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# Synthesis and Some Reactions of 3-Thiabicyclo[3.2.0]hepta-1,4-diene. A Case for Revival of the Mills-Nixon Effect?[1]

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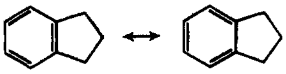
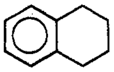
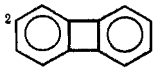
3-Thiabicyclo[3.2.0]hepta-1,4-diene (**10**) has been synthesized by a Wittig reaction between cyclobuta-1,2-dione (**8**) and the bisylide **9**, derived from dimethyl thioether $\alpha,\alpha'$-bis(triphenylphosphonium) dichloride. The compound **10** was oxidized to the sulfone **11**. Compound **10** underwent electrophilic substitution with benzoyl chloride to give the ketone **12**, but it added bromine to give the tetrabromide **13**. It is suggested that the addition, rather than the substitution, of bromine to **10** indicates that delocalization of the electrons in the thiophene ring of **10** has been decreased by annelation.

The fusion of a three- or four-membered ring onto a benzene ring might be expected to drastically alter its aromatic character. Many years ago Mills and Nixon[3,4] suggested that some differences in chemical properties which they observed between indan (**1**) and tetralin (**2**) derivatives arose from the destabilization of the aromatic ring in the indan systems.[5] This destabilization they supposed to be due to the strain induced by the five-membered ring, and the Kekulé structure (**1b**) was considered to be the predominant resonance contributor. Although the basis for their conclusions was later shown to be unfounded,[6] Longuet-Higgins and Coulson[7] deduced from a theoretical study of the effects of strain that there would be some disruption of the aromatic system on annelation. However, these authors concluded that the Kekulé form **1a** would be favored.


**1a** **1b**


**2**

At the time the Mills-Nixon proposal was made, compounds containing three- or four-membered rings fused to a benzene ring were thought to be unknown,[8] despite many attempts to prepare them. Subsequently, biphenylene (**3**),[9] benzocyclobutene (**4**),[10] and benzocyclopropene (**5**)[11] have all been prepared. The nmr proton-proton coupling constants indicate that there is an increase in ring strain on passing from **4** to **5**,[12,13] and subsequent $^{13}C$ nmr studies can also be interpreted in the same way.[14,15] It was also suggested that the proton nmr spectrum supported the view that in **5** the Kekulé structure with the central double bond (*cf.* **1a**) was preferred,[12,13] but an X-ray crystallographic structural analysis of a derivative showed that the bond lengths do not alternate in the way expected if this form predominated.[16] It has also been observed that the chemical reactivities of aryl positions adjacent to the fused ring are affected and, for example, the kinetic acidity of position 1 in biphenylene (**3**) is greater than that expected from model systems.[17,18] Taylor[17] has attributed this difference to the strain effects due to the four-membered ring which favor those transition states with least double-bond character between the carbon atoms at the ring junctions.[19] Finnegan[20] and Streitweiser and his coworkers[18] have suggested that these effects can be accounted for by a model in which the $\sigma$ bonds of the small ring have more p character, with the consequence that the adjacent aryl $\sigma$ bonds have more s character. Riecke and his coworkers[21] have presented evidence in support of the Finnegan-Streitweiser model, and it has also been suggested that both models may be operative.[22] It can thus be seen that changes in both the chemical and physical properties of the aromatic ring occur when it is annelated by a small ring, but it does not appear at present that any of these changes imply a measurable degree of double-bond localization.[23]



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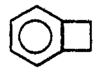
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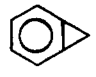
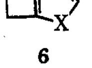
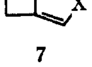

**5**

Although these results tend to discredit the operation of a Mills-Nixon effect based on bond localization in benzenoid systems, it seemed possible that such an effect might be more pronounced, and therefore more readily observed, in heterocyclic systems. In particular the five-atom 6-$\pi$ heterocycles, such as pyrrole, have only one uncharged Kekulé structure, and offer two modes of annelation. Thus fusion of the small ring at the 2,3 position forms a system (**6**) with a formal double bond in the annelating ring (4), whereas fusion at the 3,4 position forms a system (**7**) with a formal single bond in the annelating ring. A synthesis of these types of systems would then be expected to give



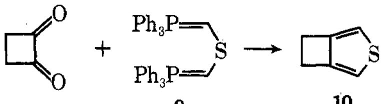
**6**



**7**

some insight into the nature of delocalization in this type of heteroaromatic ring. We now report the synthesis of 3-thiabicyclo[3.2.0]hepta-1,4-diene (**10**), and discuss some of its reactions.[24]

A Wittig reaction of cyclobutene-1,2-dione (**8**)[25] with the bisylide **9**,[26] derived from dimethyl thioether $\alpha,\alpha'$-bis-(triphenylphosphonium) dichloride, gave *ca.* 5% (see Experimental Section) of 3-thiabicyclo[3.2.0]hepta-1,4-diene (**10**) as a colorless oil. The analytical and mass spectral data were in accord with the assigned structure, and the nmr spectrum ($CDCl_3$) showed two singlets at $\tau$ 3.23 and 6.98 in the ratio 1:2.

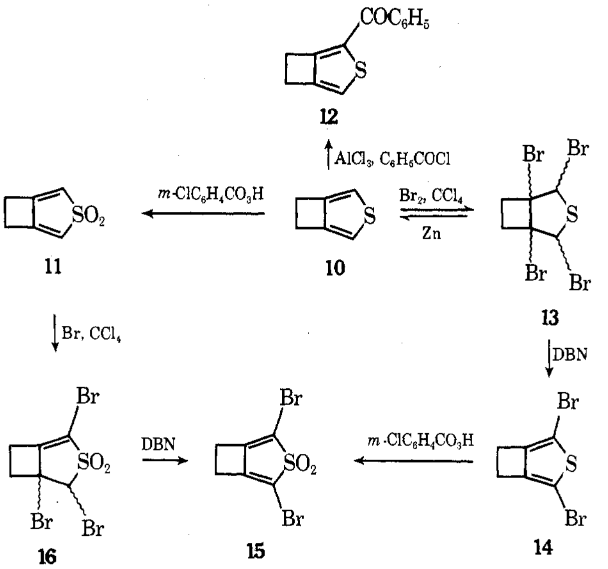


**8** **9** **10**

Oxidation of **10** with *m*-chloroperoxybenzoic acid at room temperature gave the sulfone **11**, mp 127.5–128.5°, in 80% yield. Compound **11** could also be obtained by oxidation of **10** with hydrogen peroxide, and in neither case was the sulfoxide observed. The nmr spectrum ($CDCl_3$) of **11** also showed two singlets, in this case at $\tau$ 3.98 and 6.67, respectively, in the ratio 1:2.

The compound **10** underwent electrophilic substitution with benzoyl chloride in the presence of aluminum chloride to give, in 19% yield, the monobenzoyl derivative **12**, mp 50–52°. Compound **12** could also be obtained using stannic chloride as a catalyst, but the yield was lower. The nmr spectrum ($CCl_4$) of **12** showed multiplets at $\tau$ 2.2 (2 H) and 2.6 (3 H) due to the phenyl protons, a singlet at $\tau$ 2.92 due to the thiophene proton, and a singlet at $\tau$ 6.95 due to the cyclobutyl protons.

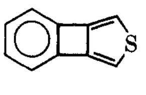
The compound **10** readily reacted with bromine to give the tetrabromide **13** in *ca.* 90% yield (nmr). The compound **13** had the correct molecular weight, as determined by the mass spectrum. The nmr spectrum ($CDCl_3$) showed a singlet at $\tau$ 4.73 and a multiplet at $\tau$ 6.8–7.7, and this was also consistent with the assigned structure. However, **13** was extremely labile and could not be isolated in a pure form. Treatment of **13** with zinc dust regenerated the thiophene **10**. Reaction of **13** with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) gave 2,4-dibromo-3-thiabicyclo[3.2.0]hepta-1,4-diene (**14**) as a colorless oil in 67% yield. The nmr spectrum ($CDCl_3$) of **14** showed only a singlet at $\tau$ 7.12 for the cyclobutyl protons. The compound **14** could also be obtained in lower yield (21%) directly from **10** by treatment with *N*-bromosuccinimide. Besides **14** a number of polybromo compounds were observed in this latter reaction.



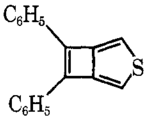
Oxidation of **14** with *m*-chloroperoxybenzoic acid gave the sulfone **15**, mp 176.5–177.5°, in 60% yield. The nmr spectrum ($CDCl_3$) of **15** again showed only a single resonance at $\tau$ 6.74. Compound **15** could also be obtained from the sulfone **11**. Bromination of **11** gave the tribromide **16**, mp 158–159°, in 75% yield. The nmr spectrum ($CDCl_3$) of **16** showed a singlet at $\tau$ 4.53, assigned to the proton on the five-membered ring, and a multiplet at $\tau$ 6.15–7.42, assigned to the cyclobutyl protons. Treatment of **16** with DBN gave **15**, identical in all observed respects with that obtained previously. When the solution obtained by bromination of **11** was treated directly with DBN, **15** was obtained in 70% yield.

3-Thiabicyclo[3.2.0]hepta-1,4-diene (**10**) is thermally stable, being recovered unchanged after heating at 235° for 90 min. It was also recovered unchanged upon photoirradiation, and did not react with tetracyanoethylene (TCNE) under a variety of conditions. By contrast the sulfone **11** decomposes when it is heated to 120° for 5 min, and it is also decomposed on photoirradiation. However, it also does not appear to react with TCNE.

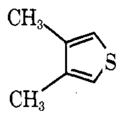
Comparison of the nmr spectra of **10** and **11** shows that the protons on the heterocyclic ring move upfield by 0.75 ppm on oxidation. This substantiates our earlier suggestion that the high field position ($\tau$ 3.51) of the thiophene proton in the nmr spectrum of **17** is due to a paratropic contribution from the potential cyclobutadiene ring in this molecule,[27] since oxidation of **17** to the corresponding sulfone leads to only a small (0.09 ppm) upfield shift. The paratropic origin of the high field position of the thiophene proton in the nmr spectrum of **18** is also substantiated.[28] The small downfield shift of the cyclobutyl ring protons (0.31 ppm) is probably due to a change in ring strain in the four-membered ring on going from **10** to **11**. A similar shift (0.38 ppm) is observed between **14** and **15**.



**17**



**18**



**19**

We had previously considered that the ready addition of bromine to 2-thianorbiphenylene (**17**) was probably due to the electronic destabilization inherent in this 12-$\pi$-electron system.[27] However, the finding that **10** also adds bromine readily suggests that the source of this unusual reactivity is not due to $4n$ destabilization, but to the strain induced by the four-membered ring. It can be considered that the effect of annelation is to reduce the extent of delocalization in the thiophene ring, which is essentially a restatement of the Mills-Nixon effect, and as a consequence the thiophene ring exhibits some double-bond character. It is well known that thiophene reacts much more readily with bromine than does benzene to give the products of electrophilic substitution, and it seems likely that the first formed product is the 2-substituted thiophene.[29] 3,4-Dimethylthiophene (**19**) reacts immediately with bromine, but the product is again that of substitution, namely 2,5-dibromo-3,4-dimethylthiophene, and no addition products could be detected.[30] It is known that chlorination of thiophene gives addition as well as substitution products,[31] although no addition products were observed on bromination.[32] Both substitution and addition reactions probably involve addition of the halonium ion, followed by subsequent loss of a proton or addition of halide. The formation of addition rather than substitution products may thus indicate a decreased tendency to reform the aromatic sextet. Thus, although the differences between the energies of the transition states in these reactions must be small, nevertheless it appears as though **10** does exhibit chemical properties consistent with a diminished delocalization of the $\pi$ electrons in the thiophene ring.[33] Comparison of the nmr spectra of **10** and 3,4-dimethylthiophene (**19**) shows that the thiophene protons in **10** are at slightly higher field ($\tau$ 0.07). The electronic spectra of **10** and **19** are similar [**10**, 244 nm ($\epsilon$ 7800); **19**, 242 (6400)], as are those of the corresponding sulfones. The spectral properties thus give little indication of any large change in the structure of the thiophene ring in these two compounds.

It may be inferred that, whereas in the annelated benzene systems it is the requirements of the benzene ring which dominate and therefore define the structure of the systems, in the thiophene case the requirements of the small ring also assume importance. The only available uncharged Kekulé structure for **10** has a single bond at the site of annelation, and if the Longuet-Higgins–Coulson calculation[7] can be transferred to the thiophene system, this is a disfavored arrangement.[34] It will be of interest to compare the properties of **10** with those of cyclobuta[*b*]thiophene (**6**, X = S) which has one Kekulé structure with a double bond in the preferred position at the site of annelation. The synthesis of **6** and of other strained heterocycles is currently under investigation.

## Experimental Section

Nmr spectra were obtained on either a Varian T-60 or HA-100 spectrometer and are recorded in $\tau$ units as solutions in $CDCl_3$ with TMS as internal standard. Mass spectra were taken on an AEI MS-12 or MS-9 spectrometer at 70 eV. Infrared spectra were recorded on a Unicam SP 200 spectrophotometer, only strong and medium bands being reported, and electronic spectra were determined on a Unicam SP 800 recording spectrophotometer.

Silica for preparative thin layer chromatography (ptlc) was Merck Kieselgel $PF_{254}$ (type E). Solvents were purified and dried by standard methods.

**Wittig Reaction between Cyclobutane-1,2-dione (8) and the Bisylide 9. Synthesis of 3-Thiabicyclo[3.2.0]hepta-1,4-diene (10).** Dimethyl thioether $\alpha,\alpha'$-bis(triphenylphosphonium) dichloride (32.75 g, 50 mmol, dried at 110°, 0.05 mm over $P_2O_5$) was suspended in dry ether (2 l.) under dry $N_2$. *n*-Butyllithium (100 mmol) in hexane was added to the stirred mixture, and stirring was continued for 35 min. The deep-red solution was then cooled to *ca.* −65° for 15 min, and a solution of cyclobutane-1,2-dione (**8**, 4.2 g, 50 mmol) in ether (100 ml) was then added in one portion to the stirred solution. The red color was discharged, and the solution was allowed to warm to room temperature and then stirred for a further 2 hr. The ethereal solution was then washed with water (4 × 200 ml) and dried ($MgSO_4$). Part of the solvent was removed under reduced pressure to leave a volume of *ca.* 40 ml, and ether–chloroform (60 ml, 1:1) was added to the resulting inhomogeneous mixture. The resulting solution was chromatographed on alumina (300 g) eluting with petroleum ether (bp 40–60°), when a mixture of **10** with some triphenylphosphine was obtained. The eluent (*ca.* 300 ml) was concentrated (*ca.* 50 ml) using a Vigreux column and rechromatographed on alumina (300 g), again eluting with petroleum ether. The eluent (*ca.* 300 ml) was concentrated to small volume (*ca.* 1 ml), again using a Vigreux column, and the residue was then distilled to give 3-thiabicyclo[3.2.0]hepta-1,4-diene (**10**, 270 mg, 6%). In most experiments a solution of **10** of this purity was used, but further purification by glc (Carbowax 6 ft, column 82°) gave **10** (colorless oil, 90 mg, 2%): mass spectrum *m/e* 110.019 (calcd for $C_6H_6S$, 110.019); ir (liquid film) 3080, 2940, 2830, 1504, 1430, 1365, 1210, 1142, 820, 790, 775 and 730 cm$^{-1}$; nmr, see discussion; $\lambda_{max}$ (EtOH) 233 sh nm ($\epsilon$ 6400), 244 (7800).

*Anal.* Calcd for $C_6H_6S$: C, 65.41; H, 5.49; S, 29.10. Found: C, 65.42; H, 5.59; S, 29.05.

**Oxidation of 10 with *m*-Chloroperoxybenzoic Acid. 3-Thiabicyclo[3.2.0]hepta-1,4-diene 3,3-Dioxide (11).** Compound **10** (11 mg, 0.1 mmol) was dissolved in chloroform (1 ml), *m*-chloroperoxybenzoic acid (52 mg, 0.3 mmol) was added, and the mixture was shaken at room temperature for 48 hr. The solvent was removed by evaporation, and ptlc of the residue on silica eluting with $CHCl_3$ gave 3-thiabicyclo[3.2.0]hepta-1,3-diene 3,3-dioxide (**11**): mp 127.5–128.5° (11.5 mg, 80%); mass spectrum *m/e* 142.009 (calcd for $C_6H_6SO_2$, 142.009); ir (KBr) 3075, 1622, 1440, 1415, 1280, 1253, 1185, 1135, 1055, 1015, 825, 798, and 710 cm$^{-1}$; nmr spectrum, see discussion; electronic spectrum $\lambda_{max}$ (EtOH) 225 nm ($\epsilon$ 3300) and 292 (1300).

*Anal.* Calcd for $C_6H_6O_2S$: C, 50.68; H, 4.25; O, 22.50. Found: C, 50.85; H, 4.35; O, 22.72.

**Benzoylation of 10.** Compound **10** (16.5 mg, 0.15 mmol) and benzoyl chloride (67 mg, 0.47 mmol) were dissolved in chloroform (2 ml), the solution was cooled to 0° and stirred, and $AlCl_3$ (84 mg, 0.78 mmol) was added. The $AlCl_3$ dissolved rapidly to give a red solution which was stirred for a further 5 min at 0° and then for 45 min at room temperature. The solution was then poured into ice-water, the resulting mixture was extracted with ether and dried ($MgSO_4$), and the solvent was removed under reduced pressure. Ptlc of the residue on silica eluting with ether–light petroleum (1:3) gave **2-benzoyl-3-thiabicyclo[3.2.0]hepta-1,4-diene (12**, 6 mg, 19%): mp 50–52°; mass spectrum *m/e* 214; ir (KBr) 1635, 1600, 1585, 1540, 1490, 1410, 1362, 1320, 1295, 1210, 1175, 1155, 1125, 1075, 1005, 945, 845, 815, 780, 720, 698, and 672 cm$^{-1}$; nmr, see discussion; $\lambda_{max}$ (EtOH) 220 sh nm ($\epsilon$ 4800), 260 sh (7500), 268 (11,500).

A second fraction was also isolated which appeared to be a mixture of **12** and the 2,4-dibenzoyl derivative.

When stannic chloride was used in place of $AlCl_3$, the reaction being run in benzene, a 3% yield of **12** was obtained, identical in all observed respects with that obtained previously.

**Bromination of 10.** Compound **10** (40 mg, 0.37 mmol) was dissolved in $CCl_4$ (1.5 ml) and a solution of bromine (120 mg, 0.75 mmol) in $CCl_4$ (1.2 ml) was then added with stirring. The bromine color was discharged, and the solvent was rapidly removed under a stream of $N_2$. The residue was chromatographed on silica eluting with ether–light petroleum (5:95) to give **13** as a yellow oil (120 mg, 77% yield): mass spectrum *m/e* 434, 432, 430, 428, 426 (1:4:6:4:1), 352, 350, 348, 346 ($M^+ - HBr$, 1:4:4:1), 270, 268, 266 ($M^+ - 2HBr$); nmr $\tau$ 4.73 (s, 2 H), 6.8–7.7 (m, 4 H). Attempts to purify **13** led to decomposition, and it was used as prepared in subsequent experiments.

**Dehydrobromination of 13. Synthesis of 2,4-Dibromo-3-thiabicyclo[3.2.0]hepta-1,4-diene (14).** Compound **13**, prepared from **10** (40 mg) as described previously, was dissolved in dry tetrahydrofuran (4 ml), 1,5-diazabicyclo[4.3.0]non-5-ene (124 mg, 1 mmol) was added, and the mixture was stirred at room temperature for 24 hr. The solvent was removed under a stream of $N_2$, and ptlc of the residue on silica eluting with light petroleum gave an oil, which on distillation gave **14** as a colorless oil (68 mg, 67%): mass spectrum *m/e* 267.839 (calcd for $C_6H_4{}^{79}Br^{81}Br^{32}S$, 267.838); ir (liquid film) 2950, 1567, 1525, 1422, 1315, 1212, 1050, 1028, and 880 cm$^{-1}$; nmr $\tau$ 7.12 (s); $\lambda_{max}$ (EtOH) 247 nm ($\epsilon$ 10,800).

Compound **14** (29 mg, 21%) was also obtained directly from **10** (55 mg, 0.5 mmol) by treatment with *N*-bromosuccinimide (404 mg, 2.2 mmol) and benzoyl peroxide in $CCl_4$ (3.5 ml). A fraction containing polybromo compounds (mass spectrum) was also obtained in this preparation.

**Debromination of 13.** Compound **13**, prepared from **10** (40 mg) as described, was dissolved in chloroform (1.5 ml), and dimethylformamide (1 ml) and zinc dust (100 mg) were added. The mixture was shaken at room temperature for 16 hr, the solid was recovered by filtration, and the filtrate was concentrated. Glc (carbowax 6 ft, column 82°) gave **10** (10.5 mg, 26%).

**Oxidation of 14.** Compound **14** (108 mg, 0.4 mmol) was dissolved in chloroform (5 ml), *m*-chloroperoxybenzoic acid (308 mg, 1.8 mmol) was added, and the mixture was shaken for 48 hr. The solvent was removed by evaporation and ptlc of the residue on silica eluting with $CHCl_3$ gave **2,4-dibromo-3-thiabicyclo[3.2.0]hepta-1,4-diene 3,3-dioxide (15**, 73 mg, 60%): mp 176.5–177.5° ($CHCl_3$–$Et_2O$); mass spectrum *m/e* 299.829 (calcd for $C_6H_6O_2{}^{79}Br^{81}Br^{32}S$, 299.828): ir (KBr) 1655, 1428, 1412, 1320, 1210, 1160, 1100, 1060, 880, 830, and 735 cm$^{-1}$; nmr, see discussion; $\lambda_{max}$ (EtOH) 225 nm ($\epsilon$ 4150), 319 (4500).

*Anal.* Calcd for $C_6H_4Br_2O_2S$: C, 24.02; H, 1.34; Br, 53.27. Found: C, 23.96; H, 1.27; Br, 53.23.

Compound **15** could also be obtained by dehydrobromination of **16** (see below) with DBN.

**Bromination of 11.** Compound **11** (10.7 mg, 0.075 mmol) was dissolved in $CDCl_3$ (0.3 ml) and bromine (30 mg, 0.187 mmol) in $CCl_4$ (0.3 ml) was added. The mixture was kept at *ca.* 37° for 40 min, and then ptlc on silica eluting with $CHCl_3$–light petroleum gave 16 (10.2 mg, 75%): mp 158–159° (CHCl$_3$–petroleum ether); mass spectrum *m/e* 379.757 (calcd for $C_6H_5{}^{79}Br_2{}^{81}BrSO_2$, 379.754); ir (KBr) 1600, 1465, 1422, 1380, 1333, 1240, 1205, 1175, 1100, 1015, 895, 850, 790, 735, and 722 cm$^{-1}$; nmr, see discussion.

**Dehydrobromination of 16.** Compound 16 (14.2 mg) was dissolved in CCl$_4$ (0.3 ml), DBN (1 drop) was added, and the solution was shaken at room temperature for 30 min. Ptlc on silica eluting with CHCl$_3$ gave **15** (7.5 mg, 70%) identical in all observed respects with the previous sample.

**Registry No.**—8, 33689-28-0; 9, 51593-74-9; 10, 38828-44-3; 11, 38828-45-4; **12,** 51593-75-0; 13, 38916-88-0; 14, 51593-76-1; 15, 51593-77-2; 16, 51593-78-3.

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(1) For a preliminary account of part of this work see P. J. Garratt and D. N. Nicolaides, *J. Chem. Soc., Chem. Commun.*, 1015 (1972).

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(33) It should be pointed out that benzocyclopropene (**5**) does add iodine across the tetrasubstituted double bond to give 1,6-diiodocycloheptatriene.[11] However, initial attack on this double bond provides a carbonium ion which cannot readily eliminate a proton to reestablish the benzenoid system. If the initial attack on **10** was at the ring junction, a similar argument could be applied, but such an attack appears unlikely in view of the relative stabilities of the carbonium ions formed.

(34) It could, however, be argued that delocalization in **10** would lead to a shortening of the 1,5 bond and thus to a decrease in strain in comparison to the bond-fixed structure.

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# Imino-1,2,4-dithiazoles. I. Alkylation

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A series of 5-(dialkylamino)-3-(substituted imino)-1,2,4-dithiazoles were alkylated with alkyl halides to give the 3,5-bis(dialkylamino)-1,2,4-dithiazolium halides **3a–h**. The scope and limitations of the reaction are discussed.

A number of 3,5-bis(substituted amino)-1,2,4-dithiazolium salts (**3**) are housefly (*Musca domestica L.*) sterilants.[1,2] The most active compounds have been those in which both of the exocyclic nitrogens were fully substituted, and we have employed two methods (paths a and b, Scheme I) for preparing these materials.[1,3,4] In each case the substituent NR$^1$R$^2$ was derived from the corresponding secondary amine; thus the accessibility of a given dithiazolium salt depended on the availability of the secondary amine. An obvious alternative synthesis would be the alkylation of iminodithiazoles **2** (path c, Scheme I). Alkylation on the imino nitrogen, as opposed to ring alkylation, would be expected, since an aromatic dithiazolium salt would result from the former process.

We have found that 5-(dimethylamino)-3-(alkyl- or arylimino)-1,2,4-dithiazoles (**2**) are smoothly alkylated by reactive alkyl halides to give the dithiazolium salts **3a–h** shown in Table I. Yields were good to excellent with methyl iodide, benzyl chloride, allyl bromide, and ethyl bromoacetate. That alkylation occurred on the imino nitrogen as expected was confirmed in two cases by comparing the products with dithiazolium salts previously prepared by the standard methods: **3a** had been synthesized earlier by oxidation of 1,1,5,5-tetramethyl-2,4-dithiobiuret