Similar treatment of **16c** gave **16b** (60%) and α-methyl-β-phenylsulfonylpropionic acid (30% yield), mp 107–109° (reported[8] mp 113°).

Registry No.—**1**, 35347-56-9; **5**, 38434-93-4; **6a**, 38434-94-5; **6b**, 38434-95-6; **7**, 38434-96-7; **8a**, 38434-97-8; **8b**, 38434-98-9; **9a**, 38434-99-0; **9b**, 38435-00-6; **10**, 27943-35-7; **11**, 38435-02-8; **12**, 38435-03-9; **13a**, 38435-04-0; **13b**, 38435-05-1; **14a**, 38435-06-2; **14b**, 38435-07-3; **15a**, 38435-08-4; **15b**, 38435-09-5; **15c**, 38435-10-8; **16a**, 10154-72-0; **16b**, 10154-73-1; **16c**, 38435-13-1; **16d**, 38435-14-2; pivalolactone, 1955-45-9.

The Reactions of Bromothianaphthenes with Piperidine. A Reinvestigation[1]

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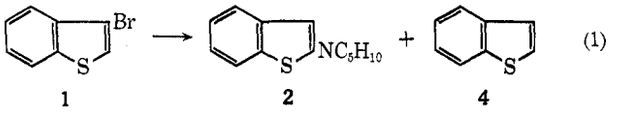
The reaction of 3-bromothianaphthene (**1**) with piperidine was reinvestigated and found to give primarily the normal (**3**) but also some of the cine-substitution product **2** which is also the only product from the reaction of 2-bromothianaphthene (**5**). The previously reported results can be rationalized by the effects of air, metals, and impure starting material on the reaction. 2,3-Dibromothianaphthene (**6**) also gives **2** under these conditions, probably *via* the bromamine **7** which was isolated under milder conditions, could be converted to **2** in high yield, and was synthesized from **2** *via* the iminium salt **9**. The diamine **8** was isolated in trace amounts from the reactions of **6** and **7** with piperidine. Possible mechanisms for some of these reactions are discussed.

Although five-membered hetarynes have been proposed as reaction intermediates for over 70 years,[2-4] closer examination[5,6] has invariably revealed these claims to be false.[7] One of those cases which has not been reexamined is the reaction of 3-bromothianaphthene (**1**) with piperidine, which, because it was reported[8] to give exclusively the cine (**2**) rather than the normal (**3**) substitution product (eq 1), might[4] involve



1 **2** **4** (1)

an elimination–addition mechanism *via* 2,3-dehydrothianaphthene. As part of the study of the reactions of halothiophenes[9-11] and halothianaphthenes[12-13] with bases a reexamination of the reactions of bromothianaphthenes with piperidine therefore was undertaken (Table I).

In agreement with the report of Brower and Amstutz[8] 2-bromothianaphthene (**5**) reacted cleanly with piperidine to give the normal substitution product **2** (expt 1). In contrast to this report (eq 1), however, the major product from 3-bromothianaphthene (**1**) was also that of normal substitution, 3-piperidinothianaphthene (**3**). A small amount of the 2 isomer (**2**) was found but thianaphthene (**4**) was not (expt 2). A possible explanation for this discrepancy may lie in differences in the reaction conditions and in the purity of the 3-bromothianaphthene (**1**). For example, when this reaction was repeated without precautions for removing air (expt 3), thianaphthene (**4**) was, as reported,[8] a minor product. Furthermore, when the starting material **1** was prepared, as reported,[8] by the direct bromination of thianaphthene,[14] substantial quantities of the 2 isomer (**2**) and thianaphthene (**4**) were present even after

TABLE I

REACTIONS OF BROMOTHIANAPHTHENES WITH PIPERIDINE

Expt	Reactant	Temp, °C (time, hr)	Products (yield, %)
1	**5**	220 (26)[a]	**2** (70)
2	**1**	250 (80)	**1** (73), **2** (2), **3** (15)
3	**1**	250 (80)[b]	**1** (60), **2** (5)
			3 (25), **4** (4)
4	**1**	250 (40)[a,c]	**1** (13), **2** (4)
			3 (67), **4** (9)
5	**1**	250 (40)[a,d]	**1** (70), **2** (1)
			3 (4), **4** (4)
6	**1**	250 (40)[a,e]	**1** (67), **2** (2)
			3 (15), **4** (4)
7	**6**	200 (15)	**2** (73), **8** (trace)
8	**6**	106 (60)[f]	**6** (71), **7** (5)
			2 (trace), **8** (trace)
9	**7**	180 (40)	**2** (83), **8** (trace)
10	**1** + **7** (1:1)	180 (40)	**2** (83),[g] **1** (70), **8** (trace)

[a] A Fischer and Porter aerosol compatibility tube with stainless steel valve was the reaction vessel. [b] No precautions for prior removal of air. [c] Valve top etched (see discussion). [d] 0.05 g of powdered Fe per 0.02 mol of **1**. [e] 0.05 g of $FeCl_3$ per 0.02 mol of **1**. [f] Reflux. [g] Based on added **7**.

(1) Taken in part from the Masters Thesis of W. B. M., Texas Christian University, 1969; reported in preliminary form at the 24th Southwest Regional Meeting of the American Chemical Society, Austin, Texas, Dec 1968.

(2) R. Stoermer and B. Kahlert, *Ber.*, **35**, 1633 (1902).

(3) H. J. den Hertog and H. C. van der Plas, *Advan. Heterocycl. Chem.*, **4**, 121 (1965).

(4) T. Kauffmann, *Angew. Chem., Int. Ed. Engl.*, **4**, 543 (1965).

(5) G. Wittig and M. Rings, *Justus Liebigs Ann. Chem.*, **719**, 127 (1968).

(6) D. A. de Bie, H. C. van der Plas, and G. Geurtsen, *Recl. Trav. Chim. Pays-Bas*, **90**, 594 (1971).

(7) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 293; H. J. den Hertog and H. C. van der Plas in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, p 1149.

(8) K. R. Brower and E. D. Amstutz, *J. Org. Chem.*, **19**, 411 (1954).

(9) M. G. Reinecke and H. W. Adickes, *J. Amer. Chem. Soc.*, **90**, 511 (1968).

(10) M. G. Reinecke, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), C68 (1969).

(11) M. G. Reinecke, H. W. Adickes, and C. Pyun, *J. Org. Chem.*, **36**, 2690, 3820 (1971).

(12) M. G. Reinecke and T. A. Hollingworth, *ibid.*, **37**, 4257 (1972).

(13) D. A. de Bie, H. C. van der Plas, G. Geurtsen, and K. Nijdam, *Recl. Trav. Chim. Pays-Bas*, submitted.

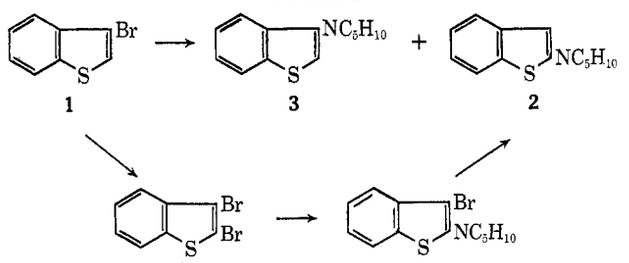
(14) G. Komppa, *J. Prakt. Chem.*, **122**, 319 (1929).

fractional distillation. Treatment of such a mixture with piperidine would have resulted in the preferential reaction of the more reactive[8] 2-bromo isomer which would have led, particularly at the shorter reaction times used by Brower and Amstutz,[8] to **2** as a major product. In our reactions (Table I) a modified bromination procedure[15] was used to prepare **1** and the last traces of 2-bromo isomer and thianaphthene were removed by reaction with piperidine and by preparative vpc, respectively.

A further example of the sensitivity of the reaction of **1** → **3** to reaction conditions was noted when (expt 4) the usual reaction vessel, a sealed glass ampoule, was replaced by a pressure tube containing a stainless steel valve which had been etched by exposure to 48% HBr at elevated temperatures for prolonged periods. The yield of **3** was more than quadrupled even though the reaction time was halved. An unetched valve had no effect on the product yield (expt 1). The possible role of either iron (expt 5) or iron salts (expt 6) in bringing about this catalysis was examined, but they had little effect on the course of the reaction.

While cine substitution therefore is not a major process in the reaction of 3-bromothianaphthene (**1**) with piperidine, it does occur to some extent. Possible mechanisms for this process include elimination–addition,[4] abnormal addition–elimination,[8] or even a mechanism involving rearrangement of **1** → **5** prior to substitution.[16] Analogy to the reactions of halothiophenes[9,10] and halothianaphthenes[12,13] with metal amides in liquid ammonia requires that a transbromination mechanism similar to that in Scheme I also be con-

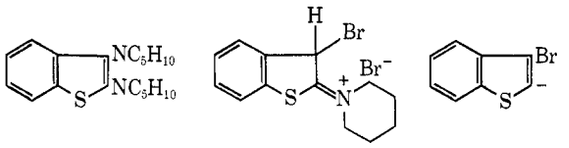
SCHEME I



sidered. As a test of the feasibility of this mechanism the reactions of the proposed intermediates 2,3-dibromothianaphthene (**6**) and 3-bromo-2-piperidinothianaphthene (**7**) with piperidine were investigated.

The feasibility of the step **6** → **2** was shown by the formation of the latter compound in 73% yield from **6** and piperidine at 200° (expt 7). A trace product detected and isolated by tlc proved to be the diamine **8** and not the proposed bromamine intermediate **7**. When the reaction temperature was reduced to 106°, however, **7** was obtained (expt 8), thereby providing evidence for its role in the step **6** → **2**. Final verification for the sequence **6** → **7** → **2** comes from the conversion of **7** to **2** in 83% yield (expt 9).

The structure of **7** was proven by independent synthesis. Bromination of **2** with dioxane dibromide gave the iminum salt **9**, which on treatment with pyridine was converted to the free base **7** in 74% yield.



8 **9** **10**

The mechanism of the step **6** → **7** may be considered as a typical nucleophilic aromatic substitution in which the more reactive 2-bromine atom[8] is preferentially removed. The debromination of **7** → **2** could be related to the radical-induced deiodination of certain aryl iodides,[17,18] but, since similar debrominations of bromothianaphthenes[12,13] and bromothiophenes[9,10] with metal amides in liquid ammonia apparently involve nucleophilic displacements on bromine, such a process is more probable. The fact that added 3-bromothianaphthene (**1**) does not increase the conversion of **7** → **2** (expt 10) indicates that *o*-halocarbanions such as **10** are not required. Mechanisms involving piperidine as the nucleophile can be written, however, and have the advantage of producing *N*-bromopiperidine as a by-product which might be capable of converting **1** to **6** under the more severe conditions of expt 2, thereby accounting for the whole process **1** → **2**.

In conclusion, cine substitution is only a minor process in the reaction of 3-bromothianaphthene with piperidine. Among the possible mechanisms for this process must be included the transbromination outlined in Scheme I.

Experimental Section

Melting points and boiling points are uncorrected. Ir spectra were recorded on a Perkin-Elmer 237 instrument as films (liquids) or KBr discs (solids) and calibrated with a polystyrene film. Nmr spectra were measured on a Varian A-60A spectrometer as 30% solutions in CCl_4 with TMS as an internal standard unless otherwise noted. Gas chromatographic analysis was performed on an Aerograph Autoprep A-700 using a 20 ft × 0.375 in. column of 30% SE-30 on Chromosorb W. Analytical tlc was carried out with Brinkman silica gel PF-254 on 1 × 3 in. plates and preparative tlc on 20 × 20 cm plates with a 1.5 mm thick layer. The plates were developed with 6:1 (v/v) low-boiling petroleum ether–benzene. Analyses were performed at M-H-W Laboratories, Garden City, Mich.

Starting Materials.—3-Bromothianaphthene (**1**),[15] 2-bromothianaphthene (**5**),[19] and 2,3-dibromothianaphthene (**6**)[20] were prepared by the cited procedures and in the latter two instances purified by recrystallization. The sample of **1** obtained by distillation (68–72°, 0.05 mm) and containing 7% **4** and 3% **5** (vpc) was heated in a sealed tube at 240° for 40 hr with half again its weight of piperidine. The neutral fraction of the resulting mixture was purified of thianaphthene (**4**) by preparative vpc to give vpc-pure 3-bromothianaphthene, bp 96.5–97° (1.4 mm) [lit.[15] bp 90–105° (1.5 mm)], $n^{20}D$ 1.6677.

Reaction of Bromothianaphthenes with Piperidine (Table I).—A mixture of the appropriate bromothianaphthene and a 4–8-fold excess of piperidine was placed in a 20 × 120 mm borosilicate glass tube, saturated with N_2 for 15 min, repeatedly frozen and

(15) J. Szmuszkovicz and E. Modest, *J. Amer. Chem. Soc.*, **72**, 571 (1950).

(16) The possibility that **2** is formed by rearrangement of **3** was eliminated by recovering the latter in 88% yield to the exclusion of **2** (vpc) under typical reaction conditions.

(17) J. F. Bunnett and C. C. Wamser, *J. Amer. Chem. Soc.*, **89**, 6712 (1967).

(18) F. Pietra, M. Bartolozzi, and F. Del Cima, *Chem. Commun.*, 1232 (1971).

(19) D. A. Shirley and M. D. Cameron, *J. Amer. Chem. Soc.*, **74**, 664 (1952).

(20) W. Reid and H. Bender, *Chem. Ber.*, **88**, 34 (1955).

thawed under vacuum, and finally sealed under vacuum. After the tube had been heated for the indicated time and temperature (Table I) it was cooled and opened and 30 ml of H_2O was added. The solution was acidified to litmus with 3 *N* HCl and extracted with three 30-ml portions of ether, and the combined ether extracts were dried (K_2CO_3), concentrated on a rotary evaporator, and analyzed by tlc and vpc. The products were separated by preparative chromatography and identified by comparison of their ir spectra with those of authentic samples or as indicated below. Yields were calculated from the vpc trace taking into account the response factors of the individual products. Variations from these reaction conditions are noted in Table I.

Product Identification.—2-Piperidinothianaphthene (**2**), mp 100–100.5° (lit.[8] mp 98–100°), and 3-piperidinothianaphthene (**3**), mp 65–66° (lit.[21] mp 64–65°), were prepared for comparison purposes by the cited methods. 2-Piperidino-3-bromothianaphthene (**7**) was compared with the independently synthesized sample described below and 2,3-dipiperidinothianaphthene (**8**), mp 101–102.5°, was identified from its nmr spectrum [δ 7.0–7.7 (m, 4, ArH), 3.2 (m, 4, CH_2N), 2.9 (m, 4, CH_2N), 1.6 (m, 12, CH_2)] and analysis.

Anal. Calcd for $C_{18}H_{24}N_2S$ (**8**): C, 71.94; H, 8.06; N, 9.33. Found: C, 72.02; H, 7.93; N, 9.17.

2-Piperidino-3-bromothianaphthene (**7**).—To a solution of 5.4 g of **2** in 25 ml of dry, distilled dioxane was added with stirring 4.0 g of Br_2 in 25 ml of dioxane over a period of 20 min. The yellow precipitate which formed was filtered and washed with dioxane and $CHCl_3$ to give 9.4 g (100%) of the highly insoluble iminium salt **9**: nmr (DMSO) δ 7.1–7.6 (m, 4, ArH), 3.8 (s, 1, CHBr), 1.5–1.8 (m, 6, CH_2); the CH_2N peaks (*ca.* 3.1) are partially blocked out by the DMSO absorption; ir 1622 cm^{-1}.

Anal. Calcd for $C_{18}H_{15}Br_2NS$ (**9**): C, 41.38; H, 4.01; N, 3.72. Found: C, 41.15; H, 4.27; N, 3.63.

To a mixture of 5.7 g of **9** and 50 ml of anhydrous ether was added 1.5 g of pyridine. After about 5 min the yellow salt **9** was replaced by white pyridinium bromide. Filtration, evaporation of the filtrate to dryness, and recrystallization of the residue from low-boiling petroleum ether gave 3.3 g (74%) of **7**: mp 76–77°; nmr δ 7.0–7.7 (m, 4, ArH), 3.0 (m, 4, CH_2N), 1.5 (m, 6, CH_2); sodium fusion indicated the presence of N, S, and Br.

Anal. Calcd for $C_{13}H_{14}BrNS$ (**7**): C, 52.68; H, 4.77; N, 4.73. Found: C, 52.90; H, 4.82; N, 4.63.

7 is unstable at room temperature and sensitive to air and moisture. It was stored under N_2 at 0°.

Registry No.—**1**, 7342-82-7; **2**, 33880-37-4; **5**, 5394-13-8; **6**, 6287-82-7; **7**, 38359-65-8; **8**, 38359-66-9; **9**, 38359-67-0.

Acknowledgment.—This research was supported by grants from the Robert A. Welch Foundation and the TCU Research Foundation.

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tert-Butylacetylene Revisited. An Improved Synthesis. Methyl Migration during Bromination

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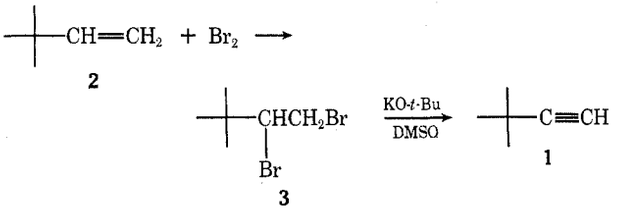
A synthesis of *tert*-butylacetylene, superior in all respects to the conventional procedure, is described involving bromination of *tert*-butylethylene (**2**), and double dehydrobromination of the *vic*-dibromide (**3**) with potassium *tert*-butoxide–dimethyl sulfoxide in overall yields of 81%. The bromination of **2** was found to give 70–90% yields of **3**, accompanied by 1-bromo-3,3-dimethylbutane and a crystalline product formulated as tetra(bromomethyl)ethylene (**4**), a new compound. The mechanism of formation of **4** and its ineffectiveness as a dienophile are described.

tert-Butylacetylene (**1**) is a highly useful synthetic reagent, serving for example as the source of the *tert*-butylethynyl group in a great many propargyl alcohols and related compounds. The usual preparation[1] of **1** involves the reaction of pinacolone with phosphorus pentachloride to form a relatively sensitive *gem*-dichloride, which is then treated with a sodium hydroxide melt to promote a double dehydrochlorination. Both steps in the sequence are only moderately efficient, owing to the lability of the intermediate dichloride and the harsh conditions required for the elimination.

We attempted to improve the overall yield by substituting potassium *tert*-butoxide in dimethyl sulfoxide (DMSO) for the sodium hydroxide, and found that this substantially increases the yield in the second step to >90%. Still, the difficulties encountered in the first step precluded significant improvement.

Recently we devised an obvious alternative preparation of **1** which is superior in all respects (simplicity, time requirements, yields, and economy) to the original method. This procedure involves the bromination of *tert*-butylethylene (**2**) and subsequent double dehydrobromination of the *vic*-dibromide with KO-*t*-Bu–DMSO. The reaction of **2** with either bromine[2] or *N*-bromosuccinimide[3] has been reported to give the desired dibromide **3**. In our hands, the addition of bromine to **2** at



−78° afforded **3** in 90% yield, and this was treated with 2 equiv of KO-*t*-Bu in DMSO, from which **1** could be isolated in 91% yield. The overall yield from olefin to acetylene was 81%.

The bromination of **2** is interesting in another regard. When the addition of bromine to **2** was carried out at room temperature, gaseous HBr was liberated in significant amounts. Moreover, two side products could then be readily isolated. The first of these, formed in 10% (isolated) yield, was found to be 1-bromo-3,3-dimethylbutane,[4] which is known to arise from the anti-Mar-

(1) (a) P. Ivitzky, *Bull. Soc. Chim. Fr.*, **35**, 357 (1924); (b) P. D. Bartlett and L. J. Rosen, *J. Amer. Chem. Soc.*, **64**, 543 (1942).

(2) M. F. Claessens, *Bull. Soc. Chim. Fr.*, **5**, 113 (1909).

(3) A. Guillemonat, G. Peiffer, J.-C. Traynard, and A. Leger, *ibid.*, 1192 (1964).

(4) Interestingly, the earlier report[2] included a vague description of a lower boiling monobromide then believed to be $C_6H_{11}Br$ on the basis of bromine content (calcd 49.08; found 46.48). We feel that compound was the same monobromide we have identified (calcd for $C_6H_{12}Br$: Br, 48.41). An allusion was also made to a liquid tribromide of unknown structure (**9**?) and an undescribed crystalline solid.