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REACTION OF TRI-2-THIENYLCARBENIUM PERCHLORATE WITH HYDROGEN AND CARBON NUCLEOPHILES

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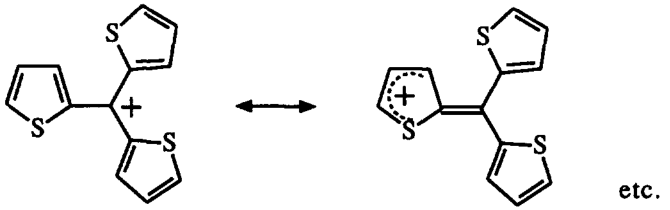
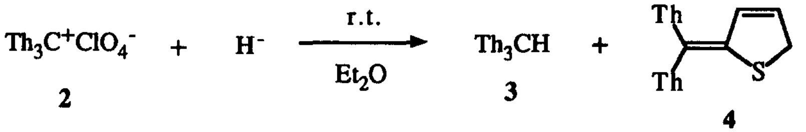
Summary: The reaction of tri-2-thienylcarbenium perchlorate (**2**) with hydrogen and carbon nucleophiles affords three types of addition products which arise from the addition of nucleophiles at the carbenium ion center and the 3- and 5-positions of the 2-thienyl group.

Although the chemistry of triphenylcarbenium salts has been investigated in great detail from a wide variety of viewpoints,[1] that of carbenium salts stabilized by three five-membered heteroaromatic substituents remains as an undeveloped field.[2] As to the tri-2-thienylcarbenium ion **1**, the formation of tri-2-thienylmethyl radical by reduction with zinc is the only reported reactivity of this cation,[3] although its structure was investigated by ^{1}H and ^{13}C NMR.[4] Here we report that it reacts with hydrogen and carbon nucleophiles not only at the carbenium ion center but also on the thiophene ring (Th denotes 2-thienyl hereafter in this paper).

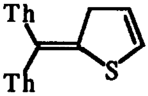


1

Addition of $LiAlH_4$ to an ethereal suspension of tri-2-thienylcarbenium perchlorate (**2**)[3a] at room temperature results in a rapid hydride addition not only to the carbenium ion center but also to the 5-position of the thiophene ring to give compounds **3**[5] (55%) and **4** (32%), respectively. ^{1}H NMR shows that **4** has an allyl system in addition to two nonequivalent 2-thienyls. The same conclusion is reached by ^{13}C NMR. **4** isomerizes to **3** quantitatively by treatment with *t*-BuOK in *t*-BuOH/C_6H_6.[6] Possibility of isomeric compound **5** which has also an allyl system and arises from hydride addition to the 3-position was ruled out by reducing **2** with $LiAlD_4$. Treatment of the resulting **4-d** with *t*-BuOK afforded **3-d** which is easily distinguishable from the product coming from deuteride addition to the 3-position. Reduction with $NaBH_4$ also afforded **3** and **4** though in decreased yields.



LiAlH$_4$	55%	32%
NaBH$_4$	27%	3%



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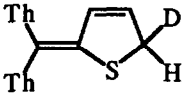
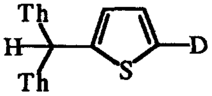
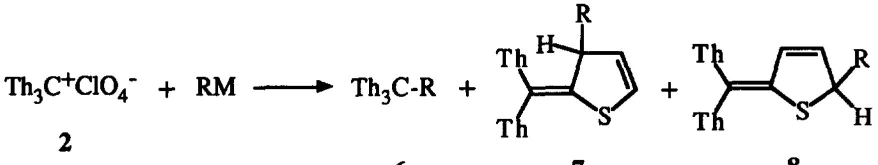


4 - d

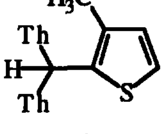


3 - d

A variety of organometallic reagents react with **2** smoothly. The reaction occurs not only at the carbenium ion center but also at the 3- and 5-positions of the thiophene ring to give compounds **6**, **7**, and **8** (Table I). Structures of these compounds were determined by spectroscopic means and also in some cases by chemical transformations. For example, **7** (R=Me) and **8** (R=Me) isomerize to **9** and **10**,[7] respectively, by treatment with *t*-BuOK, and compound **8** (R=Ph) is reduced to **11** by Raney nickel.



6 **7** **8**



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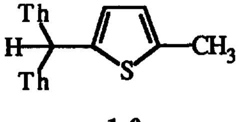

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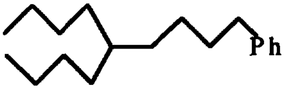

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Table I shows the following tendency. Influence of the bulkiness of an alkyl substituent in Grignard reagents on the relative ratio of **6**, **7**, and **8** becomes noticeable only when the alkyl is *t*-butyl where **7** and **8** are major products (entries 1, 4, 5, 9). When the reagent carries a β-hydogen, **3** was formed in a low yield (enties 4, 5, 9).[8] Interestingly, in aryl series, the reaction exclusively occurs on the thiophene ring (mainly at the 5-position) (entries 10, 11, 13). The use of THF as solvent or cosolvent increases the relative yields of **7** and **8**, although the effect of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) is not prominent (entries 1, 3, and 5-8).

Table I. Reaction of **2** with Organometallic Reagents[a]

		yield of products (%)[b]			
entry	RM[c]	**6**	**7**	**8**	others
1	MeMgI	54 (59)	11 (12)	26 (29)	
2	MeMgI[d]	55 (60)	11 (12)	26 (28)	
3	MeMgI[e,f]	23 (28)	21 (26)	38 (46)	
4	EtMgBr	51 (58)	17 (19)	17 (19)	**3**, 3 (3)
5	*i*-PrMgBr	35 (54)	9 (14)	17 (26)	**3**, 4 (6)
6	*i*-PrMgBr[e,f]	18 (32)	14 (24)	23 (40)	**3**, 2 (4)
7	*i*-PrMgBr[f]	19 (34)	13 (23)	21 (38)	**3**, 3 (5)
8	*i*-PrMgBr[g]	26 (35)	20 (27)	27 (36)	**3**, 2 (3)
9	*t*-BuMgCl	7 (14)	18 (35)	26 (51)	**3**, trace
10	PhMgBr	*h*	11 (12)	82 (88)	
11	*p*-TolMgBr	*h*	11 (12)	79 (88)	
12	*p*-TolMrBr[g]	*h*	10 (10)	89 (90)	
13	*o*-TolMgBr	*h*	7 (7)	91 (93)	
14	*o*-TolMgBr[g]	*h*	5 (5)	90 (95)	
15	MeLi	10 (14)	24 (33)	6 (8)	**10**,33(45)
16	Me$_2$CuLi	4 (10)	5 (13)	30 (77)	
17	Me$_2$Zn	34 (48)	10 (14)	27 (38)	

[a] Unless otherwise stated, RM in ether was added to a stirred suspension of **2** in ether at room temperature. [b] Values in parentheses refer to relative yields. [c] 5 equiv of RM was used. [d] MeMgI in ether was added at -78 °C and then the mixture was warmed to room temperature. [e] RM containing 1 equiv of TMEDA was added. [f] RM in Et$_2$O/THF (5:1) was added to a stirred suspension of **2** in ether. [g] THF as solvent. [h] Not detected.

Relative yields also depend on the nature of the organometallic reagents (entries 1, 15-17); the relative yield of **6** decreases in the order of MeMgI (59), Me$_2$Zn (48), MeLi (14), and Me$_2$CuLi (10) in accordance with the order of bulkiness of the reagents expected from solvation and aggregation.[9]

For comparison, reactions of triphenylcarbenium perchlorate with Grignard reagents were investigated. The reaction with MeMgI gave Ph$_3$CMe[10] in 41% yield and with PhMgBr an intractable mixture containing a small amount of Ph$_3$CH, no products arising from addition to the phenyl ring being formed in any amount.

The present reaction probably proceeds in a single electron transfer mechanism,[11] although, in some cases, direct addition mechanism may be also operative. Supporting evidence for the former mechanism, though indirect, comes from the formation of the dimer[12] of tri-2-thienylmethyl radical by reaction of **2** with *t*-BuLi.[13]

Our findings that **2** cleanly reacts with nucleophiles both at the carbenium ion center and on the thiophene ring, whereas triphenylcarbenium perchlorate does not show such reactivities, can be rationalized as follows. 2-Thienyl is a smaller and better electron-donating substituent than phenyl, and therefore **1** is a less crowded and more planar species than triphenylcarbenium ion as evidenced by recent ^{13}C NMR study.[4c] Consequently, the positive charge of **1** or the electron spin density of tri-2-thienylmethyl radical (if the reaction proceeds in a single electron transfer mechanism)[3] is more effectively delocalized over the whole molecule compared to that of triphenylcarbenium ion or of triphenylmethyl radical. This, along with the smaller resonance energy of thiophene compared to that of benzene, makes it easy the addition of nucleophiles to the reactive sites of **1**.

Apart from the mechanism, the present reaction which allows the preparation of a number of structurally interesting compounds having 2-methylenedihydrothiophene skeletons[15] is synthetically valuable.

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