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HETEROCYCLIC SYNTHESES VIA CARBANIONICALLY INDUCED REARRANGEMENT REACTIONS

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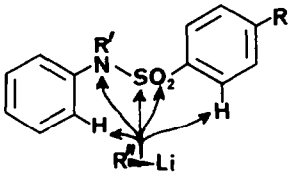
Abstract—The easily occurring [1.3]-migrations of sulfonyl and carbonyl functions to neighboring phenyl anions can be utilized for ring expansions by one benzo unit when suitably tailored precursor heterocycles are used. Thus, the 1,2-benzisothiazol dioxide systems **8** and **17** can be transformed into dibenzo[b,f][1,4]thiazepin dioxides **12** and **21**, respectively, whereas the dibenzo[c,e][1,2]- and 1,2,4-benzothiazin dioxide models **35** and **46** give rise to the tribenzo[b,e,g][1,4]thiazocin dioxide and dibenzo[c,g][1,2,6]thiadiazocin dioxide systems **38** and **47**, respectively. Unexpected formations of heterocyclic systems, namely, spiro[isoindolo[2,1-a][3,1]benzoxazin-5,1′(3H)-isobenzofuran **55**, 3,1-benzoxazin **62**, and phenanthridinium-salt **70** took place when phthalimide **52**, dibenzoylaniline **56**, and biphenylylbenzamide **65** were reacted with t-BuLi.

Background: the sulfonamide–aminosulfone and related rearrangements

Formally, N-arylarenesulfonamides of type **1** can be imagined to react with organolithium compounds in at least five different ways: ortho-metalation at either of the two phenyl groups and direct nucleophilic attack at N, S, or even O.

Experimentally it has been shown[1] that ortho-

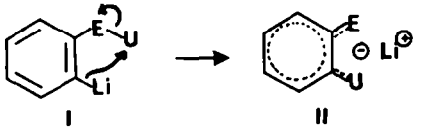


	R	R′
1a:	H	Ph
b:	Me	Ph
c:	Me	Me

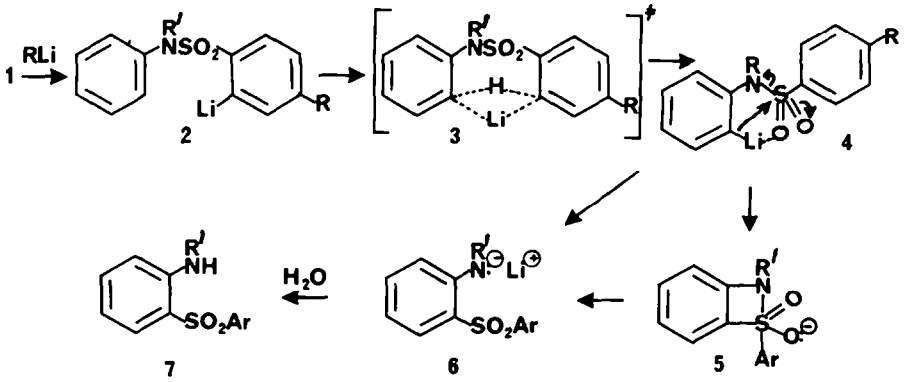
R″ = Me, Bu, Ph

metallation[2] of the phenyl group directly bound to the sulfonyl function was indeed the initial reaction step, followed by a transmetalation/rearrangement sequence which finally led to the *o*-aminodiphenylsulfones **7**. Ample support for this mechanism was provided by generating the key intermediates **2** and **4** independently from corresponding brominated or iodinated precursors via halogen metal exchange, after which the same products **7** could be isolated. Whether the benzothiazet dioxide species **5** are true intermediates or represent merely transition states remains an unsettled question. From these investigations it followed also that the [1.3]-rearrangement step proper **4**→**6** is a fast reaction and that the rate determining transmetalation through transition state **3** begins to manifest itself already at − 30° for the N,N-diarylarenesulfonamides **2a,b**, but only at temperatures above 0° for the N-methyl-N-phenylarenesulfonamide **2c**.[1] In this context it is interesting to note that similar skeleton transformations **1**→**7** can be brought about by acids,[3] thermally,[1,4] and under irradiation,[5] so that one could literally speak of a "tetrachotomous" reaction.

Particularly the carbanionically induced [1.3]-rearrangements of this type lend themselves to more systematic studies in that they seemed easily transferable to a broad variety of substrates bearing similar functional characteristics as **1**. Thus, a general concept was developed according to which any PhLi derivative **I** having in its *ortho*-position an electronegative group E bound to an unsaturated function U should rearrange readily to the isomer **II**.[6]



I II

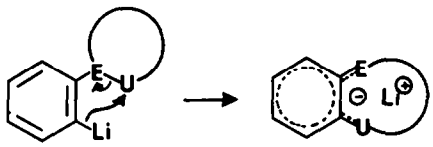


The driving force for these reactions will be provided by the transformation of the complexation-stabilized[2] PhLi compounds **I** (for example **4**) into deeply colored[1,6,7] resonance stabilized anions **II** in which the negative charge is delocalized over an extended conjugation system terminating on both ends with more or less electronegative atoms. A rough measure for this driving force can be obtained by comparing the acidity constants of the conjugate acids of **I** and **II**, respectively.[7]

So far, the above concept has been verified for the following combinations of E and U: E = O; U = -C(=O)R[6,7]. E = NR; U = $-SO_2Ar$, $-SO_2NAr_2$,[1] -COR, -C(=NR')R,[7] -C(=O)N(Li)Ph,[8] $-P(=O)Ar_2$.[6,9] Very recently, examples where E is a pure carbon group, namely CPh_2[10] or CMe_2,[11] have been reported. On the other hand these principles are also applicable when U is not π-unsaturated but a coordinatively unsaturated group such as SiR_3[7,12] and GeR_3.[13] In most cases investigated hitherto the starting materials **I** were generated by halogen metal exchange at low temperature[14] as direct metalation (hydrogen metal exchange) proved problematic because of the competition of the highly anionophilic unsaturated functions U for the attacking organolithium reagents.[15]

Designed heterocyclic syntheses

On the basis of the above general reaction scheme, it was promising to envisage structural modifications that would transform this type of intramolecular[16] rearrangements into ring-expansion reactions. Hence, after implanting the E–U combination into a cycle such as **III**, [1.3]-migration of the electrophilic fragment U to the metalated position would result in a new heterocyclic system **IV** enlarged by a benzo unit, that is, by two ring members.



III **IV**

First experiments to realize this concept were made with the 1,2-benzisothiazol dioxides **8a–c**.[1] When these compounds were treated with only one equivalent of BuLi monometalation *ortho* to the sulfonyl group led as expected to the lithio derivatives **9a–c**. Since the N-aryl group was now blocked in a too far off position, intramolecular transmetallation was not possible and the carbanionic species **9a–c** were quite persistent.

But on addition of a second equivalent of BuLi the originally only slightly colored solutions turned red and after hydrolysis the dibenzo[b,f][1,4]thiazepin derivatives **12a–c** could be isolated in good yields. From this it was concluded that [1.3]-migration of the sulfonyl function can begin only after the dimetalated derivatives **10a–c** have been formed. This view was supported by the observation that noncyclic sulfonamides **2** can rearrange much more efficiently under conditions favoring a second metalation (at the amide–phenyl group).[17]

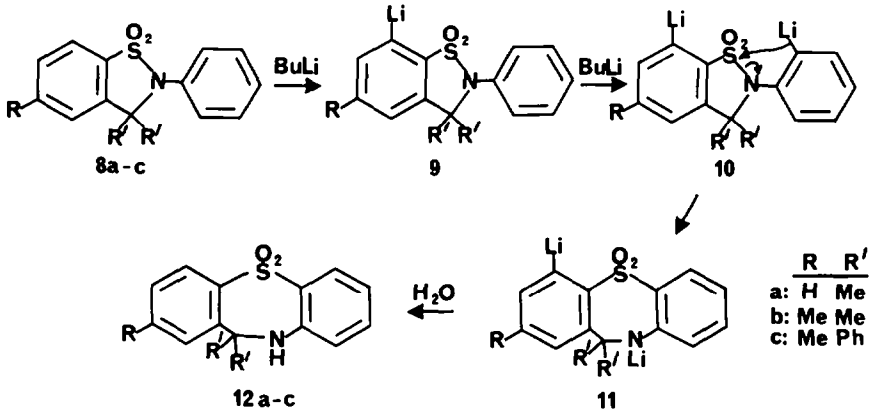
After this encouraging beginning we set about to study the synthetic potential of such rearrangement reactions in the heterocyclic field in a little more detail, which will be the subject of the next paragraphs.

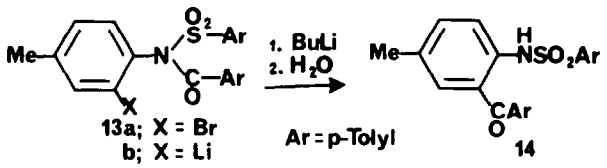
First of all we wanted to know how the migratory aptitude of the sulfonyl function would be influenced by the presence of another unsaturated function, namely a CO group, in a ring position equally suitable for rearrangement. To probe the rearrangement behavior of these two functions under unrestrained, genuine competitive conditions we chose the benzoyltosyltoluidide **13a**, as starting material. Halogen metal exchange at low temperature gave the lithio intermediate **13b** which rearranged subsequently to the benzophenone derivative **14**, proving the preferred migration of the benzoyl group. No indication, whatever, for the migration of the tosyl group could be found.[7]

For a cyclic model we selected the 1,2-benzisothiazolone dioxides **17a,b** which were synthesized from the methylbenzenamines **16a,b** and methyl 2-chlorosulfonylbenzoate (**15**) in the presence of pyridine.

Again, external nucleophilic attack on **17a** by n-BuLi took place at the more reactive CO function, yielding after hydrolysis the (oxopentyl)benzene sulfonamide **18** which in boiling methanol reclosed the ring to form a new 1,2-benzoisothiazole dioxide derivative **19**.

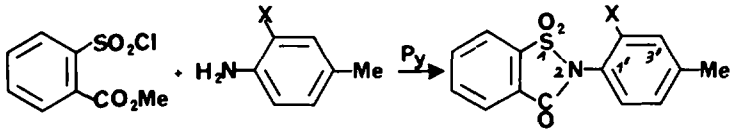
Under the more constrained conditions of intramolecular nucleophilic attack, however, **17** showed a totally different behavior. When a tetrahydrofuran solution of **17b** was subjected to halogen metal exchange with n-BuLi at low temperature, then





13a; X = Br
b; X = Li

14



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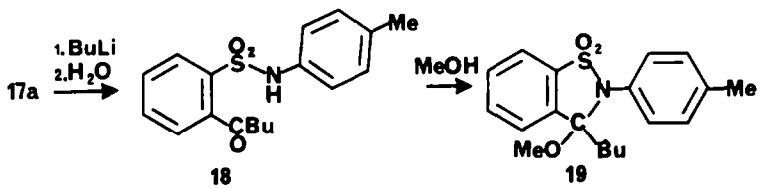
16a; X = H
b; X = Br

17a; X = H
b; X = Br
c; X = Li



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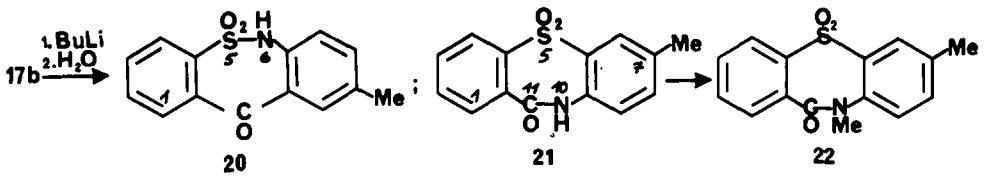


20

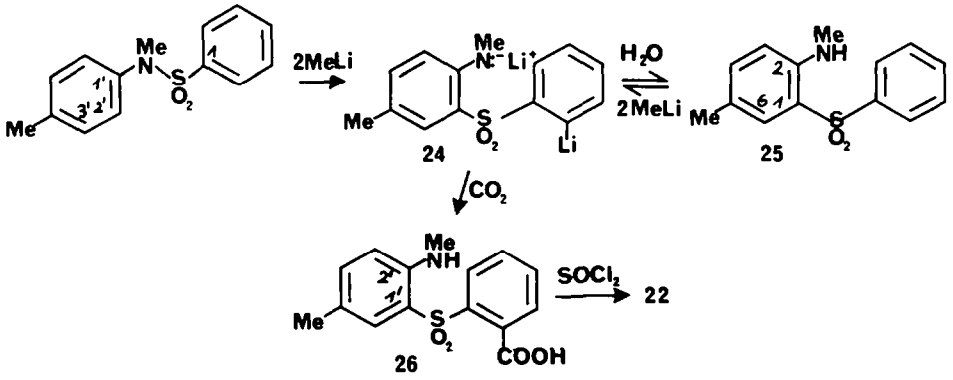
21

22

warmed to room temperature and hydrolyzed, a new product was obtained, which, according to the rather inconclusive spectroscopical data, could have been either the dibenzo[c,f][1,2]thiazepin derivative **20** or the dibenzo[b,f][1,4]thiazepin derivative **21**.

Therefore a classical structure proof was provided by virtue of an independent synthesis, which in itself illustrated a further application of the above rearrangement principles. Accordingly, N-methyl-N-*p*-tolylbenzenesulfonamide (**23**) was rearranged with two equivalents of methyllithium to give high yields of N-methyl-2-phenylsulfonyltoluidine (**25**).[17] Renewed dimetallation of **25** with MeLi produced again **24**, which represents the ultimate intermediate in the rearrangement sequence **23**→**25**. Treatment with carbon dioxide yielded amino acid **26** whose cyclization was performed by prolonged heating with thionyl chloride in dimethylformamide. The thus obtained 7,10 - dimethyldibenzo[b,f][1,4]thiazepin - 11(10H) - one 5,5-dioxide (**22**) was in every respect identical with the derivative generated by methylation of the rearrangement product **21**, thus proving its constitution.

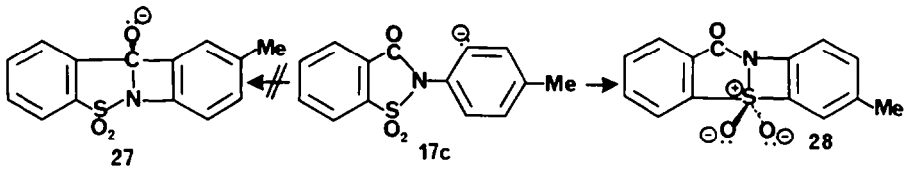
Why does intramolecular nucleophilic substitution in the cyclic case **17** occur exclusively via attack at the sulfonyl center in contradistinction to the results obtained with the noncyclic analog **13**, where only the carbonyl function migrates? Considering the actual rearrangement precursor **17c** it is evident that attack by the phenyl anion at the carbonyl group could



24

25

26



27 17c 28

occur solely from a position sidewise to, and more or less near the nodal plane of the π^*-orbital. This is very unfavorable since optimal attack is known to take place from a direction above the axis of, and including an angle around 110° with the C–O bond.[18]

Intramolecular nucleophilic attack at the sulfonyl group on the other hand is easily feasible in view of the accessibility of appropriately directed and contracted d-orbitals at the S atom.[19] Moreover, the intermediate or transition state **28** encountered here contains a nearly perfectly surrounded trigonal bipyramidal S center[20] and should therefore be much more reaction promoting then the analogous intermediate or transient species **27** comprising a strongly distorted saturated C center.

When an attempt was made to initiate a similar rearrangement sequence from the cyclic sulfenamide **30** only high yields of the 2-butylthiobenztoluidide **32** could be isolated, proving thus exclusive external nucleophilic attack at the highly polarisable S.

The corresponding sulfinamide **31** reacted with t-BuLi to a multicomponent mixture from which only a 10% yield of the disulfide **29** could be separated.

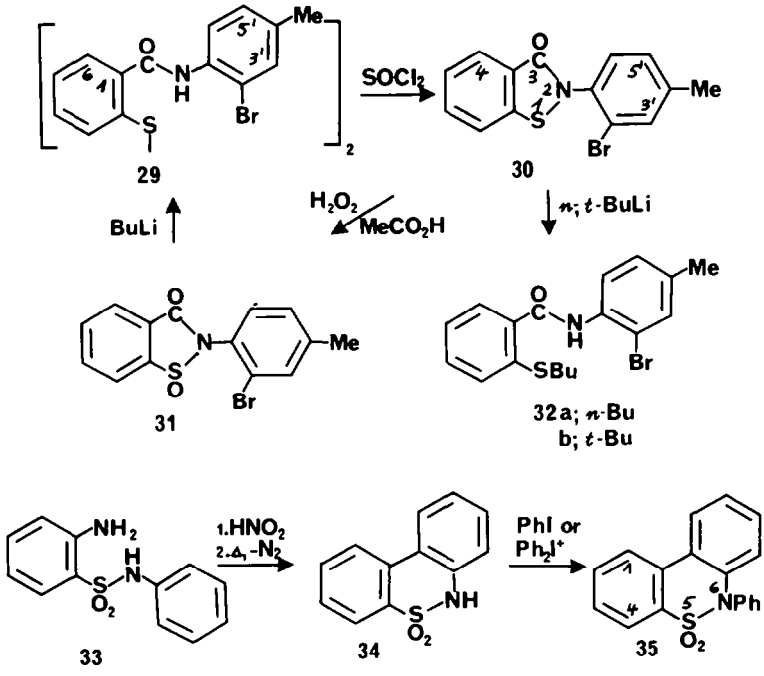
After the successful application of the sulfonamide–aminosulfone rearrangement to (5→7)-ring enlargements more generalization was sought by exploring the scope of similar (6→8)-ring expansions. A suitable model substrate was derived from 6H-dibenzo[c,e]-[1,2]thiazin 5,5-dioxide (**34**) which was easily accessible via diazotation of 2-amino-N-phenylbenzenesulfonamide (**33**).[21] Direct phenylation of **34** with iodobenzene gave only poor yields of the N-phenyl derivative **35**; treatment with diphenyliodonium bromide however led to acceptable 20–25% of **35**.

When a solution of **35** in tetrahydrofuran at − 78° was treated with 2.3 equivalents of n-BuLi, the mixture turned wine-red and, on warming to room temperature overnight, deposited a yellow precipitate. After hydrolysis, an isomeric product could be isolated (88%) whose spectroscopic and analytical data were in accordance with those expected for 14H-tribenzo[b,e,g][1,4]thiazocin 9,9-dioxide (**38**). In the ^{1}H-NMR-spectrum one observes the signal of the H–N proton at $\delta = 5.52$ and two very close signals for the protons ortho to the sulfone function at $\delta = 8.06$ and 8.15. A substantially shielded proton absorbing at $\delta = 6.81$ can be attributed to one of the positions beside the N–H function, according to models most probably position 13. Again it can be assumed that the rearrangement precursor proper is the dimetalated intermediate **36** which ring expands to the dilithio derivative **37**, the latter accounting probably for the yellow solid formed during the reaction.

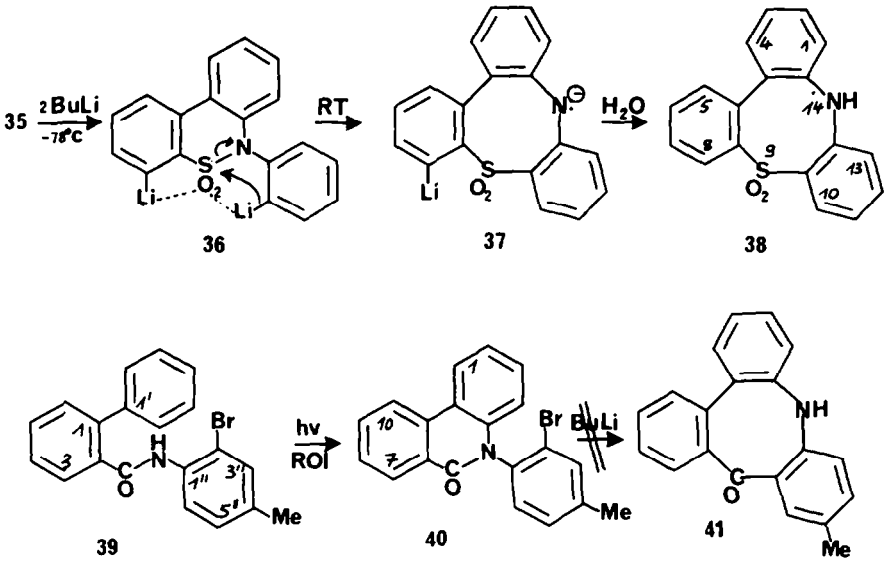
In view of the discussion relating to the inaccessibility of the "exo-directed" CO function of **17** by intramolecular nucleophilic attack it was not expected that a similar (6→8)-ring expansion could be performed with the CO analogue **40** of **35** which was synthesized by photolytic ring closure of the biphenylcarboxamide **39**.

And, indeed, when **40** was reacted with t-BuLi in the usual way, no product bearing the characteristics of the rearranged structure **41** could be isolated.

A last option for promoting intramolecular car-



29 30 31 33 34 35



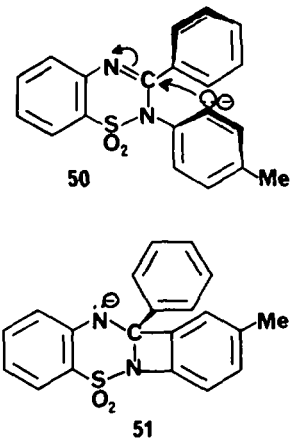
36 37 38

39 40 41

banionic attack towards a CO-like function in a 5- or 6-membered heterocycle consisted in arranging this group in such a way that only backside addition to the electrophilic carbon was possible. Such a situation was provided for in the 1,2,4-benzothiadiazin derivative **46** in which an imine grouping is modelling the CO functionality. The synthesis of **46** was straightforward, the key step being condensation of the *o*-aminobenzenesulfonamide **44** with trimethyl orthobenzoate (**45**).[22] When **46** was reacted with BuLi at − 110° and then warmed to room temperature, a high yield of 2 - methyl - 12 - phenyl - 5H - dibenzo[c,g][1,2,6]thiadiazocin 6,6-dioxide (**47**) was obtained.

The constitution of **47** followed from the very clean hydrolysis to the acyclic sulfonamide **48** which in turn could be generated independently from **42** and aminobenzophenone **49**.[23] A close inspection of the lithiated rearrangement precursor **50** indeed shows that the carbanionic function is situated suitably "behind" the C=N dipole and that the flexibility of the partly saturated thiadiazin ring and the propeller disposition of the aryl substituents facilitate off-nodal plane overlap of the nonbonding phenyl–anion-orbital and the π^*-orbital of the imine function.

Again the question whether the first result of the addition reaction, namely **51**, is an intermediate or a transition state must remain unanswered.



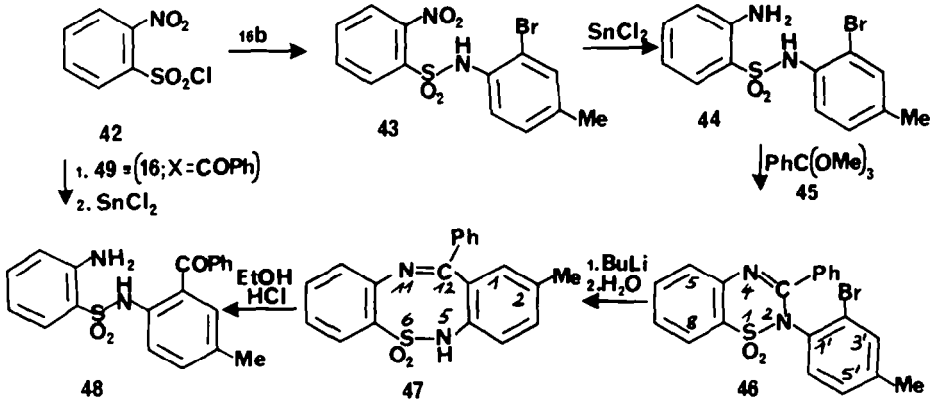
50

51

Unexpected formation of heterocycles

In the course of these investigations we encountered also several cases where the originally designed pathway was not obeyed, but where instead totally different and more complex reaction patterns were followed under formation of quite unexpected types of heterocyclic compounds.

When N-(2-bromo-4-methylphenyl)phthalimide (**52**) was reacted with one equivalent of t-BuLi under the usual conditions a multicomponent mixture was



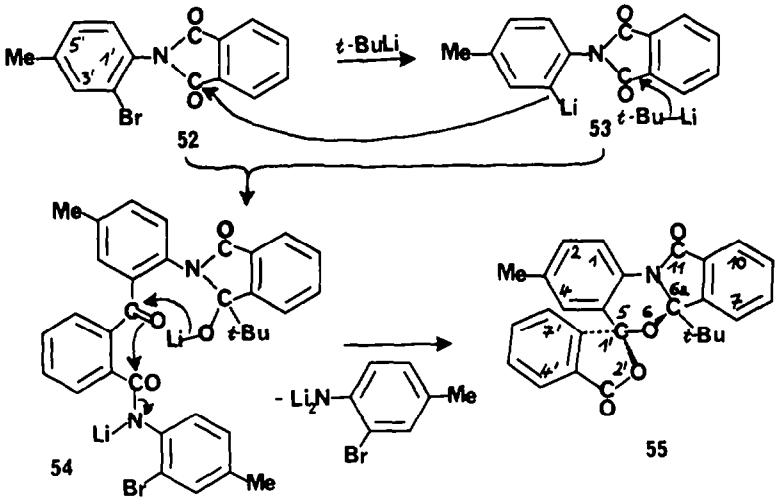
42 43 44 45

48 47 46

obtained from which besides 22% starting material only one other crystalline product could be isolated in 5% yield. The ^{1}H-NMR-spectrum of this material showed merely one Me signal, 11 aromatic protons and a signal for one t-Bu group. Together with a molecular peak of $m/z = 435$ and a base peak of $m/z = 368$ corresponding to t-Bu fragmentation these findings were strongly evidencing a sort of dimeric product which moreover had added one molecule of t-BuLi. A plausible reaction scheme begins with the usual halogen metal exchange forming the lithiated phthalimide **53**. This can now add t-Buli across one CO function and at the same time attack a second molecule of phthalimide **52** at one of its CO groups, the sequence of these two events of course being undecided. From the thus formed intermediate **54** two successive CO additions lead to the isolated 6a - t - butyl - 3 - methyl - 6a,11 - dihydro - spiro[5H - isoindolo[2,1 - a][3,1]benzoxazin - 5,1'(3H) - isobenzofuran] - 3',11 - dione (**55**).

vent the organyllithium from being deactivated by complexation with the dibenzoylamino function (see **57**). The isolated products are benzoic acid (80%), N-benzoyl-2-bromo-4-methylbenzenamine (**63**) (73%), benzamide **59** (6%), benzoxazin **62** (2%), and urea **64** (2%). A reasonable reaction scheme for the key products can be formulated as follows. Initial halogen metal exchange leads to the lithio derivative **57** which rearranges to the benzophenone **58** according to the "Leitmotiv" of this paper. Further reaction with t-BuLi results then in formation of **59**. On the other hand **58** can also be attacked by the initially formed Li compound **57** which gives rise to the intermediate **60** which stabilizes itself by intramolecular carbonyl attack (to yield **61**) and subsequent elimination of lithium benzoate ending up with **62**.

For the formation of the urea derivative **64** no conclusive explanation can be given as yet, but additional experiments have shown that similar prod-

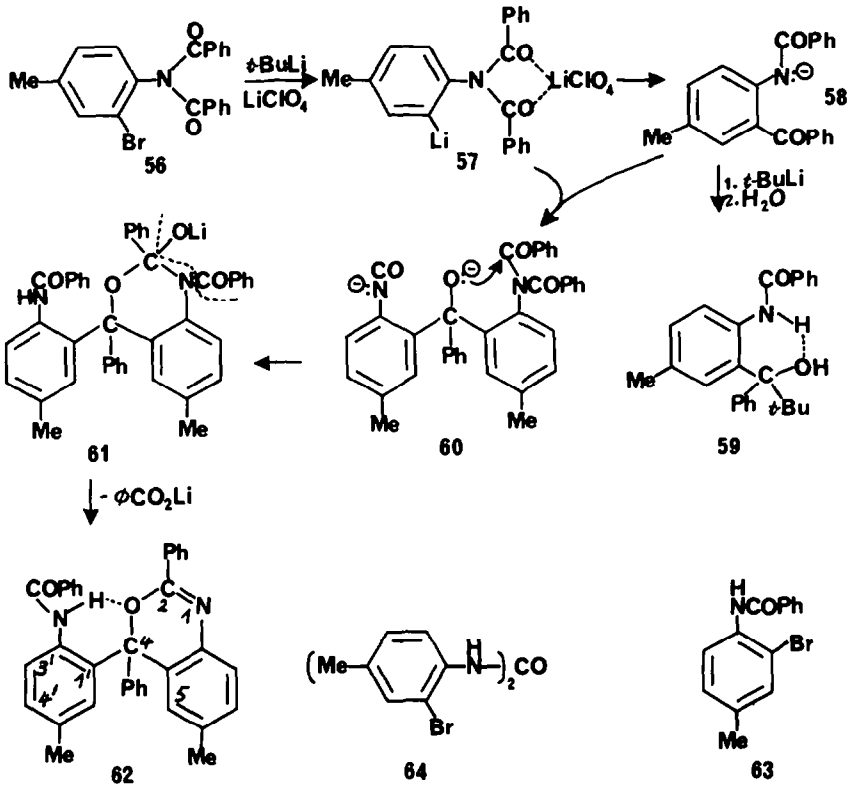


Analytical and spectroscopic data are fully in accordance with this structure. In the IR-spectrum two CO stretching frequencies are observed at 1779 and 1726 cm^{-1} which can be attributed to the 5-membered ring lactone and lactam units, respectively.[24] In the ^{13}C-NMR-spectrum the CO carbons are found at $\delta = 167.34$ and 168.21, whereas the two quaternary acetal-like carbons at C-5 and C-6a show characteristic shifts of $\delta = 96.76$ and/or 105.90.[25] Spiro compound **55** contains two asymmetric C atoms and should therefore exist in form of two diastereomeric pairs of enantiomers. In the reaction only one isomer has been formed. The significant shielding of proton H-4 ($\delta = 6.45$) strongly supports the relative configurations of the asymmetric centers C-1' and C-6a as given in the formula since molecular models show that only in this configuration H-4 is subjected to the shielding effect of the neighboring phenyl group of the isobenzofuranone system.

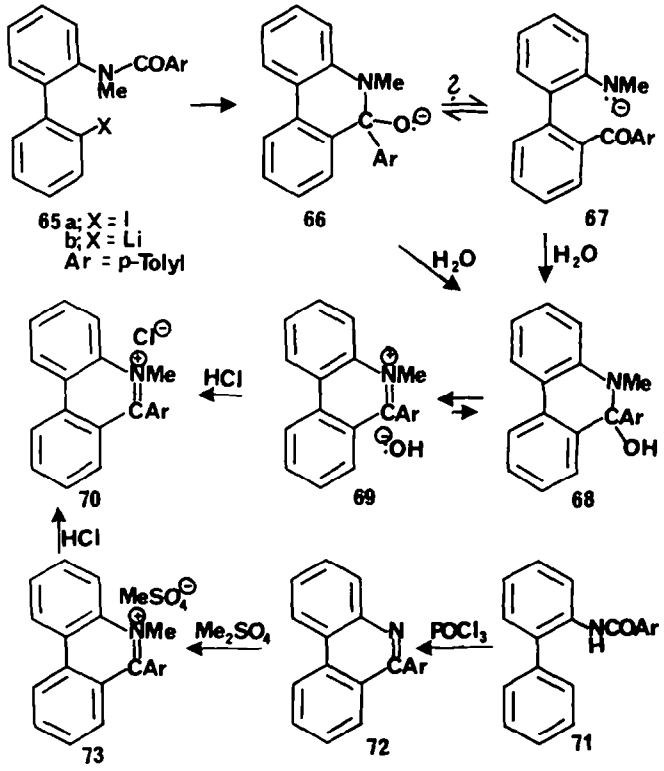
An even more complex series of inter- and intramolecular reactions seems to be effective when the acyclic analogue of **52**, N,N-dibenzoyl-2-bromo-4-methylbenzenamine (**56**) is treated with t-BuLi in the presence of lithium perchlorate. The presence of the latter is obviously necessary to pre-

ucts seem to be generally produced when N,N-dibenzoylanilines are treated with t-BuLi.[7] This reaction is now under further investigation.

All the reaction products were identified analytically and spectroscopically. In the ^{1}H-NMR spectrum **59** shows besides the t-butyl signal a characteristic AMX pattern for the protons of the tolylamino unit. The strong deshielding of the proton neighboring the amino group ($\delta = 8.12$) can be understood on the basis of a hydrogen-bridge-stabilized coplanar arrangement of the amide function with the tolyl ring, which brings this proton into the deshielding area near the CO function. A similar effect is observed for the benzoxazin **62** where the corresponding proton absorbs at $\delta = 8.32$. In addition one finds here two highly shielded broadened singlets at $\delta = 6.43$ and 6.51 for H-5 and/or H-6', which strongly support the proposed constitution. With molecular models it is easy to demonstrate that the trityl part of **62** can adopt the usual propeller conformation[26] in which the protons H-5 and H-6' are lying in the shielding cone of a neighboring aryl ring. Two strong bands in the IR spectrum at 1621 and 1671 cm^{-1} can be attributed to the amide CO and benzoxazin O–C=N functions,[27] respectively.



A more obvious cyclization reaction was finally observed when an attempt was made to apply the above reaction principles to an [1.5]acyl migration. When N - (2′ - iodo - 2 - biphenylyl) - N,4 - dimethylbenzamide (**65a**) was treated in the usual manner with t-BuLi, a blue fluorescent solution was obtained from which after hydrolysis and extraction with hydrochloric acid 46–64%, unchanged starting material **65a** could be regained. From the acid extract, however, a new substance was isolated (8–13%) which was recrystallized from dichloromethane/tetrachloromethane or concentrated hydrochloric



acid. The presence of characteristically coupled and strongly low field shifted (up to $\delta = 8.96$) signals for the aromatic protons and a low field methyl singlet ($\delta = 4.77$) in the 300 MHz ^{1}H-NMR spectrum was in favor of the phenanthridinium-salt structure **70** which was confirmed by an independent synthesis via N-(2-biphenylyl)-4-methylbenzamide (**71**).

It seems now that in this case the envisaged rearrangement **65b**→**67** had stopped midways at intermediate **66** which was then trapped by water and/or acid in form of the phenanthridinium salts **69** and **70**, respectively. It can not be excluded rigorously, though, that the reaction proceeded at least partially to the desired rearrangement product **67** which on hydrolysis reclosed the ring to form the pseudo base **68** which dissociated rapidly to the phenanthridinium hydroxide **69**.[30]

EXPERIMENTAL

All organometallic reactions were carried out under an atmosphere of dry N_2. n-BuLi in hexane and t-BuLi in pentane were purchased from Metallgesellschaft AG, Frankfurt/Main, MeLi was prepared from Li and chloromethane in diethyl ether.[31] Etheral solvents were dried with sodium wire and then distilled into the reaction vessel from LAH. Cooling baths were fed with MeOH/dry ice (− 75°) or MeOH/liquid N_2 (− 100°). Chromatographic separations were performed with neutral silica 0.05–0.2 mm (columns) or silica PF 254 and GF 254, Merck, Darmstadt (layer). Melting points are uncorrected. Elemental analyses were performed in the microanalytical laboratory of the Chemical Institutes, University of Heidelberg or by Firma I.Beetz, Kronach. IR (KBr) spectra were measured with a Beckman BE 4240. ^{1}H NMR-spectra (internal standard: TMS, δ values) were measured with the following apparatus: Varian: A 60, EM 360 (60 MHz) and EM 390 (90 MHz); Bruker: WH 300 (300 MHz). ^{13}C NMR-spectra were also determined with the Bruker WH 300 at 75.46 MHz. The spectra were generally analyzed according to first order principles. For mass spectra the following machines were used: Atlas CH4, Krupp, Bremen; CEC 21/110 B, Dupont de Nemours; ZAB, Vacuum Generators GmbH, England.

2 - (2 - *Bromo* - 4 - *methylphenyl*) - 1,2 - *benzisothiazol* - 3(2H) - *one* 1,1 - *dioxide* (**17b**) was prepared by refluxing 18.8 g (80 mmol) of **15**[32] with 14.9 g (80 mmol) of **16b**[33] and 9.3 g (0.12 mol) pyridine in 300 ml dry xylene over night. After removal of the solvent (vacuum) the paste-like residue was first extracted with 40 ml MeOH and then crystallized from MeOH containing 10% acetone, yield: 20.8 g (74%), m.p. 193°. IR: 1735 (CO); 1340, 1325, 1185 cm^{-1} (SO_2). ^{1}H-NMR (d_6-acetone): 2.49 (s, 3H); 7.50 (m, 2H, H-5',6'); 7.74 (m, 1H, H-3'); 8.1–8.3 (m, 4H). (Found: C 47.84, H 2.94, Br 22.93, N 3.69, S 9.22. Calc for $C_{14}H_{10}BrNO_3S$: C 47.74, H 2.86, Br 22.63, N 3.98, S 9.10%).

2 - (4 - *Methylphenyl*) - 1,2 - *benzisothiazol* - 3(2H) - *one* 1,1 - *dioxide* (**17a**) was similarly prepared from 8.6 g (80 mmol) *p*-toluidine (**16a**) and 18.8 g **15** in 73% yield, m.p. 194° (lit. 195.5°[34]). IR: 1740 (CO); 1345, 1315, 1186 cm^{-1} (SO_2). ^{1}H NMR (d_6-acetone): 2.40 (s, 3H); 7.4 (s, 4H, H-2',3',5',6'); 7.95–8.25 (m, 4H, H-4,5,6,7).

Reaction of **17a** *with n-butyllithium.* To a soln of 2.73 g (10 mmol) **17a** in 60 ml THF were added 20 mmol n-BuLi in hexane at − 100°. After warming to room temp overnight the mixture was hydrolyzed and the THF removed from the aqueous solution by suction. After shaking with diethyl ether the layers were separated and the aqueous layer acidified with HCl. The ppt of **18** was crystallized from cyclohexane, yield: 2.78 g (84%), m.p. 94.5°. IR: 3270 (HN); 1690 (CO); 1345, 1180, 1165 cm^{-1} (SO_2). ^{1}H NMR ($CDCl_3$): 0.8–2.00 (m, 7H); 2.23 (s, 3H); 3.00 (t, J = 7 Hz, 2H); 7.00–7.70 (m, 9H). (Found: C 65.10, H 6.50, N 4.03, S 9.41. Calc for $C_{18}H_{21}NO_3S$: C 65.23, H 6.39, N 4.23, S 9.67%).

3 - *Butyl* - 3 - *methoxy* - 2 - (4 - *methylphenyl*) - 2,3 - *dihydro* - 1,2 - *benzisothiazol* 1,1 - *dioxide* (**19**). When 1 g (3 mmol) of **18** was boiled for 30 min in 20 ml MeOH, 0.82 g (79%) **19** was obtained, m.p. 118° from MeOH. IR: 1310, 1300, 1175, 1140 cm^{-1} (SO_2). ^{1}H NMR ($CDCl_3$): 0.60–2.18 (m, 9H); 2.40 (s, 3H); 3.12 (s, 3H); 7.15–8.00 (m, 8H). (Found: C 66.00, H 6.71, N 3.82, S 9.28, OCH_3 8.82. Calc for $C_{19}H_{23}NO_3S$: C 66.06, H 6.71, N 4.05, S 9.28, OCH_3 8.98%).

Rearrangement of **17b** *to* 7 - *methyl* - *dibenzo*[b,f][1,4]*thiazepin* - 11(10H) - *one* 5,5 - *dioxide* (**21**). When 3.52 g (10 mmol) **17b** in 70 ml THF were treated at − 100° with 10 mmol n-BuLi in hexane a yellowish soln was obtained, which, on warming, deposited a colorless ppt above − 30°. After stirring overnight at room temp the mixture was hydrolyzed with 30 ml water and THF removed under suction. Acidification afforded a colorless ppt which was easily soluble in warm aqueous alkali. The product **21** could be recrystallized from acetone, yield: 2.13 g (78%), m.p. 315°C. IR: 3160 (HN); 1640 (CO); 1380, 1350, 1315, 1150, 1120 cm^{-1} (SO_2). ^{1}H NMR (d_6-acetone, 300 MHz): 2.42 (s, 3H); 7.42 (d, J = 8.2 Hz, 1H, H-9); 7.55 (dd, J = 8.2, 1.2 Hz, 1H, H-8); 7.81 (d, J = 1.2 Hz, H-6); 7.86–7.96 (m, 2H, H-2,3); 8.02–8.05 (m, 2H, H-1,4). (Found: C 61.42, H 4.32, N 4.99, S 11.90. Calc for $C_{14}H_{11}NO_3S$: C 61.52, H 4.06, N 5.12, S 11.73%).

7,10 - *Dimethyldibenzo*[b,f][1,4]*thiazepin* - 11(10H) - *one* 5,5 - *dioxide* (**22**) was prepared from 820 mg (3 mmol) **21** in 40 ml water containing 0.56 g (10 mmol) KOH with 0.63 g (5.0 mmol) Me_2SO_4 by 10 min boiling. The deposited solid was separated by filtration and recrystallized from MeOH, yield: 695 mg (81%), m.p. 168°. IR: 1640 (CO); 1355, 1325, 1308, 1167, 1130 cm^{-1} (SO_2). ^{1}H NMR ($CDCl_3$, 300 MHz): 2.40 (s, 3H); 3.68 (s, 3H); 7.32 (d, J = 8.4 Hz, H-9); 7.40 (dd, J = 8 Hz, 1.6 Hz, H-8); 7.56–7.68 (m, 2H, H-2,3); 7.81 (d, J = 1.6 Hz, H-6); 7.90–7.95 (m, 2H, H-1,4). (Found: C 62.50, H 4.88, N 4.66, S 11.18. Calc for $C_{15}H_{13}NO_3S$: C 62.70, H 4.56, N 4.87, S 11.16%).

Independent synthesis of **22**

N-*Methyl*-N-p-*tolylbenzenesulfonamide* (**23**) was prepared according to the lit[35] in 59% yield, m.p. 65°. IR: 1350, 1315, 1185, 1175, 1165 cm^{-1} (SO_2). ^{1}H NMR (CCl_4): 2.23 (s, 3H); 3.10 (s, 3H); 6.85 (d, J = 9 Hz, H-2',6'); 7.04 (d, J = 9 Hz, H-3',5'); 7.45 (s, 5H).

Rearrangement to N,4 - *dimethyl* - 2 - (*phenylsulfonyl*)*benzenamine* (**25**) was accomplished by treating 7.83 g (30 mmol) **23** in 100 ml THF under cooling with ice with 70 mmol MeLi in diethyl ether. After warming to room temp and stirring overnight the mixture was hydrolyzed and THF removed by suction. After shaking with diethylether the layers were separated and the organic solvent removed i.vac. Crystallization of the residue from CCl_4 afforded 6.35 g (81%) pure **25** having m.p. of 118–119°. IR: 3420 (HN); 1320, 1290, 1180, 1145, 1130 cm^{-1} (SO_2). ^{1}H NMR (CCl_4): 2.24 (s, 3H); 2.79 (d, J = 6 Hz, 3H, after D_2O addtn. s); 6.27 (s, 1H, D_2O-exchange); 6.46 (d, J = 8 Hz, H-6); 6.99–7.92 (m, 6H). (Found: C 64.43, H 6.06, N 5.03, S 12.28. Calc for $C_{14}H_{15}NO_2S$: C 64.34, H 5.79, N 5.36, S 12.27%).

2 - (5 - *Methyl* - 2 - *methylaminophenylsulfonyl*)*benzoic acid* (**26**). A soln of 7.83 g (30 mmol) **23** in 100 ml THF was treated with 75 mmol MeLi at − 15° and then warmed to room temp. After stirring overnight and cooling to − 78°, THF-washed lumps of dry-ice were added to the soln. After warming to room temp the whole mixture was poured into 100 ml of ice-water after which THF was removed by suction. After extraction with diethylether the aqueous layer was diluted with an equal amount of EtOH and *ca* 30 g ion exchanger (acidic, Merck Nr. 4765) were added. After thorough mixing and decantation of the soln, the ion exchanger was twice extracted with 100 ml portions of EtOH and after removal of the solvent the residue was crystallized from $CHCl_3$, yield: 5.95 g (65%), m.p. 164–166° (dec). IR: 3440 (br., HN, COOH); 1700 (CO); 1320, 1290, 1150, 1120 cm^{-1} (SO_2). ^{1}H NMR (d_6-acetone): 2.18 (s, 3H);

6.65 (d, J = 8.5 Hz, H-3'); 6.9–8.0 (m, 7H); 8.1 (s, 2H, D_2O-exchange). (Found: C 58.94, H 5.21, N 4.34, S 10.26. Calc for $C_{15}H_{15}NO_4S$: C 59.00, H 4.95, N 4.59, S 10.50%).

For cyclization, 500 mg (1.65 mmol) of **26** in 25 ml dimethylformamide were stirred for 20 min with 140 mg $NaHCO_3$ and then treated with 2 ml $SOCl_2$ for 2 hr at 65° and overnight at 100°. After removal of the solvent i.vac. the residue was boiled with EtOAc. The extract was again brought to dryness and the solid residue of **22** crystallized from $CHCl_3$, yield: 252 mg (55%), m.p. 168°. Mixed m.p. and the spectra showed this material to be identical with the product obtained from the rearrangement of **17b**.

2 - (2 - *Bromo* - 4 - *methylphenyl*) - 1,2 - *benzisothiazol* - 3(2H) - *one* (**30**) *and its* 1 - *oxide* (**31**). The *bis*-(2'-bromo-4'-methylanilide) of **29** was prepared in 80% yield like the corresponding anilide,[36] m.p. 235° (from DMF/water). IR: 3420 (HN); 1670 (CO); 1515 cm^{-1} (amide II). ^1H NMR (d_6-DMSO): 2.31 (s, 6H); 7.28 (dd, J = 9, 2 Hz, 2H, H-5'); 7.4–7.9 (m, 10H); 7.98 (dd, J = 9, 2 Hz, 2H, H-6); 10.35 (s, 2H, D_2O-exchange). (Found: C 52.16, H 3.58, Br 24.83, N 4.09, S 10.27. Calc for $C_{28}H_{22}Br_2N_2O_2S_2$: C 52.35, H 3.45, Br 24.88, N 4.36, S 9.98%).

For cyclization,[37] 9.65 g (15 mmol) **29** were refluxed for 18 hr with 60 ml $SOCl_2$. After removal of excess reagent by distillation the residual oil was dissolved in cyclohexane whereby 9% educt remained. After removal of the solvent by suction **30** was recrystallized from petrolether (70°)/CH_2Cl_2, yield: 7.2 g (75%), m.p. 139°. IR: 1670 cm^{-1} (CO). ^1H NMR (d_6-acetone): 2.40 (s, 3H); 7.25 (dd, J = 9, 1.5 Hz, H-5'); 7.4–7.9 (m, 4H); 7.62 (d, J = 1.5 Hz, H-3'); 8.05 (d, J = 8 Hz, H-4). (Found: C 52.38, H 3.22, Br 24.81, N 4.16, S 10.02. Calc for $C_{14}H_{10}BrNOS$: C 52.51, H 3.15, Br 24.95, N 4.38, S 10.01%).

For oxidation,[37] 4.80 g (15 mmol) **30** were dissolved in 60 ml AcOH containing the stoichiometric amount of 30% H_2O_2 and stirred overnight at room temp. The ppt was filtered and recrystallized from acetone, yield: 2.62 g (52%), m.p. 150–152°. IR: 1730 (CO); 1100 cm^{-1} (SO). ^1H NMR ($CDCl_3$): 2.38 (s, 3H); 7.20 (dd, J = 8.5, 1 Hz, H-5'); 7.38 (d, J = 8.5 Hz, H-6'); 7.55 (d, J = 1 Hz, H-3'); 7.7–8.1 (m, 4H); (Found: C 49.96, H 3.19, Br 23.96, N 4.03, S 9.49. Calc for $C_{14}H_{10}BrNO_2S$: C 50.01, H 2.99, Br 23.77, N 4.27, S 9.54%).

Reaction of **30** *with n- or t-butyllithium*. When 960 mg (3 mmol) **30** in 50 ml THF was treated with 3 mmol n- or t-BuLi at − 105° a yellowish soln was obtained. After gradually warming to room temp the soln was hydrolyzed, THF removed by suction and the remaining aqueous layer extracted with CH_2Cl_2. The solvent was distilled and the resulting oil purified by preparative layer chromatography with CH_2Cl_2. The products were recrystallized from petrolether (40–60°), yield: (**32a**): 905 mg (80%), m.p. 76–78°. IR: 3270 (NH); 1650 (CO); 1520 cm^{-1} (amide II). ^1H NMR (CCl_4): 0.9 (m, 3H); 1.3–1.7 (m, 4H); 2.32 (s, 3H); 2.90 (t, J = 11 Hz, H_2CS); 7.1 (dd, J = 8, 2 Hz, H-5'); 7.25–7.50 (m, 4H); 7.80 (m, H-6); 8.45 (d, J = 8 Hz, H-6'); 8.9 (s, HN, D_2O-exchange). (Found: C 57.19, H 5.48, Br 21.15, N 3.47, S 8.38. Calc for $C_{18}H_{20}BrNOS$: C 57.14, H 5.33, Br 21.12, N 3.70, S 8.47).

Yield (**32b**): 895 mg (79%), m.p. 80–81°. IR: 3240 (HN); 1660 (CO); 1515 cm^{-1} (amide II). ^1H NMR (CCl_4): 1.25 (s, 9H); 7.15 (dd, J = 9, 1.5 Hz, H-5'); 7.35 (d, J = 1.5 Hz, H-3'); 7.4–7.6 (m, 3H); 8.05 (dd, J = 8, 2 Hz, H-6); 8.43 (d, J = 9 Hz, H-6'); 9.9 (s, HN, D_2O-exchange). (Found: C 57.27, H 5.47, Br 21.01, N 3.50, S 8.49%).

When 1.01 g (3 mmol) **31** in 50 ml THF were similarly treated with 3 mmol t-BuLi only a 11% yield of **29** could be isolated (mixed m.p., IR-comparison).

6-*Phenyl*-6H-*dibenzo*[c,e][1,2]*thiazin* 5,5-*dioxide* (**35**)

(A) A mixture of 2.31 g (10 mmol) **34**,[21] 1.38 g (10 mmol) K_2CO_3, 60 mg Cu powder, and 20 g iodobenzene was refluxed for 50 hr. After steam distillation of excess iodobenzene the residue was filtered and unchanged starting material **34** was recovered from the filtrate by precipitation with AcOH. The above solid was extracted with small portions of boiling EtOH, totalling 200 ml. After treatment with activated C, filtration and concentration to 20 ml, starlike crystals were obtained on cooling, yield: 0.49 g (15%), m.p. 187°. IR: 1330, 1290, 1180, 1165, 1140 cm^{-1} (SO_2). ^1H NMR (d_6-acetone, 300 MHz): 7.04 (m, H-7); 7.22 (dd, J = 7, 2 Hz, H-2',6'); 7.40–7.51 (m, 5H); 7.71 (dt, J = 7.6, 1.2 Hz, 1H); 7.91 (m, 2H); 8.29 (m, 1H); 8.32 (d, J = 7.1 Hz, H-4?). (Found: C 70.29, H 4.54, N 4.44, S 10.21. Calc for $C_{18}H_{13}NO_2S$: C 70.34, H 4.26, N 4.55, S 10.43%).

(B) To a soln of 2.31 g (10 mmol) **34** in 30 ml EtOH and 40 ml 0.25 N KOH, aq 3.61 g (10 mmol) diphenyliodonium bromide[38] were added and the mixture was refluxed for 10 hr. After filtration from unreacted iodonium salt the filtrate was diluted with 100 ml water and extracted with ether. The solid **35** remaining after removal of the ether was crystallized from MeOH, yield: 0.77 g (25%), m.p. 187°. Reaction of the dry K-salt of **34** with diphenyliodonium bromide in dimethylformamide did not improve the yield.

Rearrangement of **35** *to* 14H-*tribenzo*[b,e,g][1,4]*thiazocin* 9,9-*dioxide* (**38**). The soln of 0.86 g (28 mmol) of **35** in 30 ml THF became wine-red on addition of 64 mmol of n-BuLi at − 78° and deposited a yellow-brown ppt on warming to − 20°. After stirring overnight, hydrolysis and removal of THF by suction, the colorless solid was dissolved in diethyl ether. After removal of the ether the resulting solid was crystallized from MeOH, yield: 765 mg (88%), m.p. 212°. IR: 3340 (NH); 1300, 1285, 1155, 1130 cm^{-1} (SO_2). MS: *m/z* = 307 (38%, M^+); 243 (100%, $M-SO_2$). ^1H NMR ($CDCl_3$, 300 MHz): 5.52 (s, NH); 6.81 (dd, J = 8, 0.9 Hz, H-13); 7.01 (dt, J = 7.6, 0.9 Hz, H-11); 7.20–7.25 (m, 1H); 7.32–7.44 (m, 4H); 7.50–7.58 (m, 2H); 7.70 (dt, J = 7.5, 1.3 Hz, H-6); 8.06 (dd, J = 8, 0.9 Hz, H-8/10); 8.15 (dd, J = 8.2, 1.5 Hz, H-10/8). (Found: C 70.48, H 4.44, N 4.31, S 10.37. Calc for $C_{18}H_{13}NO_2S$: C 70.34, H 4.26, N 4.55, S 10.43%.)

Attempted rearrangement of N-(2-bromo-4-methylphenyl)phenanthridone (**40**). Compound **39** was prepared in 80% yield from **16b** and 2-biphenylcarbonyl chloride,[39] m.p. 93–96°. IR: 3204 (NH); 1653 cm^{-1} (CO). ^1H NMR (CCl_4): 2.24 (s, 3H); 7.03 (dd, J = 8.4, 1.8 Hz, H-5''); 7.15 (d, J = 1.8 Hz, H-3''); 7.28–7.54 (m, 9H); 7.82 (m, H-3); 8.41 (d, J = 8.4 Hz, H-6''). (Found: C 65.31, H 4.67, Br 21.95, N 3.85. Calc for $C_{20}H_{16}BrNO$: C 65.59, H 4.40, Br 21.82, N 3.82%.)

Cyclization[40] *of* **39**. A soln of 10.75 g (0.1 mol) t-butylhypochlorite[41] and 28.84 g (0.112 mol) iodine in 50 ml benzene was stirred for 5 min in the dark under N_2. After addition of 17.5 g (0.154 mol) of t-BuOK and another 5 min stirring 12.2 g (33.3 mmol) of **39** were added and the mixture was then irradiated with a 300 W photo lamp for 3 hr. After renewed addition of the same amounts of hypochlorite, iodine and t-butoxide, irradiation was maintained for another 5 hr. The soln was then poured into 1/2 l water containing some sodium dithionite for the destruction of excess iodine and hypochlorite. The mixture was extracted three times with chloroform and the chloroform solution washed with water, and then dried. The solvent was distilled and the residual brown oil purified by column chromatography with CH_2Cl_2. After several fractions of oily and solid mixtures one obtained 2.84 g (23%) colorless crystals of **40**, which were recrystallized from EtOH, m.p. 153°. IR: 1668 cm^{-1} (CO). ^1H NMR ($CDCl_3$): 2.44 (s, 3H); 6.59 (m, 1H); 7.18–7.41 (m, 4H); 7.52–7.89 (m, 3H); 8.25–8.43 (m, 2H, H-1,10); 8.60 (dd, J = 7.8, 1.8 Hz, H-7). (Found: C 65.99, H 4.12, Br 21.83, N 3.61. Calc for $C_{20}H_{14}BrNO$: C 65.95, H 3.87, Br 21.94, N 3.85%.)

When a soln of 1.09 g (3 mmol) of **40** in 50 ml THF was treated with 1 equivalent of t-BuLi at − 100° a light red color evolved which changed from brown-red to orange on warming to room temp. Hydrolysis led to a yellowish soln from which a brown oil could be extracted with 15% HCl. Several attempts to crystallize this material led only to an amorphous powder having a melting area of 120–210°. Separation into definite components was not possible.

Rearrangement of 2 - (2 - *bromo* - 4 - *methylphenyl*) - 3 - *phenyl* - 2H - 1,2,4 - *benzothiadiazin* 1,1 - *dioxide* (**46**) *to* 2 - *methyl* - 12 - *phenyl* - 5H - *dibenzo*[c,g][1,2,6] - *thiadiazocin* 6,6 - *dioxide* (**47**)

N - (2 - *Bromo* - 4 - *methylphenyl*) - 2 - *nitrobenzenesulfonamide* (**43**) was prepared in 88% yield from **16b** and **42**[42] analogously to *loc cit*[21] but with pyridine as auxiliary base, m.p. 136–137°. IR: 3320 (NH); 1540, 1490 (NO_2); 1360, 1345, 1175 cm^{-1} (SO_2). ^1H NMR (d_6 - acetone): 2.31 (s, 3H); 7.20 (dd, J = 8.5, 3 Hz, H - 5'); 7.38 (s, H - 3'); 7.45 (d, J = 8.5 Hz, H - 6'); 7.78–8.05 (m, 4H). (Found: C 42.18, H 3.09, Br 21.56, N 7.36, S 8.47. Calc for $C_{13}H_{11}BrN_2O_4S$: C 42.06, H 2.99, Br 21.53, N 7.55, S 8.64%).

2 - *Amino* - N - (2 - *bromo* - 4 - *methylphenyl*)*benzenesulfonamide* (**44**) was prepared in 85% yield by reduction of **43** with $SnCl_2$ in conc HCl/EtOH,[21] m.p. 128° from EtOH. IR: 3460, 3380, 3270 (NH_2, NH); 1330, 1320, 1165, 1145 cm^{-1} (SO_2). ^1H NMR (d_6-acetone): 2.24 (s, 3H); 5.7 (br.s, 2H, H_2N, D_2O-exchange); 6.55 (ddd, J = 8.5, 8, 1.5 Hz, H-5); 6.82 (dd, J = 8.5, 1.5 Hz, H-3); 6.96–7.25 (m, 3H, H-4,3',5'); 7.38 (d, J = 8 Hz, H-6'); 7.45 (dd, J = 8, 1.5 Hz, H-6); 8.1 (br.s, HN, D_2O-exchange). (Found: C 45.53, H 3.98, Br 23.21, N 8.00, S 9.46. Calc for $C_{13}H_{13}BrN_2O_2S$: C 45.76, H 3.84, Br 23.42, N 8.21, S 9.40%.)

Condensation[22] *to* **46** was achieved by refluxing 9.5 g (28 mmol) **44** and 10 g (55 mmol) of **45** in 150 ml toluene in the presence of a little P_4O_{10} for 60 hr. The cooled mixture was treated with 5 g of solid K_2CO_3, filtrated and freed from solvent. Crystallization from cyclohexane/CH_2Cl_2, then from cyclohexane/CCl_4 afforded 9.55 g (80%) pure **46** with m.p. 138°. IR: 1580, 1560 (CN); 1360, 1190 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$, 300 MHz): 2.25 (s, 3H); 7.05 (d, J = 8.1 Hz, H-5'); 7.25 (s, H-3'); 7.3–7.4 (m, 3H, H-5,3'',5''); 7.44 (d, J = 8.1 Hz, H-6'); 7.50–7.56 (m, H-4''); 7.73–7.81 (m, 2H, H-6,7); 7.86–7.91 (m, 3H, H-8,2'',6''). (Found: C 56.41, H 3.64, Br 18.89, N 6.37, S 7.52. Calc for $C_{20}H_{15}BrN_2O_2S$: C 56.22, H 3.54, Br 18.70, N 6.55, S 7.50%.)

For rearrangement, 850 mg (2 mmol) **46** in 40 ml THF were treated at − 110° with 2 mmol n-BuLi. The soln became orange-red and gave a red ppt which dissolved only on warming to 0°. After standing overnight at room temp the soln was again cooled to 0° and hydrolyzed with satd NH_4Claq. After removal of THF by suction the aqueous soln was extracted with CH_2Cl_2, the extract dried, and freed from solvent. The resulting oily **47** crystallized from cyclohexane/CCl_4, yield: 593 mg (85%), m.p. 197–199°. IR: 3220 (NH); 1620 (CN); 1320, 1300, 1160 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$, 300 MHz): 2.28 (s, 3H); 6.05 (s, HN, D_2O-exchange); 6.89 (dd, J = 8, 1.3 Hz, H-9); 6.93 (d, J = 1.3 Hz, H-6); 7.08 (dt, J = 7.9, 1.3 Hz, H-11); 7.18 (dd, J = 8.3, 2 Hz, H-4); 7.37 (d, J = 8.3 Hz, H-3); 7.41 (dt, J = 7.1, 1.3 Hz, H-10); 7.47 (dt, J = 7.1, 1.3 Hz, 2H, H-3',5'); 7.54 (tt, J = 7.2, 1.3 Hz, H-4'); 7.86–7.89 (m, 3H, H-12,2',6'). (Found: C 68.89, H 4.67, N 8.06, S 9.11. Calc for $C_{20}H_{16}N_2O_2S$: C 68.94, H 4.63, N 8.04, S 9.20%.)

Hydrolysis of **47**. A soln of 300 mg (0.85 mmol) **47** in 15 ml EtOH and 15 ml conc HCl was kept for 20 hr at room temp. After addition of 17 g $NaHCO_3$ in 250 ml water, the mixture was extracted with CH_2Cl_2. Removal of the solvent afforded **48** as an oil, which could be crystallized from EtOH/EtOAc, yield: 265 mg (85%), m.p. 110–112°. IR: 3460, 3360, 3270 (HN, H_2N); 1690 (CO); 1320, 1160, 1150 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$): 2.25 (s, 3H); 4.85 (s, 2H, H_2N, D_2O-exchange); 6.35 (dd, J = 8.4, 1.3 Hz, H-3); 6.50 (dt, J = 8, 1.3 Hz, H-5); 6.8–7.8 (m, 10H); 9.95 (s, 1H, HN, D_2O-exchange). (Found: C 65.85, H 5.15, N 7.49, S 8.51. Calc for $C_{20}H_{18}N_2O_3S$: C 65.56, H 4.95, N 7.64, S 8.75%.)

Independent synthesis of **48**

2-*Amino*-4-*methylbenzophenone* (**49**) was prepared from *p*-toluidine and benzoylchloride,[43] m.p. 62°. IR: 3490, 3330 (H_2N); 1625 cm^{-1} (CO). ^1H NMR (CCl_4): 2.18 (s, 3H); 5.9 (br.s, H_2N, D_2O-exchange); 6.45 (d, J = 8.5 Hz, H-6); 7.05 (dd, J = 8.5, 2 Hz, H-5); 7.18 (d, J = 2 Hz, H-3); 7.35–7.70 (m, 5H).

N - (2 - *Benzoyl* - 4 - *methylphenyl*) - 2 - *nitrobenzenesulfonamide* was prepared in the usual way[21] from **49** and 2-nitrobenzenesulfonylchloride with pyridine as auxiliary base, yield: 65%, m.p. 124° from EtOH. IR: 3260 (HN); 1650 (CO); 1530, 1380 (NO_2); 1170 cm^{-1} (SO_2). ^1H NMR ($CDCl_3$): 2.29 (s, 3H); 7.15 (d, J = 1.8 Hz, H-3'); 7.30–7.55 (m, 9H); 7.70 (d, J = 8.4 Hz, H-6'); 7.8–8.0 (m, 1H); 10.0 (s, 2H, H_2N, D_2O-exchange). (Found: C 60.44, H 4.29, N 6.92, S 8.03. Calc for $C_{20}H_{16}N_2O_5O_5S$: C 60.60, H 4.06, N 7.07, S 8.09%.) *Reduction*[21] *of this nitro compound to* 2 - *amino* - N - (2 - *benzoyl* - 4 - *methylphenyl*)*benzenesulfonamide* (**48**) was performed with $SnCl_2$ in HCl/EtOH in 82% yield, m.p. 110–112° from cyclohexane/EtOAc. Mixed m.p. and spectroscopical comparisons showed the identity of this product with the hydrolysis product of **47**.

Reaction of N-(2-*bromo*-4-*methylphenyl*)*phthalimide* (**52**) *with t-butyllithium.* Phthalimide **52** was prepared by heating phthalic acid anhydride and **16b** in toluene with a drop of phosphoric acid until no more water was formed, yield: 92%, m.p. 204–205° from acetone. IR: 1791, 1774, 1728 cm^{-1} (CO).[44] ^1H NMR ($CDCl_3$): 2.42 (s, 3H); 7.29 (br.s, 2H, H-5',6'); 7.63 (br.s, H-3'); 7.75–8.12 (m, 4H). (Found: C 56.75, H 3.43, Br 25.25, N 4.22. Calc for $C_{15}H_{10}BrNO_2$: C 56.99, H 3.19, Br 25.27, N 4.43%). When 3.16 g (10 mmol) **52** in 100 ml THF were treated with 1 equiv of t-BuLi at − 100° a brown-yellow soln was formed, which on slowly warming to − 10° became red-brown. As room temperature was reached the solution was hydrolysed with NH_4Cl soln, after which THF was removed by suction. The residual aqueous layer was then treated with diethyl ether and the separated etheral layer extracted with $NaHCO_3$ aq from which surprisingly 22% unchanged starting material could be separated. Extraction with HCl removed ~ 0.1 g of a mixture of *p*-toluidine and **16b**. When the etheral layer was brought to dryness a yellow resin was obtained which after soln in CH_2Cl_2, addition of EtOH and slow evaporation formed colorless needles (0.228 g, 5%) of **55**, m.p. 274–278°. IR: 1779 (CO-lactone); 1726 cm^{-1} (CO-lactam). ^1H NMR ($CDCl_3$, 300 MHz): 0.92 (s, 9H); 2.23 (s, 3H); 6.45 (br.s, H-4); 7.37 (dd, J = 8.2, < 2 Hz, H-2); 7.52–7.54 (m, 3H); 7.68–7.74 (m, 3H); 7.86 (td, J = 7.5, < 2 Hz, H-8 or 6'); 7.91 (br.d, J = 7.5 Hz, 1H, H-10/4'); 7.94 (dd, J = 7.5, 1.8 Hz, 1H, H-4'/10). ^{13}C NMR (CD_2Cl_2): 21.27 (q); 25.73 (q); 42.09 (s); 96.76, 105.90 (s, C-5/-6a); 124.08 (d); 124.47 (d); 124.59 (d); 124.77 (d); 125.34 (d); 125.91 (d); 128.27 (s); 129.20 (s); 129.98 (d); 131.03 (s); 131.72 (d); 131.96 (d); 132.77 (d); 134.47 (s); 135.07 (d); 136.12 (s); 145.56, 147.96 (s, C-7'a/6b); 167.34, 168.21 (s, C-3'/11). MS: *m/z* = 425 (1.5%, M^+); 368 (100%, M–C_4H_9); 324 (3.8%, M–C_4H_9–CO_2); 220 (22%, M–C_4H_9–CO_2–C_6H_4CO); 192 (3.8%, $C_{14}H_{10}N$); 165 (13%, $C_{13}H_9$); 130 (3%, C_6H_4CON); 105 (6.5%, C_6H_5CO); 104 (6.3%, C_6H_4CO); 76 (3.3%, C_6H_4); 57 (5.4%, C_4H_9). (Found: C 75.86, H 5.60, N 3.01. Calc for $C_{27}H_{23}NO_4$: C 76.22, H 5.45, N 3.29%).

Reaction of N,N-*dibenzoyl*-2-*bromo*-4-*methylbenzenamine* (**56**) *with t-butyllithium.* The starting material **56** was accessible from N-(2-bromo-4-methylphenyl)benzamide and benzoylchloride in 83% yield according to *loc cit*,[45] m.p. 167° from EtOH. IR: 1708, 1670 cm^{-1} (CO). ^1H NMR ($CDCl_3$): 2.28 (s, 3H); 7.00 (m, AB part of ABX, 2H, H-5',6'); 7.2–7.5 (m, 7H); 7.8 (m, 4H, H-2,6). (Found: C 63.97, H 4.28, Br 19.98, N 3.31. Calc for $C_{21}H_{16}BrNO$: C 63.97, H 4.09, Br 20.27, N 3.55%).

On reaction of 7.88 g (20 mmol) **56** in 300 ml THF with one equivalent of t-BuLi in the presence of 5 g (47 mmol) of lithium perchlorate at − 100° a dark soln was formed which turned red-brown on slowly warming to room temp. Hydrolysis, removal of THF i.vac. shaking with diethyl ether and extraction of the etheral layer with $NaHCO_3$ aq—which was then acidified—gave 1.95 g (80%) benzoic acid. The remaining etheral soln was brought to dryness and the solid material separated by column chromatography over silica

with CH_2Cl_2. A first fraction of brown, viscous oil was discarded. A second fraction of 4.24 g (73%) consisted of N-(2-bromo-4-methylphenyl)benzamide (m.p. 141–142°), from EtOH. The third fraction was again an unidentified brown, viscous oil, whereas from the fourth fraction 0.137 g (2%) of **64** with m.p. 240° from EtOH could be isolated. An indentical reference compound was prepared from ethyl chloroformiate and **16b** by 2 h boiling in pyridine. IR: 3307 (HN); 1653 cm^{-1} (CO). ^1H NMR ($CDCl_3$, 300 MHz): 2.33 (s, 6H); 6.74 (br.s, 2H, H–N); 7.13 (dd, J = 8.1, 1.5 Hz, 2H, H-5); 7.39 (d, J = 1.5 Hz, 2H, H-3); 7.89 (d, J = 8.1 Hz, 2H, H-6). (Found: C 45.06, H 3.72, Br 39.85, N 6.90. Calc for $C_{15}H_{14}Br_2N_2O$: C 45.26, H 3.54, Br 40.14, N 7.04%.)

From the fifth chromatographic fraction a 2% yield (0.196 g) of **62** was obtained, m.p. 221° from EtOH. IR: 3422 (HN); 1671 (CN); 1621 cm^{-1} (CO). MS: m/z = 508 (3.4%, M); 403 (55.6%, M–COC_6H_5); 388 (23.5%, M–$NHCOC_6H_5$); 283 (6.4%, M–COC_6H_5–$NHCOC_6H_5$); 105 (100%, COC_6H_5); 77 (28.3%, C_6H_5); ^1H NMR ($CDCl_3$): 2.17 (s, 3H); 2.25 (s, 3H); 6.43, 6.51 (each br.s, H-5/6′); 7.1–7.5 (m, 16H); 7.94 (dd, J = 7.8, 2.2 Hz, 2H); 8.32 (d, J = 8.3 Hz, H-3′); 8.61 (br.s, HN).

The sixth chromatographic fraction finally deposited 0.41 g (6%) yellowish prisms of **59**, m.p. 190° from EtOH. IR: 3390, 3362 (HO, HN); 1662 cm^{-1} (CO). MS: m/z = 317 (7.3%, M–C_4H_8); 316 (31.3%, M–C_4H_9); 299 (2.6%, M–C_4H_8–H_2O); 298 (10.2%, M–C_4H_9–H_2O); 210 (4.3%, M–C_4H_9–$HOCC_6H_5$); 105 (100%, COC_6H_5); 77 (22%, C_6H_5). ^1H NMR ($CDCl_3$, 300 MHz): 1.25 (s, 9H); 2.37 (s, 3H); 2.89 (s, HO); 7.05 (m, 3H, H-3″,4″,5″); 7.15 (dd, J = 8.1, 1.5 Hz, H-5′); 7.25 (dd, J = 8.1, 1.5 Hz, H-2′,6′); 7.37 (t, J = 7.35 Hz, H-3,5); 7.46 (tt, J = 7.35, 2.2 Hz, H-4); 7.58 (m, 3H, H-3′,2,6); 8.12 (d, J = 8.1 Hz, H-6′); 9.65 (s, HN). (Found: C 80.57, H 7.46, N 3.58. Calc for $C_{25}H_{27}NO_2$: C 80.39, H 7.29, N 3.75%.)

Reaction of N-(2′-*iodo*-2-*biphenylyl*)-N,4-*dimethylbenzamide* (**65a**) *with t-butyllithium.* N-(2′-Iodo-2-biphenylyl)-4-methylbenzamide was prepared from 2′-iodo-2-biphenylamine[46] and *p*-toluoyl chloride in toluene, m.p. 115° from EtOH. IR: 3436 (HN); 1678, 1670 cm^{-1} (CO). ^1H NMR ($CDCl_3$): 2.36 (s, 3H); 7.0–7.7 (m, 11H); 8.09 (d, J = 6 Hz, H-3″); 8.57 (d, J = 8 Hz, H-3′). (Found: C 57.91, H 3.85, I 30.56, N 3.10. Calc for $C_{20}H_{16}INO$: C 58.13, H 3.90, I 30.71, N 3.39%). Methylation to **65a** was brought about by a phase transfer procedure using dimethyl sulfate,[47] yield: 45%, m.p. 92–93° from EtOH. IR: 1643 cm^{-1} (CO). ^1H NMR ($CDCl_3$): 2.25 (s, 3H); 3.13 (br.s, 3H); 6.9–7.3 (m, 11H); 7.85 (d, J = 7.8 Hz, H-3″). (Found: C 59.10, H 4.41, I 29.88, N 3.55. Calc for $C_{21}H_{18}INO$: C 59.03, H 4.25, I 29.70, N 3.28%.)

When 2.186 g (5 mmol) **65a** in 50 ml THF were treated with 1 equiv of t-BuLi at − 100° a yellowish soln was formed which became blue fluorescent on warming slowly to room temp. After hydrolysis the THF was removed i.vac. and the same volume of diethyl ether was added. After extraction of the separated etheral layer, first with $NaHCO_3$ aq which afforded only a small amount of unidentified oily material on acidifying, and then with 15% HCl the etheral solution was brought to dryness and the solid identified as unreacted starting material **65a** (1.41 g, 64%). The above HCl-extract was neutralized whereafter a red brown viscous oil was obtained (0.554 g) which solidified on addition of little ether. The now colorless powder could be crystallized from CH_2Cl_2/CCl_4 (m.p. 209–210°, dec) or conc HCl (m.p. 200–201°, dec) whereby 0.198 g yellowish needles were formed. According to spectroscopical and analytical data the so obtained material contained still sizable amounts of water and HCl. Only on heating these needles over KOH i.vac. to 125° for 3 days pure **70** was obtained. Final yield: 0.125 g (8%), m.p. 205–206° (dec). ^1H NMR ($CDCl_3$, 300 MHz): 2.57 (s, 3H); 4.77 (s, 3H); 7.56 (d, J = 8.1 Hz, 2H, H-3′,5′); 7.64 (d, J = 8.1 Hz, 2H, H-2′,4′); 7.76 (overlapping d, H-7); 7.80 (overlapping br.t, J = 8.1 Hz, 1H, H-8); 8.00 (br.t, J = 7.35 Hz, 1H); 8.11 (br.t, J = 7.35 Hz, 1H); 8.24 (qd, J = 8.1, 6.3 Hz, 2.2 Hz, 1H); 8.87, 8.93, 8.96 (each d, J ≈ 8.0 Hz, H-1/4/10). MS: m/z = 284 (0.1%, M–Cl); 269 (77%, M–Cl–CH_3); 268 (100%, M–Cl–CH_3–H); 254 (70%, M–Cl–2CH_3); $m/2z$ = 134 (44%); 127 (23%). (Found: C 78.53, H 5.87, Cl 11.37, N 4.27. Calc for $C_{21}H_{18}ClN$: C 78.86, H 5.67, Cl 11.09, N 4.38%).

When similar runs were, after addition of t-BuLi kept for several hours at − 100 to − 78° the yields of **70** could be improved to 11–13% besides 46–64% unchanged starting material.

Independent synthesis of **70**. **72** was prepared from **71**[48] and phosphoryl chloride in 28% yield,[28] m.p. 104° from EtOH. ^1H NMR ($CDCl_3$): 2.46 (s, 3H); 7.35 (d, J = 8.1 Hz, 2H, H-3′,5′); 7.5–7.9 (m, 6H); 8.09–8.33 (m, 2H); 8.53–8.73 (m, 2H, H-1,10). (Found: C 89.14, H 5.80, N 5.11. Calc for $C_{20}H_{15}N$: C 89.19, H 5.61, N 5.20%.)

With dimethylsulfate **72** gives 73% of its methomethylsulfate (**73**) as colorless crystals, m.p. 188–190° (lit. 191–192°).[29] IR: 1268, 1220, 1161 cm^{-1} (SO_4). ^1H NMR ($CDCl_3$): 2.57 (s, 3H); 3.43 (s, 3H); 4.57 (s, 3H); 7.61 (s, 4H, H-2′ to 6′); 7.7–7.8 (m, 2H); 7.90–8.35 (m, 3H); 8.67 (m, 1H, H-4); 8.94 (m, 2H, H-1,10). (Found: C 66.85, H 5.56, N 3.44, S 7.96. Calc for $C_{22}H_{21}NO_4S$: C 66.82, H 5.35, N 3.54, S 8.10%.) When **73** was dissolved in conc HCl, the soln neutralized with $NaHCO_3$, extracted with CH_2Cl_2 and the solvent removed (after drying) a quantitative yield of **70** could be obtained. The product could be recrystallized as before from CH_2Cl_2/CCl_4 and was then in every respect identical with the material obtained in the reaction of **65a** with t-BuLi.

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