Bromination, Deuteration, and Lithiation of the Dithienyls[1]

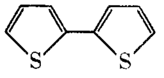
RICHARD M. KELLOGG, A. PAUL SCHAAP, AND HANS WYNBERG

Department of Chemistry, The University, Groningen, The Netherlands

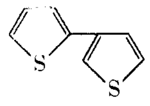
Received August 5, 1968

Reaction of 2,2′-dithienyl (**1**), 2,3′-dithienyl (**2**), and 3,3′-dithienyl (**3**) with 2 equiv of NBS in chloroform-acetic acid leads to the formation in virtually quantitative yield of 5,5′-dibromo-2,2′-dithienyl (**4**), 2′,5-dibromo-2,3′-dithienyl (**5**) and 2,2′-dibromo-3,3′-dithienyl (**7**), respectively. Reaction of **2** and **3** with excess NBS in CCl_4 for long periods leads to formation of 2′,5,5′-tribromo-2,3′-dithienyl (**6**) and 2,2′,5,5′-tetrabromo-3,3′-dithienyl (**8**), respectively. Reduction of the bromodithienyls to the respective deuterio compounds is described. The nmr spectra of **1** and **3** have been analyzed and that of **2** has been partially solved. Exchange in refluxing deuterioacetic acid with **1** leads to exchange at the 5,5 positions, with **2** to exchange at the 2′ and 5 positions, and with **3** to exchange at the 2,2′ positions. Exchange reactions with *n*-butyllithium have been carried out with **1**, **2**, and **3**; all α positions undergo exchange. Results of electrophilic substitution are compared with predictions obtained from extended Pariser-Parr-Pople calculations.

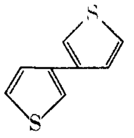
Our interest in the mechanisms of substitution reactions of thiophenes[2] led us to investigate the behavior of 2,2′-dithienyl (**1**), 2,3′-dithienyl (**2**), and 3,3′-dithienyl (**3**) in some detail. We report here the first *complete* analyses of the kinetically controlled products of electrophilic bromination and deuteration with **1**, **2**, and **3** together with a brief study of hydrogen-lithium exchange reactions with these biaryls.



1



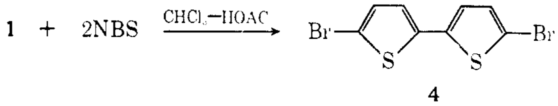
2



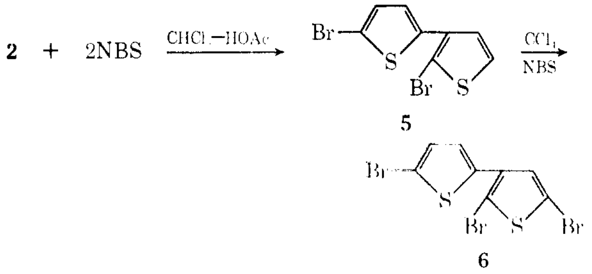
3

Results

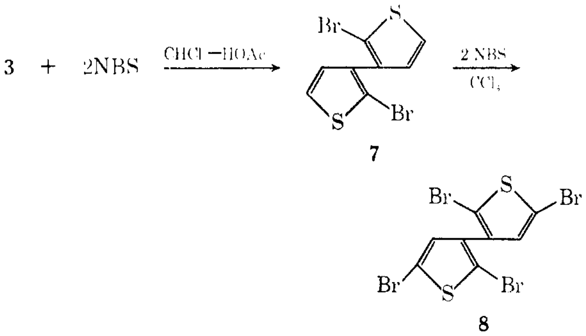
We established previously that the brominations of a number of 3-substituted thiophenes proceed with high selectivity giving the corresponding 2-bromo derivatives, the products of kinetic control. These brominations, especially with 3-aryl- and alkyl-substituted thiophenes, are complicated by concomitant acid-catalyzed rearrangements induced by hydrogen bromide released during reaction. Not surprisingly, similar difficulties are met with upon attempted direct bromination of **2** and **3** resulting in complex product mixtures.[3] Fortunately, these problems can be circumvented by use of the brominating agent N-bromosuccinimide (NBS) in mixed chloroform-acetic acid solvent.[2] Under these conditions **1**, **2**, and **3** react smoothly and essentially quantitatively within a matter of minutes at room or slightly elevated temperatures with 2 equiv of NBS to give 5,5′-dibromo-2,2′-dithienyl (**4**), 2′,5-dibromo-2,3′-dithienyl (**5**), and 2,2′-dibromo-3,3′-dithienyl (**7**), respectively (eq 1-3).[4] Succinimide (not shown) is a reaction product easily removed upon work-up. Other reaction conditions and longer times were used to form 2′,5′,5-tribromo-2,3′-dithienyl (**6**) and 2,2′,5,5′-tetrabromo-3,3′-dithienyl (**8**) (eq 2 and 3).



(1)



(2)



(3)

All products obtained from brominations of **1**, **2**, and **3** were identified by analysis of the nmr spectra.[5] Structure assignments were considered to be virtually unambiguous but, because instability[6] prevented elemental analyses of the previously unknown derivatives **5**, **6**, **7**, and **8**, we chose to confirm these structures further by reduction with zinc and deuterioacetic acid to the corresponding stable deuterated dithienyls. This reduction is known to proceed with bromothiophenes without accompanying rearrangement.[2,7] Con-

---

[1] A preliminary account of some of the results contained herein was presented at the Second IUPAC Symposium on Photochemistry, Enschede, The Netherlands, July 1967.

[2] R. M. Kellogg, A. P. Schaap, E. T. Harper, and H. Wynberg, *J. Org. Chem.*, **33**, 2902 (1968).

[3] (a) N. Gjös and S. Gronowitz, *Acta Chem. Scand.*, **21**, 2893 (1967). See ref 2 for a detailed discussion of this problem. (b) No particular difficulties are experienced with 2,2′-dithienyl (**1**) and indeed bromination products from this compound have long been known; see, for example, W. Steinkopf, "Die Chemie des Thiophens," Verlag Th. Steinkopf, Leipzig, 1941, pp 141-149, and references contained therein.

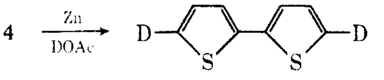
[4] Because of obvious separation difficulties no exhaustive effort was made to isolate monobromides although this is probably possible. All reactions were followed by glpc under conditions where monobromides could be observed. Dibromides appeared at a very early stage in the reaction and with **2** monobromide peaks of similar heights were observed which remained in nearly constant ratio during the course of reaction.

[5] See, for example, the discussion by S. Gronowitz, *Advan. Heterocyclic Chem.*, **1**, 1 (1963).

[6] Bromination products **5**, **6**, **7**, and **8** were indefinitely stable at −20° but began to discolor seriously within 1 hr at room temperature. In one case an old sample of **5**, after standing at room temperature, suddenly decomposed with near explosive violence; large quantites of hydrogen bromide were liberated.

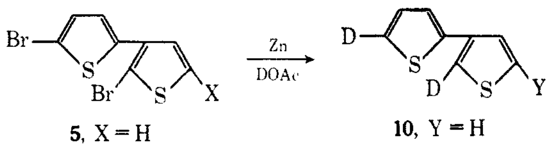
[7] B. Bak, *J. Org. Chem.*, **21**, 797 (1956).

version of **4**, **5**, **6**, **7**, and **8** into, respectively, 5,5′-dideuterio-2,2′-dithienyl (**9**), 2′,5-dideuterio-2,3′-dithienyl (**10**), 2′,5,5′-trideuterio-2,3′-dithienyl (**11**), 2,-2′-dideuterio-3,3′-dithienyl (**12**), and 2,2′,5,5′-tetradeuterio-3,3′-dithienyl (**13**) proceeded smoothly and in good yield (eq 4–6). Analysis of the nmr spectra completely substantiated the original structure assignments of the bromine-substituted precursors (see Experimental Section).



9

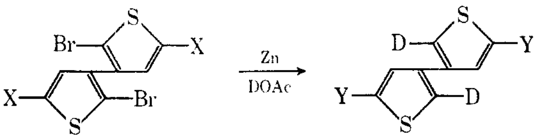
(4)



(5)

5, X = H
6, X = Br

10, Y = H
11, Y = D

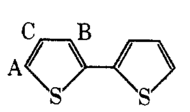


(6)

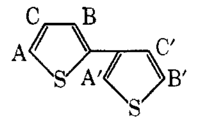
7, X = H
8, X = Br

12, Y = H
13, Y = D

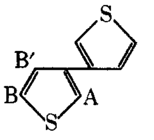
In addition to confirming the structural assignments of the bromo precursors an analysis of the nmr spectra of these deuterated derivatives allowed a complete solution of the nmr spectra of **1** and **3** as well as a partial analysis of that of **2**.[8] The ABC spectrum of **1** was first approximated as ABX and the parameters measured from 5,5′-dideuterio-2,2′-dithienyl (**9**) were used to adjust these ABX approximations. These approximate values were substituted in an ABC matrix equation and minor changes in spectral parameters were continously incorporated until the generated and experimentally obtained ABC spectra matched. The spectrum of **3** in deuterioacetone solvent is of the ABB′ type and is readily solved as described for 3-phenylthiophene;[9] the spectrum collapses to a singlet in CCl_4 solution. The spectrum of **2** is not sufficiently resolved to allow complete analysis of the overlapping ABC spectra; noteworthy, however, is the solvent sensitivity of the spectrum of **2** and deuterated derivatives **10** and **11** wherein the 4′,5′-protons collapse to a singlet in CCl_4 solution but are resolved in C_3D_6O. This is of considerable help in spectral analyses of partially deuterated derivatives. All obtainable parameters for **1**, **2**, and **3** are shown; parameters are applicable for a 10% solution of the respective compound in C_3D_6O.



$J_{AB} = 1.2$ Hz; $\nu_B - \nu_A = 7.1$ Hz
$J_{BC} = 3.4$ Hz; $\nu_C - \nu_A = 18.8$ Hz
$J_{AC} = 5.0$ Hz

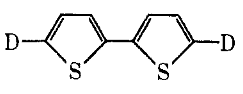


$J_{B'C'} = 5.0$ Hz; $\nu_{C'} - \nu_{B'} = 8.2$ Hz
$J_{BC} = 3.6$ Hz; $\nu_C - \nu_B = 15.9$ Hz

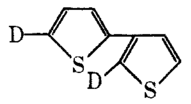


$J_{AB} + J_{AB'} = 4.3$ Hz[9]
$\nu_B - \nu_A = \nu_{B'} - \nu_A = 11.2$ Hz

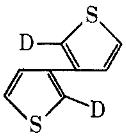
We had previously discovered that many substituted thiophenes readily undergo deuterium–hydrogen exchange in refluxing deuterioacetic acid[2] and wished to use this reaction as a second model of an electrophilic substitution reaction with the dithienyls. With the nmr spectral analyses in hand such an investigation became experimentally feasible. The results of deuterium–hydrogen exchange reactions with **1**, **2**, and **3** carried out for 5 hr in refluxing deuterioacetic acid are as shown; exchange occurred exclusively at the positions indicated.[10] Recovery of material was at least 80% and usually nearly quantitative. The amount and position of deuterium substitution were determined by analysis of nmr spectra of exchanged products taken both in CCl_4 and C_3D_6O. The partially deuterated compounds were then allowed to react with 2 equiv NBS and the dibromides obtained were shown to be identical with those obtained from non-deuterated materials; exchange is therefore established to occur only at the positions substituted by bromine.[11] From consideration of spectra and integration ratios the amounts of exchange were determined.



5,5′, *ca.* 60% exchange



5, 22%; 2′, 40% exchange



2,2′, *ca.* 60% exchange

A brief study of hydrogen–lithium exchange reactions with **1**, **2**, and **3** was carried out; the dithienyls were treated with *n*-butyllithium, warmed to room temperature, and quenched with D_2O. Recovery of starting materials was 97% or better. Determination of the position and amount of substitution was similar to that described above and the results are as shown; exchange was confined to the positions shown.

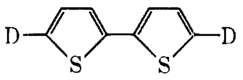
---

(8) Nmr techniques with arylthiophenes wherein deuterium labeled compounds are used in obtaining certain nmr spectral parameters have been described: R. M. Kellogg and H. Wynberg, *J. Amer. Chem. Soc.*, **89**, 3495 (1967).

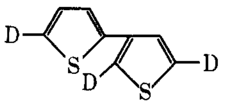
(9) Solution of the spectra gives only the combined value $J_{AB} + J_{AB'}$ while $J_{BB'}$ is not measurable. From the spectrum of 2,5′-dideuterio-3,3′-dithienyl obtained as a product of photolysis from **10**,[1] $J_{AB'}$ has been measured as 1.2 Hz requiring therefore that $J_{AB} = 3.1$ Hz. This agrees well with the spectrum of 3-phenylthiophene.[8]

(10) No conflict exists between these exchange reactions and the structure proofs of the bromodithienyls carried out by reduction with zinc in refluxing deuterioacetic acid. Exchange undoubtedly takes place in the latter reaction but is a "blind" deuterium–deuterium exchange leading to no *observable* products other than those obtained by direct bromine–deuterium substitution.

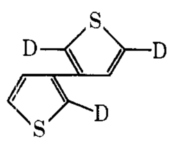
(11) We were concerned whether bromination might lead to loss of deuterium at a position other that being substituted. This point has been checked specifically with 2,5-dideuterio-3-phenylthiophene which gives *only* 2-bromo-5-deuterio-3-phenylthiophene upon bromination; no deuterium loss from the 5 position is observable: R. M. Kellogg, J. J. C. Vermeer, and H. Wynberg, unpublished results.



5,5′, 92% exchange



5, *ca.* 40%; 2′, *ca.* 40%, 5′, 33% exchange

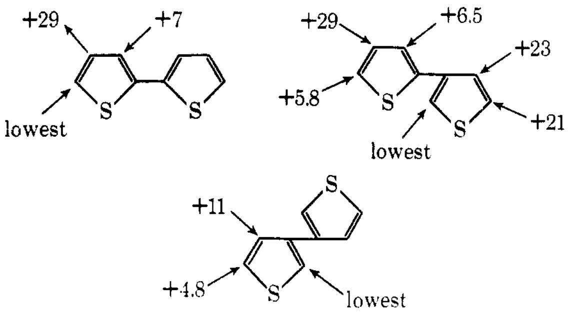


2,2′, 38%; 5,5′, 7% exchange

Discussion

The electrophilic brominations[12] and deuterations of the dithienyls proceed with high selectivity in the 5,5′ positions of **1**, the 2′,5 positions of **2**, and 2,2′ positions of **3**.[13,14] Since virtually all the starting material is accounted for as products there exists little chance that other isomers might have been missed. Electrophilic substitution in thiophenes is expected to be favored at positions adjacent to sulfur consistent with the 5,5′-substitution in **1**; the situation becomes, however, more interesting with **2** and **3** where three and four α positions are available, respectively.

The observed positions for substitution have been compared with those predicted from extended Pariser–Parr–Pople molecular orbital calculations. The relative activation energies (in kilocalories per mole) involved in electrophilic substitution at various positions were determined and the results of these calculations are as illustrated.[15] One is encouraged to see that the calculated positions of highest reactivity are the same as those found experimentally. The most notable discrepancy is the predicted reactivity of the 3,3′ positions in **1** and the 3 position of **2** while no electrophilic bromination or deuteration occur at these positions. The 3,3′ positions of **1** are reported, however, to be substituted when the 5,5′ positions are blocked.[3b] These results[16] must, of course, be treated with appropriate caution but it would appear that the positions at which substitution occur are governed primarily by energetic considerations and steric factors which *a priori* might be expected to be important with **2** and **3** do not play a major role in bromination or deuteration. These results are in contrast to those with biphenyl where *para* is highly favored over *ortho* substitution; this has been rationalized by one set of authors in terms of steric factors affecting the transition state.[17]



The lithium–hydrogen exchange experiments are not readily interpreted since no acceptable model mechanism for this reaction exists.[5] Second, one is not at all sure whether the products obtained in this case are those of kinetic control. The results obtained represent a more complete analysis of product distribution than that previously reported using carbonation as the quenching technique.[14] The present results, especially with **2** and **3**, agree well with experiments recently carried out with 3-phenylthiophene wherein substitution at the 2 and 5 positions has been observed both after quenching with deuterioacetic acid and by direct nmr spectral examination of the lithium compounds.[18]

Experimental Section

Melting points and boiling points are uncorrected. Deuterium oxide (99.7 atom %) was obtained from Carl Roth (Karlsruhe). Nuclear magnetic resonance (nmr) spectra were measured with a Varian A-60 instrument with tetramethylsilane (TMS) as an internal standard. Spectra were taken at 500-, 250- and 100-cps sweep widths and integrations were done two times going from low to high field and two times from high to low field and the average values were used. Gas–liquid partition chromatography (glpc) was done with an F & M Model 810 gas chromatograph equipped with hydrogen flame detectors. Compounds cited without reference were either prepared by standard procedures or were available in stock.

5,5′-Dibromo-2,2′-dithienyl (4) was prepared from the reaction of 2,2′-dithienyl (420 mg, 2.53 mmol) in 15 ml of a 50:50 (v/v) mixture of chloroform and acetic acid to which NBS (900 mg, 5.05 mmol) was added. Reaction started instantly at room temperature and the solution was warmed briefly to ensure complete conversion. The reaction mixture was taken up in CS_2 (used only with **4** because of its insolubility in other organic solvents), was washed with KOH solution until basic, washed once with H_2O, and was dried over $MgSO_4$. Removal of the solvent left 786 mg (96%) of **4**: mp 149–151° (lit.[14] mp 146–147.5°); nmr (CS_2) δ 6.78 (d, 2, J = 3.6 Hz, 4 H[19]), 6.92 (d, 2, J = 3.6 Hz, 3 H).

---

[12] A possible mechanism for the electrophilic brominations of thiophenes by NBS as well as evidence that the products obtained are kinetically controlled has been discussed.[2]

[13] 2,2′-Dithienyl (**1**) has received some investigation wherein halogenations,[3] nitration,[3,14] acetylations,[3] mercurations,[3] and sulfonations[3] have been examined. In virtually all cases the 5,5′ positions are most reactive. Investigation of 2,3′-dithienyl (**2**) has been confined to acetylation by Wynberg, *et al.*, where substitution at the 5 position was observed.[14] 3,3′-Dithienyl (**3**) appears not to have been studied seriously.

[14] H. Wynberg and A. Bantjes, *J. Amer. Chem. Soc.*, **82**, 1447 (1960); see also H. Wynberg, A. Logothetis, and D. VerPloeg, *ibid.*, **79**, 1972 (1957).

[15] These results were obtained with a program written by the Department of Structural Chemistry of the University of Groningen. We are grateful to Professor E. Wiebenga and Mr. E. J. Bouwhuis of this department for making results available to us. Parameters used and the approaches to building molecular orbitals were essentially those described by A. J. H. Wachters and D. W. Davies, *Tetrahedron*, **20**, 2841 (1964). Relative activation energies are those derived from assumptions of the changes involved concomitant with adjustment from sp^2 to sp^3 hybridization at a particular position upon addition of an arbitrary electrophile. Calculations were carried out both for *cis* and *trans* conformations of **1**, **2**, and **3** but energy differences were insignificant. The values given are for the *trans* conformations (sulfurs oriented in opposite directions).

[16] The positions of electrophilic substitution can, of course, be predicted correctly by the cruder expedient of considering the longest conjugated system which may be formed by addition of an electrophile; see, for example, H. Hogeveen, *Rec. Trav. Chim. Pays-Bas*, **85**, 1072 (1966).

[17] H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, **84**, 1238 (1962); for arguments that the effect derives from electronic factors, see R. C. Neuman, Jr., *ibid.*, **84**, 3025 (1962), and R. Baker, R. W. Bott, and C. Eaborn, *J. Chem. Soc.*, 2136 (1963).

[18] N. Gjös and S. Gronowitz, *Arkiv Kemi*, in press. We are grateful to Professor Gronowitz for providing us with a copy of this manuscript prior to publication; see also S. Gronowitz and A. Bugge, *Acta Chem. Scand.*, **22**, 59 (1968).

[19] These assignments are assumed by analogy to other systems.

5,5′-Dideuterio-2,2′-dithienyl (9) was prepared by reduction of **4** (280 mg, 0.77 mmol) with Zn (0.8 g, 12.2 mg-atoms) in a mixture of redistilled acetic anhydride (2 ml) and deuterium oxide (2 ml). The mixture was put in a flame-dried erlenmeyer equipped with magnetic stirring bar, reflux cooler, and drying tube. The reaction mixture was refluxed 5.5 hr after which time excess water was added and the Zn was filtered off and was thoroughly washed with ether. The reaction mixture was extracted three times with ether, the ether layer was neutralized by washing repeatedly with $KHCO_3$ solution, was washed once with water, and was dried over $MgSO_4$. Removal of the ether left 87 mg (67% yield) of **9**: nmr (C_3D_6O) δ 7.00 (d, 2, J = 3.4 Hz, 4 H), 7.20 (d, 2, J = 3.4 Hz, 3 H), (CCl_4) δ 6.90 (d, 2, J = 3.4 Hz, 4 H), 7.07 (d, 2, J = 3.4 Hz, 3 H). The doublets at δ 7.00 and 6.90 in C_3D_6O and CCl_4, respectively, were broadened by coupling to the deuterium atoms in the 5 positions.[20]

2′,5-Dibromo-2,3′-dithienyl (5) was prepared from the reaction of 2,3′-dithienyl (420 mg, 2.53 mmol) with NBS (900 mg, 5.05 mmol) in 16 ml of a 50:50 (v/v) mixture of chloroform–acetic acid. After reaction and work-up as described above there was obtained 771 mg (94%) of **5**: mp 46–47°; nmr (C_3D_6O) δ 7.13 (d, 1, J = 4.0 Hz, 4 H), 7.21 [d, 1, J = 5.8 Hz, 4′ H (absorption buried under other peaks)], 7.30 (d, 1, J = 4.0 Hz, 3 H), 7.42 (d, 1, J = 5.8 Hz, 5′ H), (CCl_4) δ 6.91 (d, 1, J = 3.8 Hz, 4 H), 6.92 (d, 1, J = 5.8 Hz, 4′ H), 7.08 (d, 1, J = 3.8 Hz, 3 H), 7.17 (d, 1, J = 5.8 Hz, 5′ H). The nmr spectrum in C_3D_6O owing to overlapping gave only six resolved peaks under all conditions while in CCl_4 at expanded sweep width and high instrument sensitivity all four sets of doublets could be observed.

2′,5-Dideuterio-2,3′-dithienyl (10) was prepared from the reduction of **5** (745 mg, 2.3 mmol) with Zn (2.0 g, 30.6 mg-atoms) in acetic anhydride (5.5 ml) and deuterium oxide (6.5 ml). After reaction and work-up as described above there was obtained 250 mg (65%) of **10**: nmr (C_3D_6O) δ 7.04 [d (broadened by coupling to deuterium), 1, J = 3.5 Hz, 4 H], 7.30 (d, 1, J = 3.5 Hz, 3 H), 7.35 (d, 1, J = 5.0 Hz, 4′ H), 7.49 [d (slightly deuterium broadened), 1, J = 5.0 Hz, 5′ H], (CCl_4) δ 6.90 [d (deuterium broadened), 1, J = 3.5 Hz, 4 H], 7.06 (d, 1, J = 3.5 Hz, 3 H), 7.20 (s, 2, 4′,5′ H).

2′,5,5′-Tribromo-2,3′-dithienyl (6) was obtained from the reaction (*ca.* 50 hr) of 2,3′-dithienyl (100 mg, 0.62 mmol) with NBS (500 mg, 2.8 mmol) in 5 ml of CCl_4 containing a trace of water–acetone.[21] Work-up of the reaction mixture (washed with aqueous KOH and water, dried over $MgSO_4$) gave 102 mg (40%) of **6**: mp 54.0–55.3°; nmr (C_3D_6O) δ 6.60 (d, 1, J = 4.0 Hz, 4 H), 6.72 (d, 1, J = 4.0 Hz, 3 H), 6.82 (s, 1, 4′ H).

2′,5,5′-Trideuterio-2,3′-dithienyl (11) was obtained by treatment of **6** (72 mg, 0.18 mmol) with excess Zn and deuterioacetic acid under conditions previously described to give 24 mg (79%) of **11**: nmr (C_3D_6O) δ 7.03 [d, 1, J = 3.5 Hz, 4 H (broadened by deuterium coupling)], 7.29 (d, 1, J = 3.5 Hz, 3 H), 7.37 [s, 1, 4′ H (broadened by deuterium coupling)].

2,2′-Dibromo-3,3′-dithienyl (7) was prepared from the reaction of 3,3′-dithienyl (420 mg, 2.53 mmol) with NBS (900 mg, 5.05 mmol) in 16 ml of a 50:50 (v/v) mixture of chloroform–acetic acid; reaction was complete within a few minutes at room temperature. Work-up gave 825 mg (101%) of **7**: mp 78–79°; nmr (C_3D_6O) δ 7.15 (d, 2, J = 5.7 Hz, 4,4′ H) and 7.62 (d, 2, J = 5.7 Hz, 5.5′ H).

2,2′-Dideuterio-3,3′-dithienyl (12) was prepared by the reduction of **7** (1.19 g, 3.67 mmol) with Zn (2.4 g, 37 mg-atoms) in a mixture of acetic anhydride (7 ml) and deuterium oxide (7 ml). After work-up 560 mg (91%) of **12** was obtained; nmr spectra in both C_3D_6O and CCl_4 consisted of singlets. Treatment of the obtained **12** with 2 equiv of NBS gave 2,2′-dibromo-3,3′-dithienyl identical with that prepared from nondeuterated material.

2,2′,5,5′-Tetrabromo-3,3′-dithienyl (8) was prepared from the reaction of 3,3′-dithienyl (1.00 g, 6.02 mmol) with NBS (4.2 g, 23.6 mmol) in 30 ml of CCl_4. After 152 hr the reaction was stopped and the mixture was worked up to yield 1.0 g (34%) of **8**: mp 133–136°; nmr spectra in both C_3D_6O and CCl_4 consisted of one singlet.

2,2′,5,5′-Tetradeuterio-3,3′-dithienyl (13) was prepared by the reduction of **8** (777 mg, 1.61 mmol) with zinc (2.44 g, 34.4 mg-atoms) in a mixture of acetic anhydride (7.5 ml) and deuterium oxide (9 ml); the mixture was refluxed 5 hr. Work-up gave 200 mg (73%) of **13**: nmr spectra in CCl_4 and C_3D_6O consisted of singlets.

Deuterium exchange with the dithienyls was carried out by treating the appropriate dithienyl (125 mg, 0.755 mmol) in a mixture of acetic anhydride (2 ml) and D_2O (2.25 ml) for 5 hr. The solutions were quenched with water and extracted with ether; the ether layer was neutralized with $NaHCO_3$ solution, washed with water, and dried over $MgSO_4$. Evaporation of the solvent left the exchanged dithienyl in 80–100% yield. The nmr spectra of the exchanged products were taken in CCl_4 and C_3D_6O and compared with the dideuterio compounds already prepared. The exchanged compounds were then allowed to react with 2 equiv of NBS to give dibromides which were shown to be identical with those obtained from nondeuterated dithienyls. This indicates that deuteration and bromination occur at identical positions. By detailed examination of the nmr spectra of the exchanged materials the amount of deuterium exchange at the reactive positions could be determined.

Lithium exchange experiments with dithienyls were carried out with the appropriate dithienyl (664 mg, 4.0 mmol) in 20 ml of dry ether. *n*-BuLi (8–9 mmol *ca.* 1.0 *M* in ether solution) was added at 0° under an N_2 atmosphere. The mixtures became turbid and then clear. After standing *ca.* 10 min the reaction mixtures were quenched with 5 ml of D_2O. The solutions were filtered, washed, and dried to give the dithienyl in not less than 97% yield. Nmr spectra in CCl_4 and C_3D_6O were taken after which the deuterated materials were brominated with 2 equiv of NBS. The spectra of the dibromides were examined to determine the amounts and location of the deuterium remaining. Careful examination of all spectra allowed the assignments given.

Registry No.—**1**, 492-97-7; **2**, 2404-89-9; **3**, 3172-56-3; **4**, 4805-22-5; **5**, 18592-84-2; **6**, 18592-85-3; **7**, 18592-86-4; **8**, 18592-87-5; **9**, 18592-88-6; **10**, 18592-89-7; **11**, 18592-90-0; **12**, 18592-91-1; **13**, 18592-92-2.

Acknowledgment.—The authors thank Mr. J. Buter for aid with certain experimental problems met within the course of this work.

---

[20] For a discussion of this phenomenon in deuteriothiophenes, see R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, **15**, 45 (1959).

[21] This method was used for a number of reactions before the catalytic effects of acetic acid were noted. The tribromination in chloroform–acetic acid did not, however, go well in our hands.