148. Diazo-Transfer Reaction with Diphenyl Phosphorazidate

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Diphenyl phosphorazidate (DPPA) was used as the azide source in a one-pot synthesis of 2,2-disubstituted 3-amino-2*H*-azirines **1** (*Scheme 1*). The reaction with lithium enolates of amides of type **2**, bearing two substituents at C(2), proceeded smoothly in THF at 0°; keteniminium azides **C** and azidoenamines **D** are likely intermediates. Under analogous reaction conditions, DPPA and amides of type **3** with only one substituent at C(2) gave 2-diazoamides **5** in fair-to-good yield (*Scheme 2*). The corresponding 2-diazo derivatives **6**–**8** were formed in low yield by treatment of the lithium enolates of *N*,*N*-dimethyl-2-phenylacetamide, methyl 2-phenylacetate, and benzyl phenyl ketone, respectively, with DPPA. Thermolysis of 2-diazo-*N*-methyl-*N*-phenylcarboxamides **5a** and **5b** yielded 3-substituted 1,3-dihydro-*N*-methyl-2*H*-indol-2-ones **9a** and **9b**, respectively (*Scheme 3*). The diazo compounds **5**–**8** reacted with 1,3-thiazole-5(4*H*)-thiones **10** and thiobenzophenone (**13**) to give 6-oxa-1,9-dithia-3-azaspiro[4.4]nona-2,7-dienes **11** (*Scheme 4*) and thiirane-2-carboxylic acid derivatives **14** (*Scheme 5*), respectively. In analogy to previously described reactions, a mechanism *via* 1,3-dipolar cycloaddition, leading to 2,5-dihydro-1,3,4-thiadiazoles, and elimination of N_2 to give the 'thiocarbonyl ylides' of type **H** or **K** is proposed. These dipolar intermediates with a conjugated C=O group then undergo either a 1,5-dipolar electrocyclization to give spiroheterocycles **11** or a 1,3-dipolar electrocyclization to thiiranes **14**.

1. Introduction. – Diphenyl phosphorazidate (DPPA), synthesized for the first time by *Yamada et al.* from diphenyl phosphorochloridate (DPPCl) and NaN_3 in acetone at room temperature [1], found wide applications in organic synthesis, especially in peptide chemistry as a coupling reagent based on the azide method (*e.g.* [2] [3]). It was also used as a reagent for the synthesis of thioesters from carboxylic acids [4] [5], in direct *C*-acylations [6] [7], in modified *Curtius*-type reactions [8] [9], as an azide source in *Mitsunobu* reactions [10], as a reagent in the electrophilic amination of aromatic or heteroaromatic organometallics [11] [12], and as an azide source in 1,3-dipolar cycloaddition reactions with enamines of various cyclic ketones [13] [14].

Recently, we described a novel synthesis of 3-amino-2*H*-azirines **1** based on the reaction between amide enolates and DPPCl followed by treatment of the chloroenamine intermediate with NaN_3 [15] [16]. A mechanism *via* the formation of the corresponding keteniminium salt was proposed for this reaction. Taking these results into account and with the aim of proving our proposed mechanism for the formation of **1**, the reaction of amide enolates with DPPA under conditions similar to those just described, was studied. We were expecting that the corresponding 3-amino-2*H*-azirines **1** would be formed in a two-step one-pot reaction, further simplifying the aminoazirine synthesis.

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2. Results. – 2.1. *Synthesis of 2,2-Disubstituted 3-Amino-2*H*-azirines* **1** *from Amide Enolates and DPPA.* In accordance with the above-mentioned prediction, on treatment of a solution of amide enolate **A** in dry THF at 0° with DPPA, N_2 evolution was observed, and a smooth reaction leading to **1** took place. Lithium diisopropylamide (LDA) was generally employed to generate enolate **A** from **2**[4]). The proposed mechanism of the reaction is shown in *Scheme 1*. Amide enolate **A** and DPPA react smoothly to give the expected azidoenamine **D** in an analogous manner to the DPPCl/NaN_3 procedure [16], most likely *via* intermediates **B** and **C**. At room temperature, **D** spontaneously loses N_2 to form **1** in good yield (*Table 1*), most probably *via* the formation of an unstable 4,5-dihydro-1,2,3-triazole [17]. All compounds were characterized spectroscopically and showed no differences to those obtained by other routes [16] [18].

2.2. *Diazo-Transfer Reactions with DPPA.* Surprisingly, different results were achieved when the enolates **E**, derived from 2-monosubstituted amides of type **3** and LDA in THF, were treated with DPPA. In these cases, not the expected 2-monosubsti-

Scheme 1

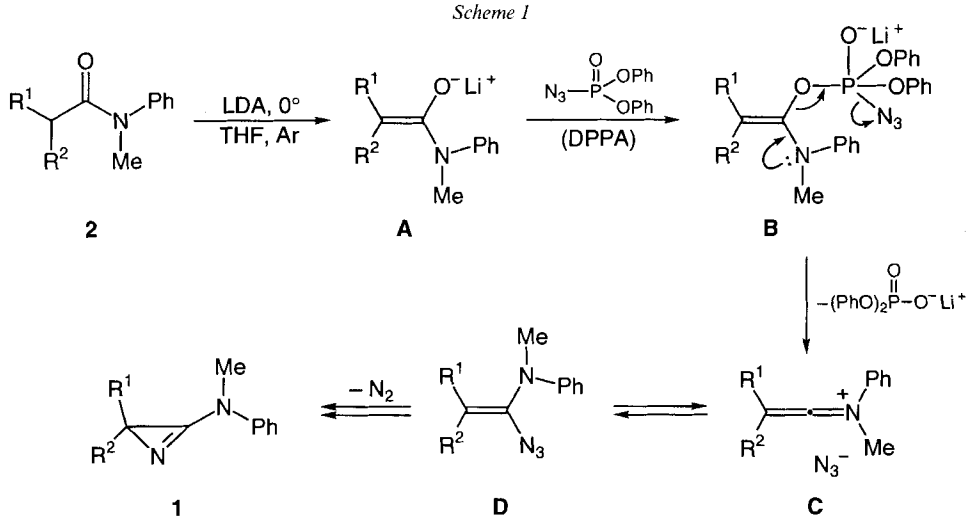


Table 1. *3-Amino-2*H*-azirines* **1** *Synthesized by the 'DPPA Method'*

	R^1	R^2	Yield [%]
1a	Me	Me	94
b	Me	$PhCH_2$	87
c	$PhCH_2$	Et	82
d	$-(CH_2)_4-$		86
e	$-(CH_2)_5-$		47

[4]) The use of lithium hexamethyldisilazanide (LiHMDS), NaHMDS, or KHMDS as a base had very little effect on the yields of the isolated products.

tuted 3-amino-2*H*-azirines **4**, but α-diazoamides of type **5** were formed in 46–76% yield (*Scheme 2*, *Table 2*). Under similar reaction conditions, *N*,*N*-dimethylphenylacetamide, methyl phenylacetate, and benzyl phenyl ketone yielded the corresponding α-diazoamide **6**, α-diazo ester **7**, and α-diazo ketone **8**, respectively, albeit in low yields[5]).

The α-diazocarbonyl compounds **5–8** were purified by chromatography (SiO_2, deactivated with NH_3), isolated as yellow-to-red oils, and characterized by means of their spectroscopic data (*e.g.* IR ($CHCl_3$): $\tilde{\nu}$(N=N) 2050–2100 cm^{-1}). In the case of **5a**, the product was partially transformed into **9a** during flash chromatography. Attempts to distill crude **5a** (110°/3·10^{-2} Torr) while avoiding chromatography resulted in a nearly

Scheme 2

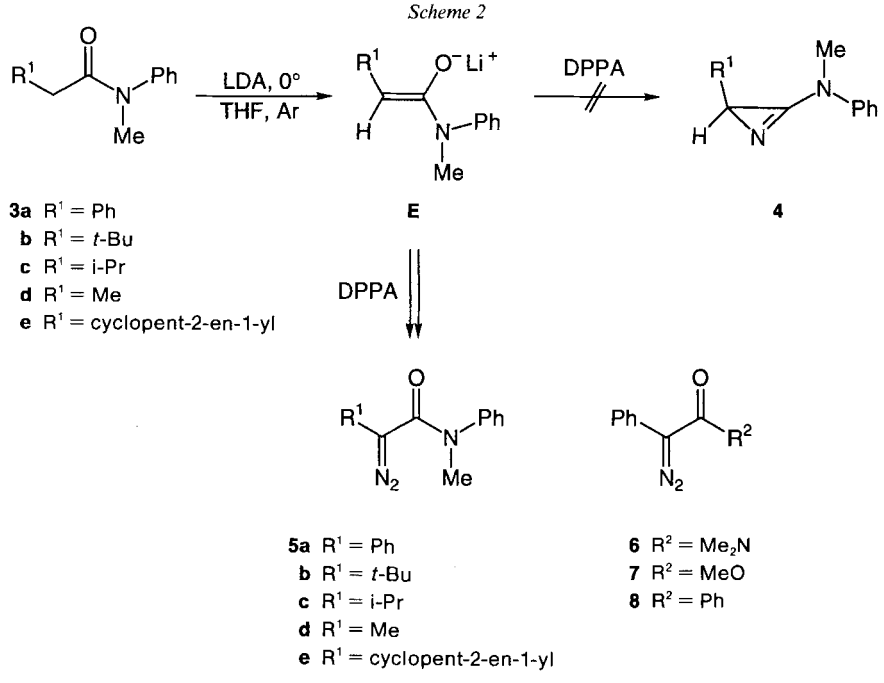
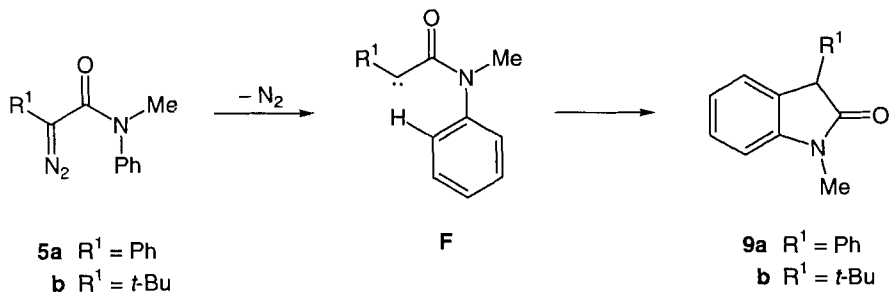


Table 2. *α-Diazocarbonyl Compounds* **5–8** *Synthesized by Diazo Transfer*

	5a (R^1 = Ph)	**5b** (R^1 = *t*-Bu)	**5c** (R^1 = i-Pr)	**5d** (R^1 = Me)	**5e** (R^1 = cyclopent-2-en-1-yl)	**6** (R^2 = Me_2N)	**7** (R^2 = MeO)	**8** (R^2 = Ph)
Yield [%]	65	76	58	61	46	6	20	27

[5]) All attempts to prepare 2-diazo-*N*,*N*-dimethylpropanamide, methyl 2-diazopropanoate, and 2-diazo-1-phenylpropan-1-one in an analogous manner failed.

Scheme 3



5a R^1 = Ph
b R^1 = *t*-Bu

9a R^1 = Ph
b R^1 = *t*-Bu

quantitative transformation into **9a**, as did treatment of the crude mixture with trifluoroacetic acid (CF_3COOH) at 0° (*Scheme 3*). The new compound **9a** was identified as 1,3-dihydro-*N*-methyl-3-phenyl-2*H*-indol-2-one by means of its spectroscopic data, and X-ray crystallography confirmed the structure (*Fig. 1*).

A likely reaction mechanism for the formation of **9a** is an intramolecular electrophilic aromatic substitution *via* carbene **F** [20–22], *i.e.*, a carbene insertion into an *ortho*-CH bond of the *N*-phenyl group. Attempts were made to generalize this attractive 1,3-dihydro-2*H*-indol-2-one (indolin-2-one, oxoindole) synthesis, which leads to **9a** in high yields by simply heating the precursor or treating it with CF_3COOH. Reactions using several other diazo compounds of type **5** (R^1 = Me, Et, i-Pr, *t*-Bu) failed under various conditions (rhodium(II) acetate or trifluoroacetate, Cu^I catalyst [20] [21]), in addition to those mentioned above. Untractable mixtures were usually obtained. Only in the case of **5b**

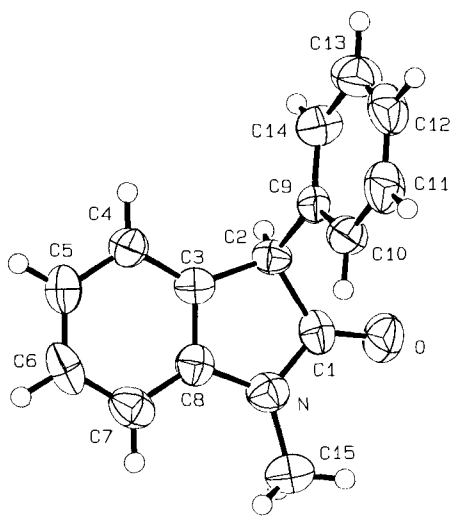


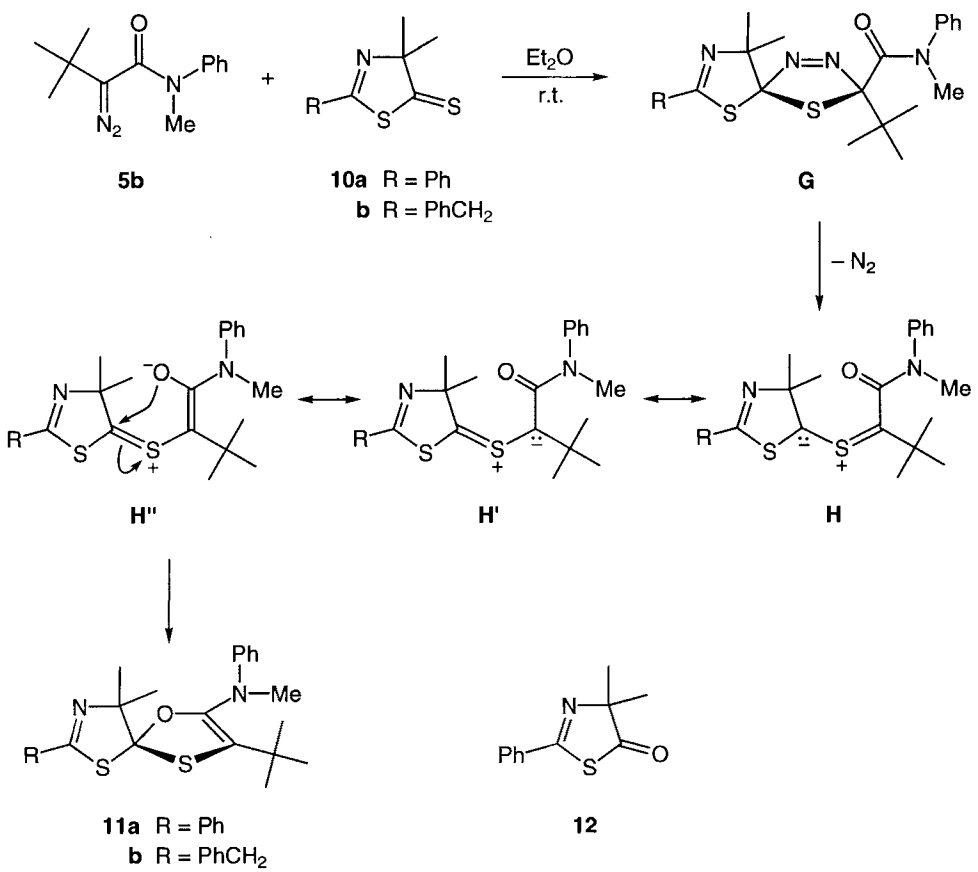
Fig. 1. *ORTEP Plot* [19] *with 50% probability ellipsoids of the crystal structure of* **9a**

(R^1 = *t*-Bu), the corresponding dihydroindol-2-one **9b** was formed on heating in toluene in the presence of $CuSO_4$.

2.3. *Reaction of α-Diazocarbonyl Compounds with 4,4-Dimethyl-1,3-thiazole-5(4H)-thiones* **10** *and Thiobenzophenone* (**13**). Recently, we reported on 1,3-dipolar cycloadditions of diazo compounds with the C=S bond of 4,4-disubstituted 1,3-thiazole-5(4*H*)-thiones (**10**) [23–27]. Depending on the nature of the diazo compound, either the primary spirocyclic adduct [23] [25], a spirocyclic thiirane, formed by N_2 elimination from the cycloadduct [23–26], or a 4,5-dihydro-5-methylidene-1,3-thiazole, the product of a 'two-fold extrusion reaction' [28] of the cycloadduct [23–27], were isolated as major products. Therefore, we also studied the reactivity of the α-diazocarbonyl compounds **5–8** towards **10** and thiobenzophenone (**13**).

Reaction between **5b** and **10a** in Et_2O at room temperature for 4 days yielded, after chromatography, the spiroheterocycle **11a** (*Scheme 4*) as a yellowish oil, which was crystallized from Et_2O/hexane. The structure of **11a** was deduced from the spectral data

Scheme 4



and corroborated by an X-ray crystal-structure determination (*Fig. 2*). The analogous product **11b** was obtained from the reaction between **5b** and **10b**. Surprisingly, **5a** and **10a** in Et_2O at room temperature yielded a complex reaction mixture from which no **11** could be isolated. Under more drastic conditions[6]), the major product – albeit in low yield – was 4,4-dimethyl-2-phenyl-1,3-thiazol-5(4*H*)-one (**12**).

A likely reaction mechanism for the formation of **11** is shown in *Scheme 4*: the 1,3-dipolar cycloaddition of **5b** with the C=S group of **10** leads to the unstable spirothiadiazole **G**, which looses N_2 spontaneously to give the resonance-stabilized 'thiocarbonyl ylid' **H**. A 1,5-dipolar electrocyclization [29] then yields **11**.

It is well known that thioketones are very reactive dipolarophiles ('superdipolarophiles') [30]; *e.g.* the reaction between thiobenzophenone (**13**) and diazo compounds

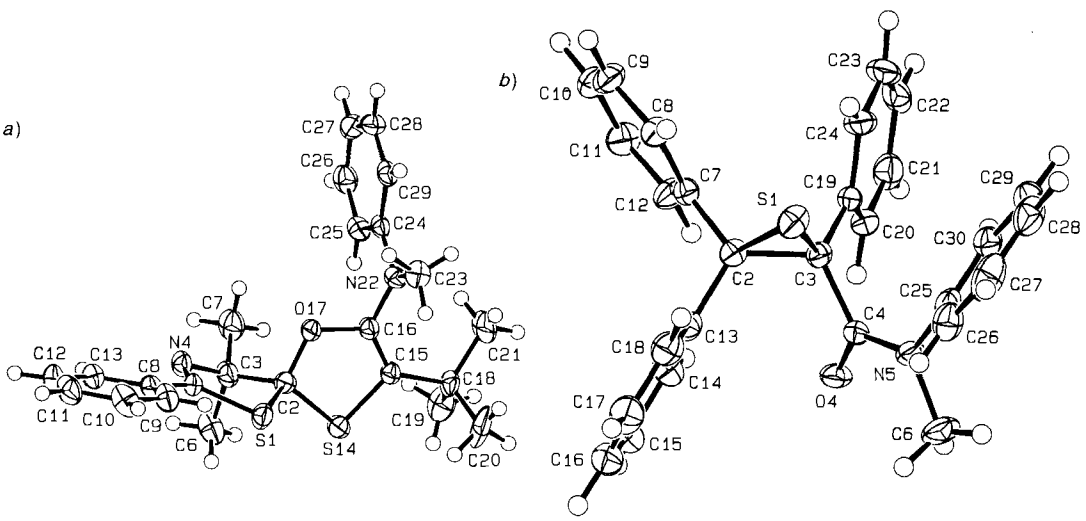


Fig. 2. *ORTEP Plots* [19] *with 50% probability ellipsoids of the crystal structure of* a) **11a** *and* b) **14a**.Only one orientation of the disordered *t*-Bu group in **11a** is shown.

Table 3. *Thiiranes* **14** *from the Reaction of α-Diazocarbonyl Compounds and Thiobenzophenone* (**13**)

α-Diazocarbonyl compound	Thiirane **14**	R^1	R^2	Yield [%]
5a	**a**	Ph	Ph(Me)N	41
5b	**b**	*t*-Bu	Ph(Me)N	30
5d	**c**	Me	Ph(Me)N	48
7	**d**[a])	Ph	OH[a])	77
8	**e**	Ph	Ph	5

[a]) The corresponding carboxylic acid was isolated instead of the ester.

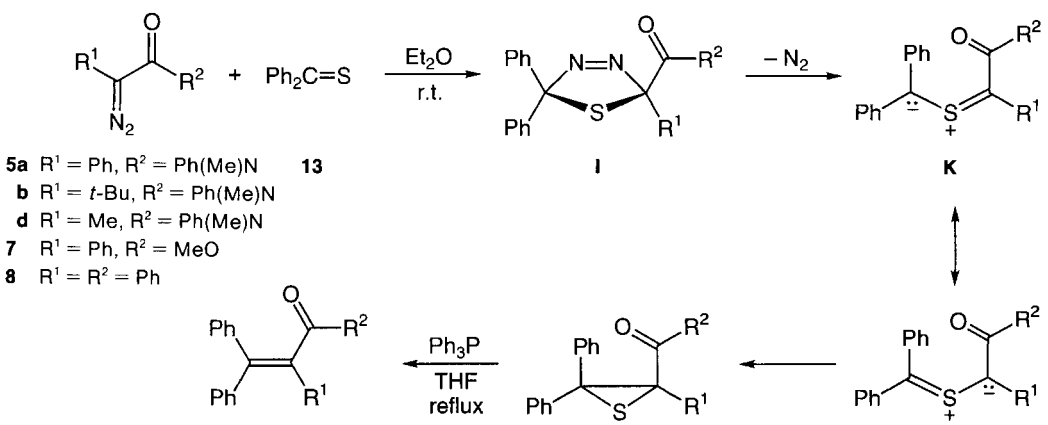
[6]) The reaction of **5a** was performed without solvent at room temperature for 4 days, in THF at 55° for 6 days, and in toluene at 90° for 2 days. The i-Pr derivative **5c** and **10a** in Et_2O at room temperature yielded also **12** as the major product.

was studied many years ago [31] [32]. For that reason, solutions of **13** and α-diazocarbonyl compounds **5**, **7**, or **8** in Et_2O were stirred under Ar at room temperature for 3–4 days. After chromatographic workup, thiiranes **14** were isolated in fair yields (*Scheme 5*, *Table 3*). The structure of **14** was elucidated from the spectral data and an X-ray crystal-structure determination of **14a** (*Fig. 2*). As a chemical proof of the thiirane structure, desulfurization of **14a** and **14b** with Ph_3P in refluxing THF gave the α,β-unsaturated carboxamides **15a** and **15b**, respectively (*Scheme 5*).

The reaction mechanism of formation of thiiranes from 2,5-dihydro-1,3,4-thiadiazoles is well known (*cf.* [23–27] and ref. cit. therein). Therefore, we believe that the cycloadduct **I** of **13** and **5**, **7**, and **8**, respectively, eliminates N_2 to give the resonance-stabilized 'thiocarbonyl ylide' **K**, which undergoes a 1,3-dipolar electrocyclization to **14**.

3. Discussion. – Whereas DPPA behaves as the expected azido-transfer reagent in the reaction with enolates **A** of 2,2-disubstituted amides (*Scheme 1*), it acts as a diazo-transfer reagent with enolates **E** of 2-monosubstituted amides, esters, and ketones, leading to α-diazocarbonyl compounds (*Scheme 2*). This type of diazo compound has been known since 1888, when *Curtius* published the synthesis of ethyl diazoacetate [33]. Since then, several syntheses of α-diazocarbonyl compounds have been described (*cf.* [34]). Among other methods, diazo-transfer reactions [35] attracted attention; suitable reagents for this purpose are sulfonyl azides [36] [37] and azidinium salts [38] [39]. Little is known about the use of phosphoryl azides as diazo-transfer reagents: in a very slow reaction with alkoxyethenes (alkyl ethenyl ethers), diazomethane was produced in low yield [40]. It is likely that the capability of diazo-transfer reagents is dependent on the electrophilicity of its diazo group. Reagents such as *Balli*'s reagent [38], in which the 'diazo function' is part

Scheme 5



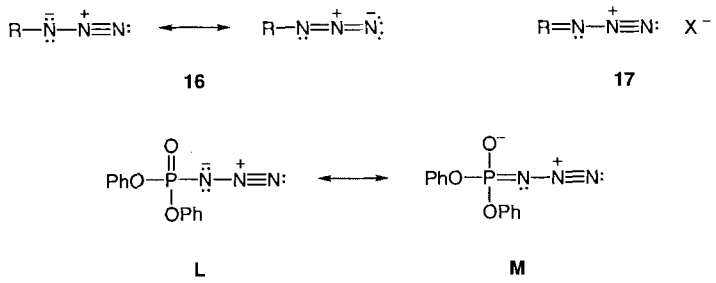
5a R^1 = Ph, R^2 = Ph(Me)N **13**
b R^1 = *t*-Bu, R^2 = Ph(Me)N
d R^1 = Me, R^2 = Ph(Me)N
7 R^1 = Ph, R^2 = MeO
8 R^1 = R^2 = Ph

I **K** **K'**

15a R^1 = Ph, R^2 = Ph(Me)N
b R^1 = *t*-Bu, R^2 = Ph(Me)N

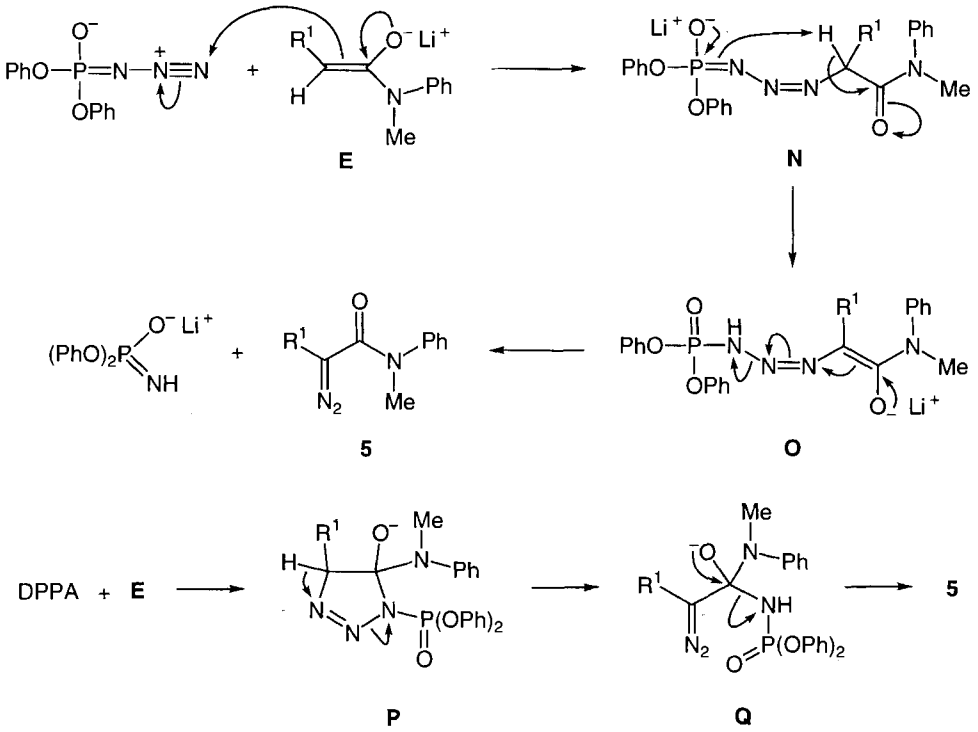
14a R^1 = Ph, R^2 = Ph(Me)N
b R^1 = *t*-Bu, R^2 = Ph(Me)N
c R^1 = Me, R^2 = Ph(Me)N
d R^1 = Ph, R^2 = OH
e R^1 = R^2 = Ph

of a *N*-diazonioimine (*cf.* **17**), are more electrophilic than those in which the 'diazo function' is part of an azide (*cf.* **16**). The potential of DPPA[7]) as a diazo-transfer reagent can be explained by considering the influence of resonance structure **M**.



Thus, the overall diazo-transfer process with enolates **E** may proceed as shown in *Scheme 6*: attack of **E** onto the terminal N-atom of DPPA, followed by proton transfer in intermediate **N** leads to intermediate **O**, which, after elimination of [bis(phenyloxy)-phosphoryl]aminide, yields the diazo compound **5**. As discussed in [36], a mechanism *via* 1,3-dipolar cycloaddition of DPPA and **E** is also possible (*Scheme 6*). Ring opening of

Scheme 6



[7]) The same arguments are valid for sulfonyl azides (RSO_2N_3).

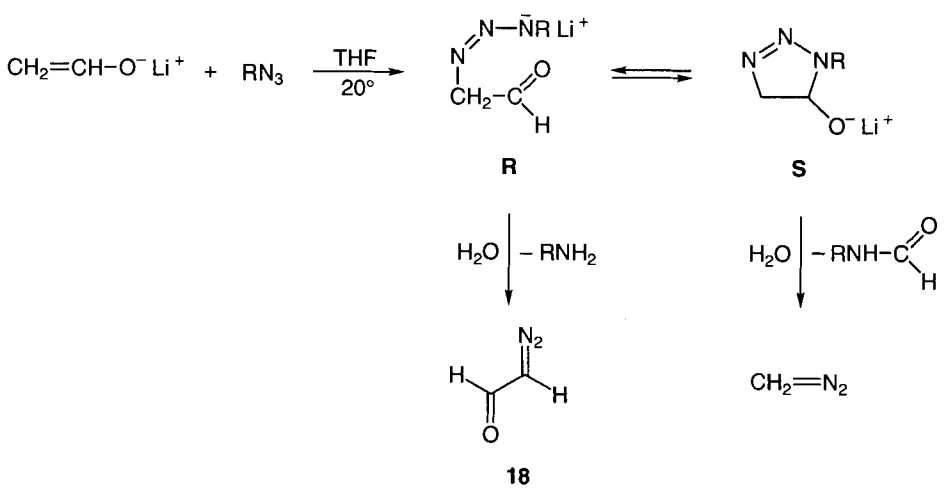
the cycloadduct **P** leads to **Q** which forms **5** by elimination of [bis(phenyloxy)phosphoryl]aminide.

A similar reaction was observed between the lithium enolate of acetaldehyde, generated *in situ* from THF and BuLi at 20°, and organic azides [41] (*Scheme 7*). In addition to diazomethane (*ca.* 20–70%) and the corresponding formamides (*ca.* 20–90%), formed *via* decomposition of adduct **S**, primary amines were detected in yields of up to 24%. It was proposed that these amines result from a competing decomposition of intermediate **R**[8]).

New syntheses of 1,3-dihydro-2*H*-indol-2-ones are of current interest [20–22] [42] because of their occurrence in alkaloids [43] and other pharmacologically active compounds [44]. Therefore, the formation of **9** in a convenient two-step synthesis starting with easily obtainable carboxamides (*Scheme 3*) is an attractive method. Unfortunately, the scope of this reaction seems to be rather limited, and the reaction conditions need further optimization.

The results of the reactions of α-diazocarbonyl derivatives with thiocarbonyl compounds **10** and **13** fit very well into the scope of our investigations of the 1,3-cycloaddition of diazo compounds and C=S groups (for reviews on 1,3-dipolar cycloadditions, see [45]). It was previously shown that 1,3-thiazole-5(4*H*)-thiones **10** are powerful dipolarophiles, similar to thioketones, towards nitrilium betaines [46–48], organic azides [49] [50], 'thiocarbonyl ylides' [51], azomethin ylides [52], and diazoalkanes (alkylidene diazenes) [23–27]. Whereas the spirocyclic adducts are stable enough in some cases to be isolated, the cycloadducts with diazo compounds usually decompose *via* elimination of N_2. The 'thiocarbonyl ylides' thereby formed react further *via* cycloaddition, dimerization, electrocyclic ring closure to thiiranes, and other rearrangements. The stabilized 'thiocarbonyl

Scheme 7



[8]) So far the postulated diazoacetaldehyde (**18**) has not been detected.

ylides' **H** and **K** (*Schemes 4* and *5*), which bear a conjugated C=O group, are able to undergo electrocyclizations to give either a 1,3-oxathiole (*via* 1,5-dipolar electrocyclization, *Scheme 4*) or a carbonyl-substituted thiirane (*via* 1,3-dipolar electrocyclization, *Scheme 5*). It is worth mentioning that only the first type of ring closure was observed with **10**, whereas with **13** only products of the latter type are formed. So far, it is not clear which factors are decisive for the type of ring closure[9]).

The formation of **12** in the reaction of **5a** and **10a** can be explained *via* hydrolysis of a 'thiocarbonyl ylide' of type **H** (R = Ph) or *via* decomposition of the spirocyclic product of type **11**. Precedents for both pathways are known: a 1,3-addition of H_2O with *in situ* generated 'thiocarbonyl ylides' leads to the corresponding carbonyl derivatives [27] [54]. Results of reactions of **10a** with various diazo compounds suggest that the susceptibility for hydrolysis is higher for stabilized 'thiocarbonyl ylides', because the other reactions were slowed down. For intermediates of type **H** (*Scheme 4*), this could mean that the less stabilized **H** undergoes a fast intramolecular cyclization to **11**, whereas the corresponding intermediate with a Ph instead of the *t*-Bu group is stabilized by conjugation. Therefore, the lifetime should be longer, and the probability of hydrolysis increases. On the other hand, the stability of the spiroheterocycles of type **11** is influenced decisively by the substituents. It is well known that *t*-Bu groups stabilize ring systems (*cf.* [25] [26] and ref. cit. therein). Thus, **11a, b** are stabilized, but the 8-Ph and 8-(i-Pr) derivatives of type **11**, formed in the reaction of **10a** with **5a** and **5c**, respectively, readily decompose to **12**. This is analogous to reactions described by *Battaglia* and *Dondoni* [55].

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Experimental Part

General. See [56]. Unless otherwise stated, IR spectra in $CHCl_3$, ^1H- (300 MHz) and ^{13}C-NMR (50, 4 MHz) in $CDCl_3$. EI-MS at 70 eV, and CI-MS with 2-methylpropane or NH_3 as carrier gas.

1. *2,2-Disubstituted 3-(*N*-Methyl-*N*-phenylamino)-2*H*-azirines* **1**: *General Procedure.* To a soln. of 5 mmol of an *N*-methyl-*N*-phenylcarboxamide **2** in 20 ml of dry THF, 1.2 equiv. (4 ml) of LDA (1.5M in cyclohexane) or LiHMDS, NaHMDS, or KHMDS (1M in THF) were added slowly at 0° under Ar. The mixture was stirred at 0° for 1 h. Then, 1.18 ml (1.1 equiv.) of diphenyl phosphorazidate (DPPA) were added. The mixture was stirred at 0°→r.t. for 3 days (N_2 evolution at the beginning), then, Et_2O/hexane 1:1 was added, the suspension filtered over a *Celite* pad, the filtrate evaporated, and the residue partitioned between Et_2O and H_2O. The org. layer was separated, dried ($MgSO_4$), and evaporated and the residue purified by flash chromatography (FC) or distillation ('Kugelrohr'). Azirines **1a–e** were obtained in the yields shown in *Table 1*, and their spectra were identical with those previously described (see [16]).

2. *Reaction of DPPA with Enolates of α-Monosubstituted Amides, Esters, and Ketones.* 2.1. *General Procedure.* To a soln. of 3 mmol of carboxamide **3** (prepared from the corresponding acyl chloride and *N*-methylaniline in AcOEt/Et_3N at *ca.* 0°) in 9 ml of dry THF, 1.1 equiv. of LDA (1.5M in cyclohexane) were added at 0° under Ar. After stirring the mixture for 1 h, 1.1 equiv. of DPPA were added slowly. The mixture was stirred for 65 h, raising the temperature from 0° to r.t., then Et_2O/hexane 1:1 was added and the suspension filtered over a *Celite* pad. The filtrate was evaporated and the residue purified by chromatography (SiO_2, desactivated with NH_3).

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[9]) The scope and limitation of the 1,3- and 1,5-dipolar electrocyclization of 'thiocarbonyl ylides' with π-substituents are under investigation [53].

2.2. *2-Diazo-*N*-methyl-*N*,2-diphenylacetamide* (**5a**). Chromatography with hexane/AcOEt 1:1: 500 mg (65%). Red oil. IR: 2070*s*, 1655*m*, 1630*s*, 1595*s*, 1495*s*, 1470*w*, 1450*w*, 1420*w*, 1365*s*, 1290*m*, 1270*m*, 1185*m*, 1160*w*, 1120*m*, 1080*m*, 1025*w*, 1010*w*, 955*m*, 900*w*, 830*w*, 695*s*, 660*m*. ^{1}H-NMR: 7.4–7.1 (*m*, 10 arom. H); 3.43 (*s*, MeN). ^{13}C-NMR: 165.2 (*s*, C=O); 143.7, 127.0 (2*s*, 2 arom. C); 129.6, 128.5, 126.6, 125.5, 125.4, 124.7 (6*d*, 10 arom. CH); 77.6 (*s*, C(2)); 38.4 (*q*, MeN). EI-MS: 223 (32, $[M-28]^+$), 107 (100), 77 (46). CI-MS: 252 (100, $[M+1]^+$).

2.3. *2-Diazo-*N*,3,3-trimethyl-*N*-phenylbutanamide* (**5b**). Chromatography with hexane/AcOEt 6:1: 526 mg (76%). Orange oil. IR: 2060*s*, 1620*s*, 1590*s*, 1490*m*, 1470*w*, 1455*m*, 1420*w*, 1350*s*, 1310*m*, 1280*m*, 1240*w*, 1180*w*, 1165*w*, 1150*w*, 1100*m*, 1070*w*, 1030*w*, 1000*w*, 975*m*, 885*w*, 860*w*, 830*w*, 700*s*, 660*m*. ^{1}H-NMR: 7.4–7.35 (*m*, 2 arom. H); 7.3–7.25 (*m*, 2 arom. H); 7.2–7.1 (*m*, 1 arom. H); 3.29 (*s*, MeN); 1.25 (*s*, Me_3C). ^{13}C-NMR: 156.1 (*s*, C=O); 144.5 (*s*, 1 arom. C); 129.8, 126.3, 125.4 (3*d*, 5 arom. CH); 80.7 (*s*, C(2)); 38.4 (*q*, MeN); 30.6 (*s*, Me_3C); 28.6 (*q*, Me_3C). EI-MS: 232 (80, $[M+1]^+$), 204 (51, $[(M+1)-28]^+$), 188 (21), 160 (15), 147 (100), 118 (16), 41 (26). CI-MS: 232 (100, $[M+1]^+$), 204 (49, $[(M+1)-28]^+$).

2.4. *2-Diazo-*N*,3-dimethyl-*N*-phenylbutanamide* (**5c**). Chromatography with hexane/Et_2O 1:1: 370 mg (58%). Orange oil. IR: 2050*s*, 1610*s* (br.), 1580*s*, 1490*s*, 1450*m*, 1415*m*, 1360*s*, 1290*m*, 1275*w*, 1235*w*, 1180*m*, 1155*m*, 1095*m*, 1020*m*, 1010*m*, 1005*m*, 960*s*, 885*w*, 820*w*, 690*s*, 655*w*. ^{1}H-NMR: 7.4–7.25 (*m*, 3 arom. H); 7.2–7.15 (*m*, 2 arom. H); 3.33 (*s*, MeN); 2.87 (*sept.*, $J=7$, Me_2CH); 1.04 (*d*, $J=7$, Me_2CH). ^{13}C-NMR: 166.3 (*s*, C=O); 144.2 (*s*, 1 arom. C); 129.7, 127.0, 126.2 (3*d*, 5 arom. CH); 95.2 (*s*, C(2)); 38.6 (*q*, MeN); 25.8 (*d*, Me_2CH); 20.0 (*q*, Me_2CH). CI-MS: 218 (100, $[M+1]^+$), 190 (22, $[(M+1)-28]^+$).

2.5. *2-Diazo-*N*-methyl-*N*-phenylpropanamide* (**5d**). Chromatography with hexane/Et_2O 71:6: 342 mg (61%). Yellow oil. IR: 2070*s*, 1640*m*, 1605*s*, 1590*s*, 1490*m*, 1470*w*, 1455*w*, 1420*w*, 1365*m*, 1310*w*, 1180*w*, 1150*w*, 1115*m*, 1070*w*, 1010*w*, 965*m*, 880*w*, 685*m*, 660*w*. ^{1}H-NMR: 7.4–7.35 (*m*, 2 arom. H); 7.3–7.25 (*m*, 1 arom. H); 7.2–7.15 (*m*, 2 arom. H); 3.32 (*s*, MeN); 1.79 (*s*, Me). ^{13}C-NMR: 167.2 (*s*, C=O); 144.0 (*s*, 1 arom. C); 129.6, 127.7, 126.3 (3*d*, 5 arom. CH); 91.6 (*s*, C(2)); 38.8 (*q*, MeN); 10.9 (*q*, Me). CI-MS: 190 (100, $[M+1]^+$), 162 (48, $[(M+1)-28]^+$).

2.6. *2-(Cyclopent-2-en-1-yl)-2-diazo-*N*-methyl-*N*-phenylacetamide* (**5e**). Chromatography with hexane/AcOEt 3:1: 330 mg (46%). Orange oil. IR: 2060*s*, 1590*s* (br.), 1485*s*, 1450*w*, 1360*m*, 1280*m*, 1180*s*, 1160*m*, 1105*s*, 1070*w*, 1020*w*, 1005*w*, 960*m*, 930*s*, 900*w*, 685*m*, 660*m*. ^{1}H-NMR: 7.4–7.2 (*m*, 5 arom. H); 5.83, 5.55 (2*d*, $J=6$, CH=CH); 3.33 (*s*, MeN); 2.27, 1.61 (2*m*, CH, 2 CH_2). EI-MS: 242 (2, $[M+1]^+$), 213 (13, $[M-28]^+$), 107 (100), 77 (12), 67 (16), 65 (8), 53 (7), 51 (14).

2.7. *2-Diazo-*N*,N-dimethyl-2-phenylacetamide* (**6**). In analogy to *2.1*, 490 mg (3.0 mmol) of *N,N*-dimethyl-2-phenylacetamide were treated with 3.3 mmol of LDA and 980 mg (3.3 mmol) of DPPA. Chromatography with hexane/AcOEt 6:1: 34 mg (6%). Orange oil. IR: 2020*m*, 1635*s* (br.), 1590*m*, 1485*s*, 1450*m*, 1395*w*, 1285*m*, 1260*m*, 1250*m*, 1185*s*, 1155*s*, 1100*s*, 1070*w*, 1020*m*, 1005*m*, 965*s*, 920*m*, 820*w*, 685*m*, 655*w*. ^{1}H-NMR: 7.4–7.3 (*m*, 2 arom. H); 7.3–7.15 (*m*, 3 arom. H); 2.97 (*s*, Me_2N). ^{13}C-NMR: 165.7 (*s*, C=O); 129.1 (*d*, 2 arom. CH); 127.6 (*s*, 1 arom. C); 125.6, 124.4 (2*d*, 3 arom. CH); 94.1 (*s*, C(2)); 37.7 (*q*, Me_2N). CI-MS: 190 (100, $[M+1]^+$), 162 (34, $[(M+1)-28]^+$).

2.8. *Methyl 2-Diazo-2-phenylacetate* (**7**). In analogy to *2.1*, 450 mg (3.0 mmol) of methyl 2-phenylacetate were treated with 3.3 mmol of LDA and 980 mg (3.3 mmol) of DPPA. Chromatography with hexane/Et_2O 3:1 yielded 110 mg (20%) of **7**. Orange oil. IR: 2090*s*, 1730*s* (br.), 1450*w*, 1435*m*, 1350*s*, 1245*s*, 1185*m*, 1155*s*, 1070*w*, 1050*w*, 1010*m*, 965*m*, 910*w*, 880*w*, 685*m*, 660*m*. ^{1}H-NMR: 7.65–7.45 (*m*, 2 arom. H); 7.45–7.3 (*m*, 2 arom. H); 7.2–7.15 (*m*, 1 arom. H); 3.87 (*s*, MeO). ^{13}C-NMR: 128.8, 125.7 (2*d*, 3 arom. CH); 125.4 (*s*, 1 arom. C); 123.9 (*d*, 2 arom. CH); 51.9 (*q*, MeO); C=O and C(2) could not be localized. EI-MS: 176 (68, $M^{+\cdot}$), 148 (11, $[M-28]^+$), 105 (100), 77 (28).

2.9. *2-Diazo-1,2-diphenylethanone* (**8**). In analogy to *2.1*, 590 mg (3.0 mmol) of 1,2-diphenylethanone, prepared by *Friedel-Crafts* acylation of benzene with benzoyl chloride, were treated with 3.3 mmol of LDA and 980 mg (3.3 mmol) of DPPA. Chromatography with hexane/Et_2O 6:1 yielded 190 mg (29%) of **8**. Orange oil. IR: 2100*m*, 1730*s*, 1590*s*, 1530*w*, 1485*m*, 1445*m*, 1380*w*, 1330*w*, 1290*s*, 1180*s*, 1160*s*, 1100*m*, 1055*m*, 1020*m*, 960*s*, 930*w*, 900*w*, 860*w*, 830*w*, 685*s*. ^{1}H-NMR: 7.65–7.55 (*m*, 1 arom. H); 7.35–7.25 (*m*, 2 arom. H); 7.25–7.05 (*m*, 6 arom. H); 6.95–6.9 (*m*, 1 arom. H).

3. *3-Substituted 1,3-Dihydro-*N*-methyl-2*H*-indol-2-ones*. 3.1. *1,3-Dihydro-*N*-methyl-3-phenyl-2*H*-indol-2-one* (**9a**). According to *2.1*, 500 mg (2.22 mmol) of *N*-methyl-*N*,2-diphenylacetamide were transformed into **5a**. The crude red oil was heated *i.v.* to 150–160°: 396 mg (80%) of **9a**. Yellowish solid. Crystallization from MeOH gave colorless crystals. M.p. 120°. IR: 1710*s*, 1650*w*, 1615*m*, 1495*m*, 1470*m*, 1450*w*, 1420*w*, 1375*m*, 1350*m*, 1305*w*, 1260*w*, 1250*w*, 1185*w*, 1175*w*, 1130*m*, 1090*m*, 1075*w*, 1020*w*, 960*w*, 930*w*, 915*w*, 885*w*, 700*m*, 660*w*. ^{1}H-NMR: 7.35–7.3 (*m*, 5 arom. H); 7.3–7.05 (*m*, 3 arom. H); 6.82 (*d*, $J=8$, 1 arom. H); 4.54 (*s*, 1 H); 3.18 (*s*, MeN). ^{13}C-NMR: 175.9 (*s*, C=O); 144.4, 136.5, 129.2 (3*s*, 3 arom. C); 128.7, 128.3, 127.4, 124.9, 122.6, 108.0 (6*d*, 9 arom. CH); 51.9 (*q*, MeN); 26.3 (*d*, CH). EI-MS: 223 (100, $M^{+\cdot}$), 194 (52), 118 (11), 107 (29), 106 (15), 96 (12), 94 (11), 91 (26), 89 (11), 77 (41), 76 (10), 65 (18), 63 (14), 57 (15), 51 (24), 41 (13).

In an analogous experiment, the reaction of *N*-methyl-*N*,2-diphenylacetamide, LDA, and DPPA was quenched with CF_3COOH after 30 min at 0°. Crude **9a** was obtained in nearly quantitative yield.

In a 3rd experiment, 520 mg (1.9 mmol) of **5a** were heated to 110°/3 · 10^{-2} Torr. Crystallization of the crude product from MeOH yielded 389 mg (89%) of **9a**. The cyclization of **5a** to **9a** also was partly achieved by chromatography of crude **5a** on SiO_2.

3.2. *3-(*tert*-Butyl)-1,3-dihydro-*N*-methyl-2*H*-indol-2-one* (**9b**)[10]. A mixture of 605 mg (2.7 mmol) **5b** and 46 mg of $CuSO_4$ in 5 ml of toluene was refluxed for 20 h. Evaporation and chromatography with hexane/Et_2O yielded 173 mg (35%) of **9b**. Yellowish oil. IR: 1690*m*, 1640*s* (br.), 1625*s*, 1590*s*, 1460*m*, 1430*w*, 1415*w*, 1375*s*, 1360*s*, 1315*w*, 1270*m*, 1180*w*, 1160*w*, 1120*m*, 1090*w*, 1070*w*, 1020*w*, 1010*w*, 965*s*, 905*w*, 890*w*, 680*m*, 660*w*. ^{1}H-NMR: 7.35–7.2 (*m*, 2 arom. H); 7.05–7.0 (*t*-artig, J = 6, 1 arom. H); 6.8–6.75 (*d*-artig, J = 6, 1 arom. H); 3.17 (*s*, MeN); 3.12 (*s*, 1 H); 1.10 (*s*, Me_3C). ^{13}C-NMR: 176.8 (*s*, C=O); 145.0, 127.6 (2*s*, 2 arom. C); 127.8, 126.6, 121.5, 107.5 (4*d*, 4 arom. CH); 55.4 (*q*, MeN); 34.9 (*s*, Me_3C); 30.1 (*d*, CH); 27.4 (*q*, Me_3C). CI-MS: 221 (9, $[M + NH_4]^+$), 204 (100, $[M + 1]^+$), 203 (9, $M^{+\cdot}$).

4. *Reaction of* **5a** *and* **5b** *with 4,4-Dimethyl-1,3-thiazole-5(4*H*)-thiones* **10**. 4.1. *8-(*tert*-Butyl)-4,4-dimethyl-7-(*N*-methyl-*N*-phenylamino)-2-phenyl-6-oxa-1,9-dithia-3-azaspiro[4.4]nona-2,7-diene* (**11a**). To a soln. of 250 mg (1.13 mmol) of **10a** in 1 ml of dry Et_2O (Ar), a soln. of 265 mg (1.15 mmol) of **5b** in 0.5 ml of Et_2O was added at r.t., and the mixture was stirred for 3–4 d. Then, the solvent was evaporated and the residue purified by FC (hexane/AcOEt 14:1): 334 mg (70%) of **11a**. Colorless crystals. M.p. 213°. IR: 1665*w*, 1600*s* (br.), 1575*w*, 1500*s*, 1475*w*, 1450*m*, 1395*w*, 1380*w*, 1360*m*, 1325*w*, 1300*w*, 1265*m*, 1175*w*, 1120*s*, 1025*s*, 955*m*, 870*m*, 690*m*, 670*m*, 620*w*. ^{1}H-NMR: 7.75–7.7 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 7.25–7.2 (*m*, 2 arom. H); 6.85–6.8 (*m*, 3 arom. H); 3.03 (*s*, MeN); 1.70, 1.46 (2*s*, 2 Me); 1.19 (*s*, Me_3C). ^{13}C-NMR: 163.5 (*s*, C=N); 147.2 (*s*, C(7)); 139.0, 133.7 (2*s*, 2 arom. C); 131.9 (*s*, C(8)); 131.1, 128.9, 128.3, 128.0, 118.8, 113.5 (6*d*, 10 arom. CH); 98.5 (*s*, C(5)); 82.0 (*s*, C(4)); 39.0 (br. *q*, MeN); 33.2 (*s*, Me_3C); 30.0 (*q*, Me_3C); 24.0, 21.3 (2*q*, 2 Me). EI-MS: 424 (15, $M^{+\cdot}$), 222 (12), 203 (11), 147 (65), 145 (100), 134 (35), 131 (12), 130 (15), 77 (15), 57 (37), 41 (76). CI-MS: 425 (100, $[M + 1]^+$), 220 (72). Anal. calc. for $C_{24}H_{28}N_2OS_2$ (424.60): C 68.37, H 5.98, N 6.64, S 15.21; found: C 68.66, H 6.22, N 7.00, S 15.34.

4.2. *2-Benzyl-8-(*tert*-butyl)-4,4-dimethyl-7-(*N*-methyl-*N*-phenylamino)-6-oxa-1,9-dithia-3-azaspiro[4.4]-nona-2,7-diene* (**11b**). In analogy to *4.1*, 250 mg (1.06 mmol) of **10b** and 265 mg (1.15 mmol) of **5b** were reacted at r.t. Purification by prep. TLC (hexane/AcOEt 4:1): 333 mg (72%) of **11b**. Yellowish oil. IR: 1660*m*, 1615*s*, 1600*s*, 1500*s*, 1475*m*, 1455*m*, 1380*w*, 1365*m*, 1350*m*, 1325*w*, 1300*w*, 1270*w*, 1240*w*, 1190*w*, 1160*w*, 1120*s*, 1035*s*, 970*m*, 870*m*, 700*s*, 660*w*, 615*m*. ^{1}H-NMR: 7.35–7.1 (*m*, 8 arom. H); 6.75–6.6 (*m*, 3 arom. H); 3.76 (*s*, PhCH_2); 2.87 (br. *s*, MeN); 1.35, 1.29 (2*s*, 2 Me); 1.04 (*s*, Me_3C). ^{13}C-NMR: 165.0 (*s*, C=N); 147.1 (*s*, C(7)); 138.8, 135.6 (2*s*, 2 arom. C); 134.2 (*s*, C(8)); 129.0, 128.9, 128.5, 126.9, 118.8, 113.6 (6*d*, 10 arom. CH); 80.6 (*s*, C(4)); 42.0 (*t*, PhCH_2); 37.6 (br. *q*, MeN); 33.3 (*s*, Me_3C); 30.1 (*q*, Me_3C); 24.0, 21.3 (2*q*, 2 Me); C(5) could not be detected. CI-MS: 439 (4, $[M + 1]^+$), 341 (17), 340 (100), 323 (49), 322 (30).

4.3. *Reaction of* **5a** *and* **10a**. A soln. of 400 mg (1.39 mmol) of **5a** and 250 mg (1.13 mmol) of **10a** in 2 ml of Et_2O was stirred for 4 d under Ar. No defined product could be isolated from the complex reaction mixture. Similarly, heating a soln. of 350 mg (1.39 mmol) of **5a** and 250 mg (1.13 mmol) of **10a** in THF (6 d, 55°), led to an untractable mixture.

In another experiment, a soln. of 294 mg (1.13 mmol) of **5a** and 250 mg (1.13 mmol) of **10a** in toluene was heated to 90° for 2 d. Chromatography of the complex mixture (hexane/AcOEt 25:1) gave 63 mg (27%) of *4,4-dimethyl-2-phenyl-1,3-thiazol-5(4*H*)-one* (**12**) [27]: ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.5–7.45 (*m*, 3 arom. H); 1.52 (*s*, 2 Me). ^{13}C-NMR: 211.6 (*s*, C=O); 161.0 (*s*, C=N); 133.6 (*s*, 1 arom. C); 131.9, 128.8, 128.1 (3*d*, 5 arom. CH); 84.2 (*s*, C(4)); 24.7 (*q*, 2 Me). CI-MS: 224 (41, $[M + NH_4]^+$), 206 (100, $[M + 1]^+$), 178 (13).

Reaction of 300 mg (1.14 mmol) of **5a** and 250 mg (1.13 mmol) of **10a** without solvent for 4 d at r.t. yielded, after chromatography (hexane/AcOEt 25:1), 61 mg (26%) of **12**.

4.4. *Reaction of* **5c** *and* **10a**. Stirring a mixture of 260 mg (1.2 mmol) of **5c** and 250 mg (1.13 mmol) of **10a** without solvent for 4 d at r.t. yielded, after chromatography, 74 mg (30%) of **12**.

5. *Reaction of* **5a, b, d**, **7**, *and* **8** *with Thiobenzophenone* (**13**). 5.1. *General Procedure*. A soln. of *ca.* 2.0 mmol of **5**, **7**, or **8** and *ca.* 1 equiv. of **13** in 2 ml of dry Et_2O at r.t. under Ar was stirred for 4 d. Then, the solvent was evaporated and the residue purified by chromatography.

5.2. *N-Methyl-N,2,3,3-tetraphenylthiirane-2-carboxamide* (**14a**). From 500 mg (2.0 mmol) of **5a** and 400 mg (2.0 mmol) of **13**. Chromatography with hexane/AcOEt 14:1: 341 mg (41%) of **14a**. Colorless crystals. M.p. 148°.

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[10]) No **9b** could be detected after distillation of **5b** at 115°/3 · 10^{-2} Torr.

IR: 1645*s* (br.), 1595*m*, 1495*s*, 1445*m*, 1420*w*, 1370*m* (br.), 1315*w*, 1295*w*, 1230*w*, 1140*w*, 1110*w*, 1075*w*, 1030*w*, 1020*w*, 1000*w*, 965*w*, 865*w*, 700*s*, 650*m*. ^{1}H-NMR: 7.55–7.35 (*m*, 4 arom. H); 7.3–7.0 (*m*, 14 arom. H); 6.95–6.75 (*m*, 2 arom. H); 3.13 (*s*, MeN). ^{13}C-NMR: 176.9 (*s*, C=O); 144.8, 139.4 (2*s*, 4 arom. C); 130.9, 129.0, 128.7, 127.6, 127.3, 126.9, 126.4 (7*d*, 20 arom. CH); 38.5 (*q*, MeN); C(2), C(3) of the thiirane could not be localized. CI-MS: 424 (8), 423 (26), 422 (100, $[M + 1]^+$), 391 (6), 390 (24, $[(M + 1) - S]^+$).

5.3. *2-(*tert*-Butyl)-*N*-methyl-*N*,3,3-triphenylthiirane-2-carboxamide* (**14b**). From 523 mg (2.0 mmol) of **5b** and 297 mg (1.5 mmol) of **13**. Chromatography with hexane/AcOEt 40:1: 241 mg (30%) of **14b**. Colorless oil. IR: 1630*s* (br.), 1590*s*, 1495*s*, 1470*w*, 1445*m*, 1395*w*, 1365*s*, 1315*w*, 1290*w*, 1275*w*, 1240*w*, 1175*w*, 1135*w*, 1110*w*, 1080*w*, 1060*w*, 1025*w*, 965*w*, 875*w*, 830*w*, 705*m*, 695*s*, 655*w*. ^{1}H-NMR: 7.85–7.7 (*m*, 2 arom. H); 7.65–7.55 (*m*, 2 arom. H); 7.3–7.1 (*m*, 9 arom. H); 6.75–6.65, 6.35–6.25 (2*m*, 2 arom. H); 3.46, 2.77 (2*s*, MeN); 1.08 (*s*, Me_3C). ^{13}C-NMR[11]): 168.4 (*s*, C=O); 144.5, 142.9, 141.0 (3*s*, 3 arom. C); 130.8–126.2 (15 arom. CH); 67.2, 64.2 (2*s*, C(2), C(3) of thiirane); 42.2 (*q*, MeN); 38.7 (*s*, Me_3C); 30.4 (*q*, Me_3C). CI-MS: 419 (5, $[M + NH_4]^+$), 404 (8), 403 (30), 402 (100, $[M + 1]^+$).

5.4. *N,2-Dimethyl-N,3,3-triphenylthiirane-2-carboxamide* (**14c**). From 100 mg (0.5 mmol) of **5d** and 100 mg (0.5 mmol) of **13**. Chromatography with hexane/AcOEt 10:1: 88 mg (48%) of **14c**. Yellowish, viscous oil. IR: 1635*s* (br.), 1595*s*, 1495*s*, 1445*m*, 1420*w*, 1380*s*, 1300*w*, 1280*w*, 1245*w*, 1190*w*, 1160*w*, 1110*w*, 1075*w*, 1030*w*, 1010*w*, 965*w*, 900*w*, 860*w*, 835*w*, 700*s*, 660*w*. ^{1}H-NMR: 7.4–7.1 (*m*, 13 arom. H); 7.0–6.4 (*m*, 2 arom. H); 3.13 (*s*, MeN); 2.99 (*s*, Me). ^{13}C-NMR: 142.4, 140.9, 140.3 (3*s*, 3 arom. C); 130.2–125.6 (15 arom. CH); 39.0 (*q*, MeN); 20.6 (*q*, Me); C=O, C(2), C(3) of the thiirane could not be localized. CI-MS: 360 (13, $[M + 1]^+$), 359 (15, M^+), 328 (14), 221 (46), 193 (27), 178 (45), 165 (65), 161 (100), 115 (92), 91 (48), 77 (43).

5.5. *2,3,3-Triphenylthiirane-2-carboxylic Acid* (**14d**). From 350 mg (2.0 mmol) of **7** and 396 mg (2.0 mmol) of **13**. Chromatography with hexane/AcOEt 10:1: 530 mg (70%) of **14d**. Colorless crystals. M.p. 58°. IR: 3380*m* (br.), 1705*m* (br.), 1590*m*, 1490*s*, 1445*w*, 1410*s*, 1280*m*, 1240*w*, 1185*s*, 1160*m*, 1130*w*, 1070*w*, 1025*w*, 1010*m*, 965*s*, 905*w*, 880*w*, 850*w*, 700*s*, 685*w*, 670*w*. ^{1}H-NMR: 7.35–7.05 (*m*, 13 arom. H); 6.9–6.75 (*m*, 2 arom. H). CI-MS: 301 (2, $[(M + 1) - S]^+$), 300 (20, $[M - S]^+$), 299 (100), 281 (8). Anal. calc. for $C_{21}H_{16}O_2S$ (332.42): C 76.13, H 4.83; found: C 76.17, H 4.66.

5.6. *Phenyl (2,3,3-Triphenylthiiran-2-yl) Ketone* (**14e**). From 440 mg (2.0 mmol) of **8** and 400 mg (2.0 mmol) of **13**. Chromatography with hexane/AcOEt 10:1: 39 mg (5%) of **14e**. Yellow oil. IR: 1700*s*, 1590*m*, 1490*s*, 1445*w*, 1410*s*, 1280*w*, 1185*s*, 1160*m*, 1125*w*, 1070*w*, 1025*w*, 1010*m*, 965*s* (br.), 905*w*, 880*w*, 700*m*, 690*w*, 670*w*. ^{1}H-NMR: 7.85–7.7 (*m*, 7 arom. H); 7.6–7.3 (*m*, 13 arom. H). ^{13}C-NMR: 196.6 (*s*, C=O); 137.5, 134.4 (2*s*, 4 arom. C); 132.3, 131.3, 130.7, 130.0, 129.5, 129.4, 128.9, 128.6, 128.2 (9*d*, 20 arom. CH).

6. *Desulfurization of Thiiranes* **14**. 6.1. *N-Methyl-N,2,3,3-tetraphenylprop-2-enamide* (**15a**). A soln. of 65 mg (0.15 mmol) of **14a** and 59 mg (2.25 mmol) of Ph_3P in 7 ml of abs. THF was refluxed for 20 h. Then, the solvent was evaporated and the residue crystallized from Et_2O: 17 mg (30%) of **15a**. Colorless crystals. M.p. 130°. ^{1}H-NMR: 7.3–7.1 (*m*, 3 arom. H); 7.1–6.7 (*m*, 17 arom. H); 3.23 (*s*, MeN). EI-MS: 389 (1, M^+), 183 (100), 107 (25), 77 (27).

6.2. *2-(Diphenylmethylidene)-N,3,3-trimethyl-N-phenylbutanamide* (**15b**). In analogy to *6.1*, 41 mg (0.1 mmol) of **14b** and 40 mg (0.22 mmol) of Ph_3P in 5 ml of abs. THF yielded 15 mg (47%) of **15b**. Colorless crystals. M.p. 148°. ^{1}H-NMR: 7.75–7.65 (*m*, 5 arom. H); 7.5–7.4 (*m*, 8 arom. H); 7.3–7.1 (*m*, 2 arom. H); 3.23, 3.05 (2*s*, MeN); 2.21 (*s*, Me_3C). CI-MS: 371 (25), 370 (100, $[M + 1]^+$).

7. *Crystal-Structure Determination of* **9a**, **11a**, *and* **14a** (see *Table 4* and *Figs. 1* and *2*)[12]). The intensities were collected on a *Rigaku-AFC5R* diffractometer in the $\omega/2\theta$- (**9a**, **14a**) and ω-scan mode (**11a**) using graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) and a 12-kW rotating anode generator. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction was applied for **9a** using DIFABS [57]. Data collection and refinement parameters are listed in *Table 4*, views of the molecules are shown in *Figs. 1* and *2*. The structures were solved by direct methods using SHELXS86 [58], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. In **9a**, all of the H-atoms were fixed in geometrically calculated positions with a C–H distance of 0.95 Å and individually refined isotropic temperature factors. In **11a**, the *t*-Bu group is disordered; two orientations of the group were refined successfully (occupation ratio 0.55:0.45). The H-atoms of the disordered *t*-Bu group were placed in geometrically calculated positions with fixed temperature factors of 1.2 B_{eq} of the parent C-atom. All other H-atoms were located in a difference electron density map

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[11]) Most of the signals are doubled (two conformations).

[12]) Atomic coordinates, bond lengths, and bond angles were deposited with the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, England.

and were refined isotropically. In **14a**, all of the H-atoms were located in a difference electron density map and were refined isotropically. All refinements were carried out on F using full-matrix least-squares procedures [59]. Neutral atom scattering factors for non-H-atoms were taken from [60a] (for **9a**) and [61a] (for **11a** and **14a**) and the scattering factors for H-atoms from [62]. Anomalous dispersion effects were included in F_{calc} [63]; the values for $\Delta f'$ and $\Delta f''$ were those of [60b] (for **9a**) and [61b] (for **11a** and **14a**). All calculations were performed using the TEXSAN crystallographic software package [64].

Table 4. *Crystallographic Data for Compounds* **9a**, **11a**, *and* **14a**

	9a	**11a**	**14a**
Crystallized from	MeOH	hexane/Et_2O	hexane/Et_2O
Empirical formula	$C_{15}H_{13}NO$	$C_{24}H_{28}N_2OS_2$	$C_{28}H_{23}NOS$
Formula weight	223.27	424.62	421.56
Crystal color, habit	colorless, plate	colorless, plate	colorless, irregular prism
Crystal temp. [K]	294(1)	173(1)	173(1)
Crystal dimensions [mm]	0.13 × 0.43 × 0.45	0.11 × 0.27 × 0.32	0.33 × 0.33 × 0.35
Crystal system	monoclinic	monoclinic	monoclinic
Lattice parameters			
Reflections for cell determination	18	25	25
2θ range [°]	$20 < 2\theta < 36$	$26 < 2\theta < 37$	$34 < 2\theta < 40$
a [Å]	4.738(2)	7.975(5)	11.170(2)
b [Å]	13.644(7)	24.910(6)	12.402(2)
c [Å]	9.216(3)	11.293(7)	16.714(1)
β [°]	97.63(3)	96.69(6)	105.842(7)
V [Å^3]	590.5(4)	2228(2)	2227.4(5)
Space group	Pc	$P2_1/n$	$P2_1/n$
Z	2	4	4
D_x [g cm^{-3}]	1.256	1.266	1.257
Absorption coefficient μ (MoK_α) [mm^{-1}]	0.0735	0.256	0.165
Absorption correction min, max	0.475, 1.415	–	–
2θ (max) [°]	55	55	60
Total reflections measured	1588	5600	7093
Symmetry-independent reflections	1427	5112	6497
Reflections observed	901	2934	3311
Criterion	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Variables	165	365	372
Final R	0.0595	0.0435	0.0448
R_w[a])	0.0662	0.0384	0.0363
Goodness of fit s	2.143	1.479	1.574
p for $1/w = \sigma^2(F_o) + (pF_o)^2$	0.015	0.005	0.005
Final Δ_{max}/σ	0.0001	0.0004	0.0002
$\Delta\rho$ (max, min) [e Å^{-3}]	0.21, −0.31	0.23, −0.30	0.34, −0.30

[a]) Function minimized $\Sigma w(|F_o| - |F_c|)^2$.

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