114° (hexane).

Anal. Calcd for $C_{11}H_{12}Cl_2OS$: C, 50.21; H, 4.60. Found: C, 50.38; H, 4.53.

5,7-Dibromo-1,3-dichloro-5,7-dimethyl-5,6,7,8-tetrahydro-4H-cyclohepta[*c*]thiophen-6-one (4c).—Ketone **4b** above, 500 g, (19.0 mmoles) in 35 ml of acetic acid was treated with 6.65 g (41.5

mmoles) of bromine in 15 ml of acetic acid. The mixture was stirred 3 hr and treated with chloroform and with sodium bisulfite solution. A mixture of *cis*- and *trans*-dibromo ketones [mp 132–141° (hexane), 6.64 g ,15.8 mmoles, 83.0%] resulted.

Anal. Calcd for $C_{11}H_{10}Br_2Cl_2OS$: C, 31.58; H, 2.39. Found: C, 31.52; H, 2.60.

1,3-Dichloro-5,7-dimethyl-6H-cyclohepta[*c*]thiophen-6-one (6b) (Dichlorodimethyl-2-thiaazulen-6-one).—The above dibromo ketone (6.64 g, 15.8 mmoles), lithium chloride (2.0 g), calcium carbonate (4.0 g), and dimethylformamide (80 ml) were heated under nitrogen on a steam bath for 20 min. The mixture was treated with chloroform and dilute hydrochloric acid to give 3.59 g (13.9 mmoles, 87.8%) of pale yellow needles, mp 163–164° (hexane).

Anal. Calcd for $C_{11}H_8ClOS$: C, 50.98; H, 3.11. Found: C, 50.81; H, 3.05.

1,3-Dichloro-5,7-dimethyl-6-phenyl-6H-cyclohepta[*c*]thiophen-6-ol (9b).—The reaction of the above thiaazulenone (520 mg, 2.00 mmoles) and phenyllithium (2.14 mmoles) was carried out as in the preparation of **9a** to give 522 mg (1.55 mmoles, 77.5%) of coloress crystals, mp 155–157° (chloroform–heptane).

Anal. Calcd for $C_{17}H_{14}Cl_2OS$: C, 60.53; H, 4.18. Found: C, 61.08; H, 4.09.

Registry No.—2-Thiaazulen-6-one, 10095-83-7; **4a,** 10095-84-8; **4b,** 10095-92-8; **5,** 10095-85-9; **7,** 5368-72-9; **6a,** 10095-87-1; **6b,** 10095-95-1; **9a,** 10095-88-2; **9b,** 10095-96-2; **10a,** 10095-89-3; **3b,** 10095-90-6; 3-chloromethyl-2,5-dichlorothiophene, 10095-91-7; *cis* **4c,** 10095-93-9; *trans* **4c,,** 10095-94-0.

Friedel–Crafts Isomerization. XV.[1] Aluminum Chloride Catalyzed Isomerization of Methyldiphenylmethanes

GEORGE A. OLAH AND JUDITH A. OLAH

Department of Chemistry, Western Reserve University, Cleveland, Ohio 44106

Received September 27, 1966

No previous reports exist on the investigation of the Friedel–Crafts isomerization of methyldiphenylmethanes. Brown and Bolto[2] investigating the gallium bromide catalyzed benzylation of toluene with benzyl bromide suspected concurrent (or consecutive) isomerization and used short reactions times (in a flow system) to minimize this effect.

Olah, Kuhn, and Flood[3] investigated the aluminum chloride catalyzed benzylation of toluene with benzyl chloride in nitromethane solution. They found that the isomer distribution of the formed methyldiphenylmethanes in this solvent was typically *ortho–para* (43.5% *ortho,* 4.5% *meta,* and 52.0% *para*) in sharp contrast with the observations of Brown and Bolto[2] (41% *ortho,* 19.5% *meta,* and 39.5% *para*), obtained in excess aromatic hydrocarbon as solvent. At the same time, the relative reactivity of the benzylation of toluene and benzene was found to be around 3.2 both from competitive[3] and absolute[4] rate determinations. The question, whether the Friedel–Crafts benzylation of toluene in hydrocarbon solvent gave isomer distribution affected by isomerization, thus obviously became an important one.

TABLE I

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF METHYLDIPHENYLMETHANES AT 0°

Reaction time	% Methyldiphenylmethane isomer distribution (normalized) *ortho*	*meta*	*para*
	2-Methyldiphenylmethane		
0	>99.0		
30 sec	91.7	3.2	5.1
1 min	88.7	4.1	7.2
2	85.1	5.3	9.6
3	70.1	12.1	17.8
4	49.3	23.9	26.8
5	46.3	25.3	28.4
6	36.4	35.1	28.5
8	26.4	42.1	31.5
10	19.4	50.7	29.9
12	13.2	61.4	25.4
15	10.2	65.7	24.1
20	9.8	67.7	22.5
30	9.2	66.3	24.5
1 hr	10.4	65.5	25.1
24	9.7	65.5	24.8
	3-Methyldiphenylmethane		
0		>99.0	
5 min	0.9	96.8	2.3
10	1.5	93.6	4.7
15	1.6	92.8	5.6
30	2.9	88.4	8.7
45	4.3	83.7	12.0
1 hr	5.5	80.7	13.9
1.5	7.4	73.7	18.9
2	7.7	70.3	22.0
6	8.3	68.5	23.2
24	9.7	66.1	24.2
	4-Methyldiphenylmethane		
0	<0.1	<0.1	99.9
30 sec	2.1	2.4	95.5
1 min	4.5	8.5	87.0
2	7.8	12.0	80.2
3	11.5	21.7	66.8
5	12.5	36.3	51.2
7	12.7	45.4	41.9
10	11.3	57.7	31.0
15	10.2	62.7	27.1
30	9.9	65.5	24.6
24 hr	9.7	65.4	24.9

In the continued investigation of the Friedel–Crafts isomerization of disubstituted benzenes[5] we now investigated the aluminum chloride catalyzed isomerization of the isomeric methyldiphenylmethanes.

Results and Discussion

The needed high purity isomeric methyldiphenylmethanes were prepared by standard methods, the best suited being the following.

2-Methyldiphenylmethane was prepared from α-chloro-*o*-xylene and phenylmagnesium bromide.

3-Methyldiphenylmethane was prepared by the $ZnCl_2$-catalyzed Friedel–Crafts reaction of α-chloro-*m*-xylene with benzene.

4-Methyldiphenylmethane was obtained by the catalytic (palladium on charcoal) hydrogenation of 4-methylbenzophenone.

The aluminum chloride catalyzed isomerization of the isomeric methyldiphenylmethanes was carried out

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[1] Part XIV: G. A. Olah, J. C. Lapierre, and H. Schreier, *J. Org. Chem.,* **31,** 1268 (1966).

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[3] G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.,* **84,** 1688 (1966).

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[5] Parts II and XIV of this series.