Heteroatom Chemistry
Volume 17, Number 5, 2006

1,3-Dipolar Cycloadditions of Diphenyldiazomethane to Thioketones: Rate Measurements Disclose Thiones to be Superdipolarophiles

Rolf Huisgen and Elke Langhals

Department Chemie und Biochemie der Ludwig-Maximilians-Universität München, Butenandtstr. 5-13, D-81377 München, Germany

Received 2 January 2006; revised 6 February 2006

ABSTRACT: *1,3-Dipolar cycloadditions of diphenyldiazomethane to thioketones afford 2,5-dihydro-1,3,4-thiadiazoles* **8**, *which rapidly lose* N_2. *The liberated thiocarbonyl ylides* **10** *furnish thiiranes* **9** *by electrocyclic ring closure. The rate constants, measured by spectrophotometry (DMF, 40°C) for 16 cycloaliphatic and aromatic thioketones and one cyclic trithiocarbonate, stretch over five powers of 10 with fluorene-9-thione at the top and 2,2,5,5-tetramethylcyclopentanethione at the bottom. Electron-releasing substituents decrease the cycloaddition rate of thiobenzophenone; thus, the ambiphilic diphenyldiazomethane reacts as nucleophilic partner with the electrophilic thioketone. The influence of substituents and ring size on the reactivity of cycloalkanethiones, which are sterically hindered by two gem-dimethyl groups, will be discussed. Compared with electron-deficient C=C and C≡C bonds, thiones are superdipolarophiles.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:433–442, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20262

INTRODUCTION

The superior dipolarophilic activity of the CS double bond has been demonstrated by the measurement of cycloaddition rates with several 1,3-dipoles: *N*-methyl-*C*-phenylnitrone [1], thiobenzophenone *S*-methylide [2,3], and, in a preliminary communication, diphenyldiazomethane [4]. For the 1,3-cycloadditions of diphenyldiazomethane, kinetic data for an extended set of thiones and a characterization of the reaction products will be discussed here.

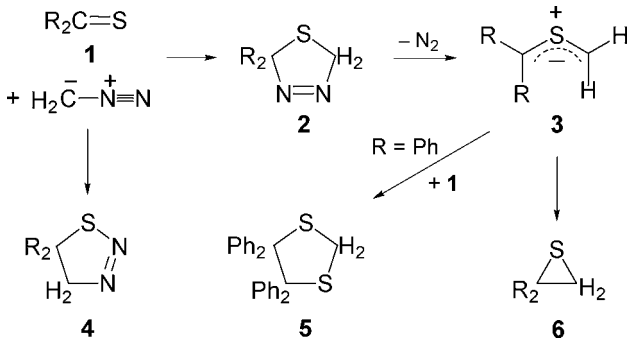
In the MO discussion, the major reason for thiones to appear as "superdipolarophiles" was found in the low HO–LU energy distance of the CS double bond [5,6]. Thioketones are also "superdienophiles" in the Diels–Alder reaction, e.g., fluorene-9-thione beats maleic anhydride in the additions to 1,3-dienes [7].

The reactions of diazomethane with aliphatic thioketones **1** furnish regioisomeric cycloadducts, 2,5-dihydro-1,3,4-thiadiazoles **2** and 4,5-dihydro-1,2,3-thiadiazoles **4** (Scheme 1). The ratio of **2**:**4** shifts toward **2**, when solvent polarity and temperature are low and R is a voluminous substituent [8–11]. The sterically hindered cycloaliphatic thioketones—our main model compounds—afford virtually only the 1,3,4-thiadiazole derivatives **2**. Nitrogen extrusion from **2**, $R_2C=$cycloalkylidene, takes place at 40–70°C and produces thiiranes **6** via thiocarbonyl ylides **3**. The latter are a class of

1,3-Dipolar Cycloadditions, 133. For part 132 see Giera, H; Huisgen, R.; Polborn, K. Eur. J Org Chem 2005, 3781–3790.

Correspondence to: Rolf Huisgen; e-mail: Rolf.Huisgen@cup.uni-muenchen.de

Dedicated to Lubor Fisera, Slovak University of Technology, Bratislava, on the occasion of his 60th birthday.



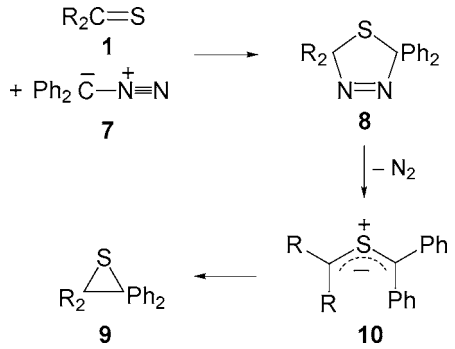
SCHEME 1

nucleophilic 1,3-dipoles that cannot be isolated, since rapid electrocyclization gives rise to thiiranes **6**. However, the elusive intermediates **3** are easily intercepted by electron-poor CC multiple bonds or C=O, C=N, and C=S bonds as dipolarophiles; a wealth of five-membered heterocycles is accessible [12–14].

With R = Ph in Scheme 1, the heteroallyl anion system of the 1,3-dipole **3** profits from phenyl conjugation, and the elimination of N_2 from **2** requires a lower activation energy: compound **2**, R = Ph, in THF extruded N_2 at −45°C with a half-life of 56 min [15,16].

Thiocarbonyl ylide **3**, R = Ph, is easily interceptible. The reaction of thiobenzophenone with diazomethane at room temperature affords 4,4,5,5-tetraphenyl-1,3-dithiolane **5** as a 2:1 product next to quantitatively ("Schönberg reaction") [17,18]. At 20°C the N_2 loss of **2**, R = Ph, and the cycloaddition with a second molecule of **1**, R = Ph, are much faster than the initial cycloaddition that gives rise to **2**, R = Ph [15,16].

In 1920, Staudinger and Siegwart combined thiobenzophenone **1** (R = Ph) with diphenyldiazomethane **7** and obtained 2,2,3,3-tetraphenylthiirane **9** (R = Ph, Scheme 2) [19].



SCHEME 2

Schönberg et al. broadly varied the reactants: diarylthioketones and diaryltrithiocarbonates were reacted with diaryldiazomethanes (59 pairs) and provided the tetrasubstituted thiiranes, as reviewed in 1957 [20]. The intermediacy of dihydrothiadiazoles **8** and thiocarbonyl ylides **10** was not recognized at that time. Beyond the analogy with the diazomethane reaction (Scheme 1), the reaction of thiobenzophenone with diphenyldiazomethane at −78°C (CH_2Cl_2) is quoted, which led to the precipitation of the colorless, nearly insoluble **8**, R = Ph. In a suitable solvent, e.g., methanol, N_2 evolution is fast even at −78°C, and **9**, R = Ph, is the product [21].

1,3-Dipolar cycloadditions are sensitive to steric effects. Tetrasubstituted thiocarbonyl ylides **10** are less inclined to undergo cycloadditions (for some exceptions cf. [22,23]). They are not planar, but assume a twisted conformation, which may well be the first phase of the conrotatory electrocyclization **10** → **9** (conrotation has been established by Kellogg et al. [24]). Thus, the rate-determining step, **1** + **7** → **8**, is followed by a fast elimination of N_2.

MEASUREMENT AND DISCUSSION OF RATE CONSTANTS

Diazomethane exceeds diphenyldiazomethane in the rate of cycloaddition to thioketones. Thiobenzophenone **1** (R = Ph) in THF at −78°C can be titrated with a diazomethane solution for the fading of the blue color. The second-order reaction of **1**, R = Ph, with diphenyldiazomethane **7** proceeds at 40°C with the rate constant $k_2 = 4.05$ L mol^{-1} s^{-1} ($CHCl_3$, Table 1), i.e., slower by orders of magnitude. Rate constants for the cycloadditions to some olefinic CC bonds were measured for both diazomethane (DM) and diphenyldiazomethane (DDM) under identical conditions (DMF, 40°C): $k_{2,\mathrm{DM}}/k_{2,\mathrm{DDM}} = 266$ for ethyl acrylate, 117 for 1-phenylbutadiene, and 17 for norbornene [25]. The log $k_{2,\mathrm{DM}}$ (DMF, 25°C) and log $k_{2,\mathrm{DDM}}$(DMF, 40°C) for reactions with 16 olefinic dipolarophiles showed a fairly linear relation, and diazomethane is the more selective species [26].

Originally, the high solubility of diazomethane in dimethylformamide (DMF) was responsible for the choice of this solvent. To keep the conditions comparable to the rate measurements of diphenyldiazomethane with CC double and triple bonds—and here with thiones—DMF at 40°C was chosen as standard conditions.

With T and D as concentrations of thione and diphenyldiazomethane, the integrated rate equation

of second order takes the form:

$$k_2 t = \frac{1}{D_0 - T_0} \ln\left[\frac{T_0}{D_0}\left(\frac{D_0 - T_0}{T} + 1\right)\right] \qquad (1)$$

The rates were measured by UV–Vis spectrophotometry. Both reactants contribute to the measured absorbance A according to their molar absorption coefficients, ε_T and ε_D, at the chosen wavelength. With $A = T\varepsilon_T + D\varepsilon_D$, Eq. (2) is obtained.

$$T = \frac{A - \varepsilon_D(D_0 - T_0)}{\varepsilon_T + \varepsilon_D} \qquad (2)$$

The ε_D of diphenyldiazomethane is larger than that of the cycloaliphatic thiones; therefore, λ_{max} of the former was used. For aromatic thioketones, $\varepsilon_T > \varepsilon_D$, a wavelength close to the λ_{max} of the thione was chosen. Rate constants k_2 were evaluated by linear regression. Table 1 provides average values of two to six independent kinetic runs and scheme 3 defines the seventeen thiones.

Difficulties occurred when 4,5-dioxo-1,3-dithiolane-2-thione **1r** or ethenetetracarbonitrile (TCNE) served as dipolarophiles. Since the reaction of **7** with TCNE in $CHCl_3$ or acetonitrile furnished 3,3-diphenylcyclopropane-1,1,2,2-tetracarbonitrile in high yield [27], the experiment in DMF as solvent provided rather tetraphenylethylene, benzophenone, and diphenylcarbinol. Kinetic measurements showed that the color of **7** disappeared in a first-order reaction, a decomposition of **7** catalyzed by TCNE in DMF. Electron transfer was reported for TCNE in DMF [28], and probably the DMF radical cation is the active reagent. Therefore, the cycloaddition rates of these highly electrophilic dipolarophiles were measured in $CHCl_3$ at 40°C. Thiobenzophenone **1l** was measured in both solvents: the reaction with **7** in DMF was 2.5 times faster than in $CHCl_3$ (Table 1).

Table 1 does not list the rate constants for the cycloadditions of **7** with electron-deficient ethylene and acetylene derivatives; the previous comparison [4] will not be repeated here. It may just be mentioned that thiofluorenone **1p** as the top thione surpasses k_2 of TCNE 113-fold, and **7** reacts with thiobenzophenone 134 times faster than with dimethyl acetylenedicarboxylate, a notoriously reactive CC bond dipolarophile.

The rate constants of Table 1 stretch over five powers of 10; fluorene-9-thione **1p** ranks at the top and 2,2,5,5-tetramethylcyclopentanethione **1f** and thiofenchone **1k** take the lowest positions. In Fig. 1 the thiones are ordered in groups I–V to simplify comparisons.

The superiority of aromatic thioketones in the cycloadditions with **7** is evident. In group I, k_2 of thiobenzophenone **1l** surpasses those of cycloaliphatic thioketones about 100 fold. Admittedly, tetramethylcyclobutanethione **1a** and adamantanethione **1j** are not fully comparable with

TABLE 1 Rate Constants and Products for the Reactions of Thiocarbonyl Compounds and Diphenyldiazomethane in DMF (*$CHCl_3$) at 40°C; Lit. on Thiiranes **9l**–**9s** in Ref. [20]

Thione	*λ (nm)*	*k_2*	*Thiirane*		
No.	*used*	*(L mol^{-1}s^{-1})*	*No.*	*m.p. (°C)*	*% Yield*[a]
1a	525	4.77×10^{-2}	**9a**	68	93
1b	525	0.139	**9b**	80	93
1c	525	4.66×10^{-2}	**9c**	116	(74)
1d	520	1.29	**9d**	115	82
1e	520	1.05	**9e**	116	(95)
1f	525	2.35×10^{-3}	**9f**	143	83
1g	525	4.83×10^{-2}	**9g**	215	92
1h	525	0.579	**8h**	120 (dec)[b]	
1j	520	0.101	**9j**	182–184	(82)
1k	520	2.98×10^{-3}	**9k**	155–157[c]	97
1l	628	10.2	**9l**		
		4.05*			
1m	628	0.368	**9m**		
1n	620	4.41×10^{-3}	**9n**		
1p	440	450*	**9p**		
1q	520	5.51×10^{-2}	**9q**		
1r	532	0.506	**9r**		
1s	520	66.8*	**9s**		

[a] ^{1}H NMR analysis; in parentheses isolated yield.
[b] 2,5-Dihydro-1,3,4-thiadiazole.
[c] Diastereomer 1.

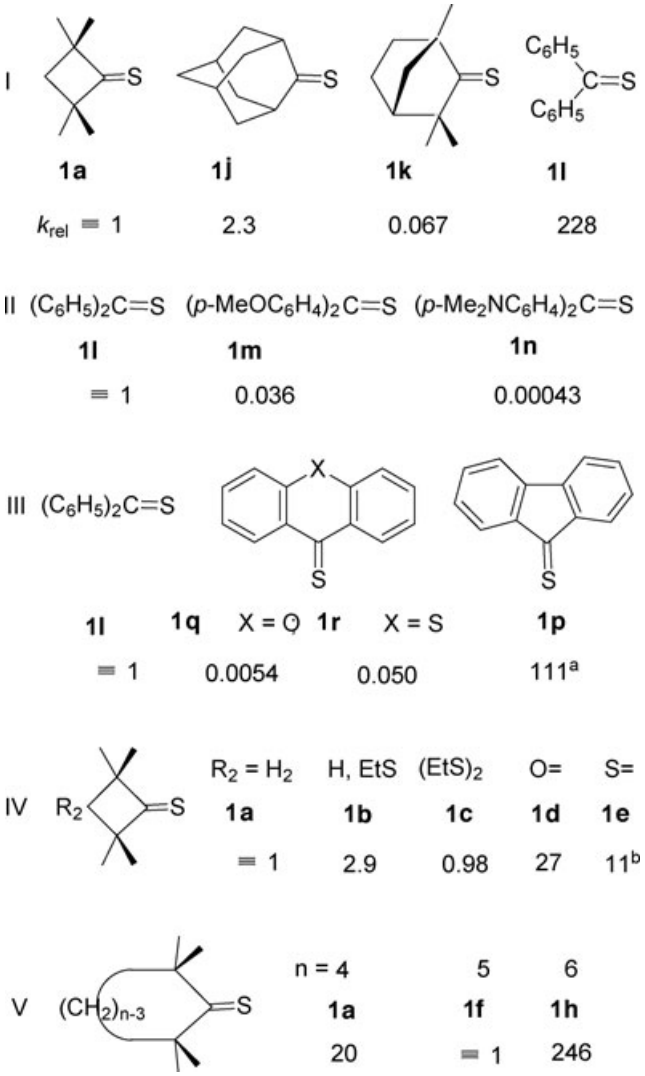


FIGURE 1 Cycloadditions of diphenyldiazomethane with thioketones in DMF at 40°C; relative rate constants.

1l in steric demand. The high ranking of aromatic thiones indicates that the additional aryl conjugation further lowers the energy of the transition structure (TS). It would be in harmony with the TS of a concerted cycloaddition in which the low HO–LU energy distance, i.e., the orbital compression in the conjugated system of **1l**, is important. The bathochromic effect of phenyl conjugation shows up in the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions [29] and is observed in the color of dilute solutions: pink for **1a** and **1j**, blue-violet for **1l**.

In group II, the strong retardation by electron-releasing substituents on the cycloaddition rate of thiobenzophenone is shown: bis(*p*-methoxy) and bis(*p*-dimethylamino) diminish by factors of 28 and 2300. A Hammett relation based on only three rate constants is not very significant, but the log k_2 fit straight lines when plotted versus $\sigma(\rho = 4.0)$ or $\sigma^+(\rho^+ = 2.0)$. No doubt, the thioketone is the electrophilic and diphenyldiazomethane the nucleophilic partner.

In xanthione **1q** (group III), the electron-releasing *o*,*o*′-oxygen function reduces the activity of thiobenzophenone **1l** 185-fold, even a greater effect than that generated by two *p*-methoxy groups in **1m**. Fluorene-9-thione **1p** is by a factor of 111 faster than **1l**. The participation of an aromatic fluorenyl-type carbanion in the TS of cycloaddition may lower the barrier height. Moreover, the bathochromic shift in the light absorption [29] demonstrates the changed π-system of **1p**, compared with **Il**. The planarity of **1p** assists the approach of the 1,3-dipole; in **1l**, the dihedral angle between the two phenyl planes amounts to 69° (X-ray [30]) and contributes to the bulk.

Inductive electron attraction across the four-membered ring may play a role in the rate modulation given by 3-substituted 2,2,4,4-tetramethylcyclobutanethiones (group IV in Fig. 1). The O= and S= function increase the electrophilicity of the dipolarophilic C-atom in **1d** and **1e** by factors of 27 and 11, respectively. Smaller is the influence of 3-SEt in **1b**; the inductive effect of two 3-SEt functions in **1c** appears to be compensated by steric hindrance.

The two *gem*-dimethyl groups in the cycloalkanethiones impede the access of the 1,3-dipole like a grate. The dependence on the ring size (group V) results from two effects. In the four-membered ring of **1a** the dimethyl groups are bent back from the reaction center, whereas in the five- and six-membered rings of **1f**–**1h** the bond angles reach "normality" in two steps. This is connected with an enhancement of steric hindrance at the dipolarophilic C=S bond. Superimposed is the change of conformational strain in the conversion of an sp^2-hybridized center to a tetrahedral C-atom, as exemplified by the reduction rates of cyclic ketones with sodium borohydride: $k_{rel} = 38{:}1{:}23$ for the four-, five-, and six-membered ring, respectively [31]. The I-strain concept of Brown et al. [32] served as interpretation for a bulk of rate and equilibrium data [33,34], but in the application to cycloalkyl solvolysis rates [35] some reserve is recommended [36].

Mayr et al. published rate constants for the reactions of *p*-substituted benzhydryl cations with diazoalkanes in the framework of their fruitful reactivity correlation, $\log k_2 = s(E + N)$ (review: [37]). The bis(*p*-dimethylamino)benzhydryl cation reacts with diazomethane 1.3×10^4 times faster than with diphenyldiazomethane **7**. The nucleophilicity parameter *N* of **7** has been determined [38], but the electrophilicity *E* of thiobenzophenone is unknown.

The knowledge of this parameter would help to answer the significant question about the nature of the cycloaddition we are dealing with here. The concert of bond-making and -breaking should reduce the activation free energy of the process calculated for the making of one bond in an initiating reaction step.

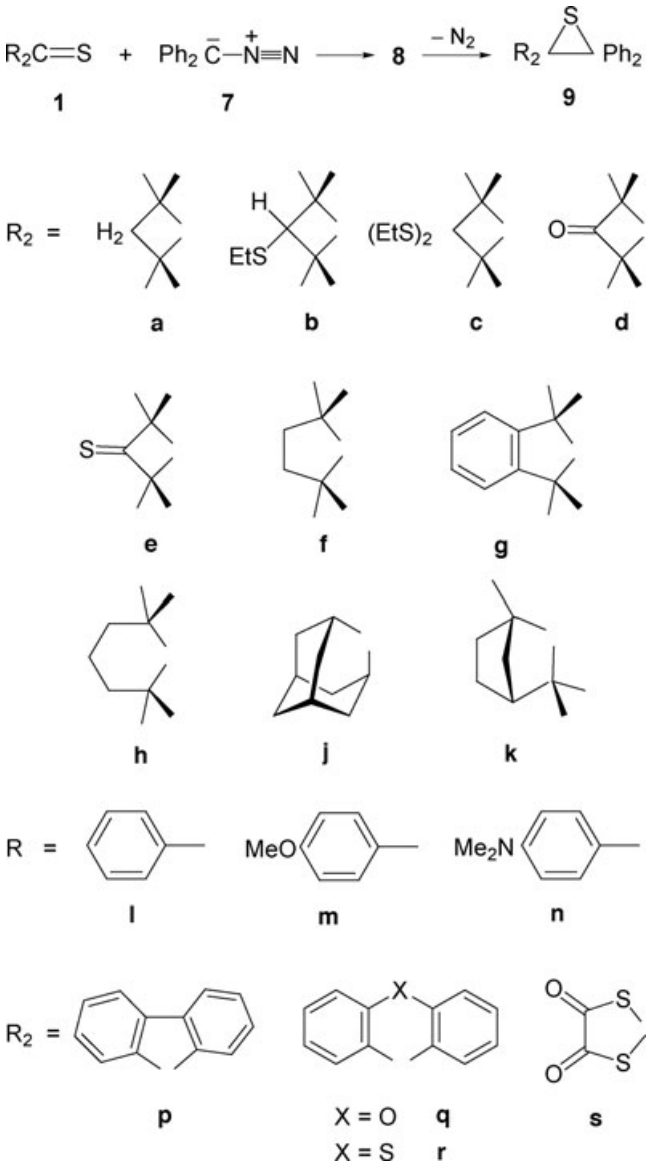
There are arguments for the concertedness of diazoalkane cycloadditions with CC double bonds: retention of dipolarophile configuration, >99.997%, in the addition of diazomethane to methyl-(*E*)-2,3-dimethylacrylate [39]; only small dependence of rate on solvent polarity for additions of phenyldiazomethane to methyl acrylate or norbornene was observed [25]. On the other hand, the high influence of solvent polarity on the reaction of dimethyl diazomalonate with 1-pyrrolidinocyclopentene indicated a switching from cycloaddition to azo-coupling [40] as a consequence of the low distance of LU (1,3-dipole) and HO (dipolarophile).

Thiiranes as Products

All thiones of Scheme 3 reacted with diphenyldiazomethane **7** in DMF at 40°C and furnished thiiranes—with one exception: 2,2,6,6-tetramethylcyclohexanethione **1h** afforded the dihydro-1,2,4-thiadiazole **8h**, i.e., the N_2 extrusion as the second step was slow in just this case. The conversion **8h** → **9h** + N_2 became measurable at higher temperature, but—oddly enough—was accompanied by formation of thiobenzophenone. Competing cycloreversions of **8h** were revealed, which will be the subject of the following paper. The reactions of **7** with aromatic thioketones **1l–1r** and the cyclic trithiocarbonate **1s** gave rise to thiiranes **9l–9s**, which have been described before (for lit., see [20]); a renewed isolation was regarded dispensable.

The thiiranes **9a–9k** are crystalline and were formed in high yields. The NMR spectra not only confirmed the structures and symmetry properties, but also allowed an assignment of all essential ^{13}C parameters. Thiirane **9b** harbors two stereocenters and occurred in two diastereomers 62:38; a σ-plane is retained in each of them. The fenchane derivative showed up in two chiral diastereoisomers (46:54). One was isolated pure and the second was enriched. The ^{13}C parameters of the pure isomer display different phenyls.

The mass spectra of thiiranes **9a–9k** exhibit the loss of sulfur, often combined with the elimination of alkyl or—in the case of **9d**—carbon monoxide. Strong M^+ peaks (up to 85%) are noteworthy. As expected from precedents, the radical cations of **9d** and **9e** lose dimethylketene and dimethylthioketene, respectively. Surprising was a fragmentation which



SCHEME 3

furnished thiobenzophenone$^+$ (*m/z* 198, in the MS of **9g** as 100% peak), accompanied by benzhydryl$^+$ (*m/z* 167, small), 9-fluorenyl (*m/z* 165, big), and PhC≡S$^+$ (*m/z* 121); these conversions of thiobenzophenone$^+$ are well known [41].

EXPERIMENTAL

General

IR spectra were recorded on a Perkin-Elmer FT 1000 instrument. ^1H NMR spectra were taken on a Bruker WP80 CW model, and ^{13}C NMR on Bruker WP80 DS; signal multiplicities were determined by comparison of H-decoupled and off-resonance spectra.

The MS are EI spectra with 70 eV recorded on Finnigan MAT 90. CC is column chromatography, and TLC is thick-layer chromatography on 20 × 20 cm glass plates with 2 mm Merck silica gel 60 PF_{254}. Melting points are uncorrected.

Materials

Diphenyldiazomethane **7** *[42].*

Dimethylformamide (DMF). The commercial solvent was purified by distillation with benzene and water according to the procedure described by Bunge [43]; b.p. 40°C/8, $n_D^{25} = 1.4267$.

New Thioketones

3-Ethylsulfanyl-2,2,4,4-tetramethylcyclobutanethione **1b**. The corresponding ketone [44] (8.08 g, 43.4 mmol) and trimethyl orthoformate (7.6 g) in abs. MeOH (70 mL) at 0°C were treated with HCl and H_2S. After several days, work-up with ice/pentane and column chromatography (silica gel, pentane) afforded **1b** (4.5 g, 51%) as red liquid, b.p. 90–95°C/12. ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ 15.3 (q, Me of Et), 24.0, 28.3 (2q, 4Me), 27.3 (t, CH_2 of Et), 59.5 (d, C-3), 62.5 (s, C-2/C-4), 283.9 (C-1).

3,3-Bis(ethylsulfanyl)-2,2,4,4-tetramethylcyclobutanethione **1c**. The corresponding ketone [44] (2.70 g, 11.0 mmol) and P_4S_{10} (3.0 g, 9.4 mmol) were refluxed in dry pyridine (15 mL) for 3 days. Work-up with pentane and chromatography with silica gel/pentane gave spectroscopically pure **1c** (0.89 g, 31%). ^{1}H NMR (CCl_4, 80 MHz): δ 1.25 (t, $^3J = 7.6$ Hz, 2Me of 2Et), 1.45 (s, 4Me), 2.60(q, $^3J = 7.6$ Hz, $2CH_2$ of 2Et). ^{13}C NMR ($CHCl_3$, 20.2 MHz): δ 13.8 (q, 2Me of 2Et), 26.0 (t, $2CH_2$ of 2Et), 26.4 (q, 4Me), 69.8 (s, C-2/C-4), 74.4 (s, C-3), 280.8 (s, C-1). MS (130°C) *m/z* (%): 262 (0.5) [M^+], 233 (80) [$M^+ -$ Et], 201 (73) [$M^+ -$ EtS], 172 (61) [$201^+ -$ Et], 157 (11) [$172^+ -$ Me], 139 (25), 115 (19), 105 (38), 96 (31), 91 (18), 85 (60), 81 (100), 79 (25), 71 (41), 59 (74).

Kinetic Measurements

The UV/Vis spectrophotometer Zeiss PMQ II with solvent compensation in the second beam and 0.1–1.0 cm quartz cuvettes were employed. The jacketed cuvette chamber was thermostatted at 40.0 ± 0.1°C, measured in the chamber. The decrease of absorbance *A* versus time was continuously recorded, and the final value, E_∞, deviated from the value precalculated for the excess reactant by not more than 1–2.5%. The concentrations of the reactants and the length of the light path were adopted to the reaction rate and to $E_o \approx 1$. The ratio of the reactants was varied to confirm the second order, as some examples in Table 2 demonstrate.

Equations (1) and (2) are valid for experiments with an excess of **7**; corresponding equations with *D* and *T* exchanged were applied for runs with an excess of thione. The evaluation of k_2 was based on 15–30 pairs of *E*/*t* up to 80–90% reaction, and a computer program was employed. Linear regression provided k_2; correlation coefficients $r^2 > 0.996$ were standard. Despite excellent correlation coefficients (Table 2) for the single runs, the reproducibility was only fair. Spreads of up to ±5% were observed for independent experiments.

TABLE 2 Reactions of Thioketones **1** with Diphenyldiazomethane **7** in DMF at 40.0°C; Details of Spectrophotometric Rate Runs for Three Thioketones

mmol L^{-1}		*λ (nm)*	*ε*		*Evaluated*		*Correlation*
1	**7**	*used*	**1**	**7**	*to % Reaction*	k_2*(L mol^{-1}s^{-1})*	*Coefficient r^2*
3-Ethylsulfanyl-2,2,4,4-tetramethylcyclobutanethione **1b**							
6.36	4.10	525	6.31	90.7	80	0.141	0.9999
7.75	2.26	525	6.31	90.7	80	0.137	0.9994
Adamantanethione **1j**							
13.98	8.16	525	4.31	90.7	90	0.103	0.9995
13.98	8.16	525	4.31	90.7	91	0.104	0.9998
27.96	4.08	525	4.31	90.7	84	0.0956	0.9998
Thiobenzophenone **1l**							
2.47	3.14	628	157.5	3.20	90	10.3	0.9991
1.83	3.14	628	157.5	3.20	96	9.86	0.9974
1.94	2.30	628	157.5	3.20	82	10.7	0.9997
0.427	0.603	628	157.5	3.20	83	10.6	0.9999
1.89	2.30	604	210	11.4	84	10.3	0.9996

Preparative Experiments: Characterization of Thiiranes

4,4,6,6-Tetramethyl-2,2-diphenyl-1-thiaspiro[2,3]-hexane **9a**. 2,2,4,4-Tetramethylcyclobutanethione [45] **1a** (440 mg, 3.09 mmol) and **7** (590 mg, 3.04 mmol), each dissolved in DMF (5 mL), were combined with stirring at 40°C; decolorization was observed after about 1 h. Water (15 mL) was added, and the product was extracted with pentane (2×10 mL). The pentane phase was washed two times with water, dried with molecular sieve (3 Å), evaporated, and left a colorless powder (870 mg). The ^{1}H NMR analysis with *sym*-tetrachloroethane as weight standard was based on two singlets at δ 0.90 and 1.11, and indicated 93% of **9a**. Recrystallization from MeOH gave analytically pure **9a**, m.p. 68°C. IR (KBr): ν 695 st, 752 m, 782 m (arom. out-of-plane deform.), 1366 m, 1444 st; 1490 m, 1595 w (arom. ring vibr.). ^{1}H NMR ($CDCl_3$, 80 MHz): δ 0.90, 1.11 (2s, 4Me), 1.69, 1.78 (AB, $^2J = 7.0$ Hz, 5-H_2), 7.64–7.85 (m, 10 arom. H). ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ 28.5, 32.7 (2q, 4Me), 40.7 (s, C-4/C-6), 49.7 (t, C-5), 66.5 (s, C-3), 126.9, 127.1, 130.9 (3d, 10 arom. CH), 140.3 (s, 2 arom. C_q). MS (50°C), *m/z* (%): 308 (10) [M^+], 276 (58) [$M^+ -$ S], 261 (19) [$276^+ -$ Me], 252 (12) [$M^+ - C_4H_8$], 237 (22) [$M^+ - C_5H_{11}$], 233 (49) [$276^+ - C_3H_7$], 220 (48) [$252^+ -$ S], 219 (41), 205 (100) [$237^+ -$ S], 191 (9) [$205^+ - CH_2$], 178 (10), 165 (18) [$C_{13}H_9^+$, fluorenyl$^+$], 155 (8), 143 (7), 129 (11), 128 (11), 105 (15) [$C_8H_9^+$], 91 (24) [$C_7H_7^+$], 77 (14) [$C_6H_5^+$]. Anal. calcd. for $C_{21}H_{24}S$ (308.47): C, 81.76; H, 7.84; S, 10.40; found: C, 81.87; H, 7.66; S, 10.37.

5-Ethylsulfanyl-4,4,6,6-tetramethyl-2,2-diphenyl-1-thiaspiro[2,3]hexane **9b**. Analogously, **2b** (2.12 mmol) and **7** (2.06 mmol) afforded crude **9b** (670 mg) as a colorless powder. The NMR spectra showed the presence of two diastereoisomers (62:38), which were not separated; the quantitat. ^{1}H NMR analysis with *sym*-$C_2H_2Cl_4$ used the q at δ 2.40 and the s at 3.05 and resulted in 93% of **9b**, m.p. 80°C (MeOH). IR (KBr): ν 692 m, 710 st, 743 m, 778 m (arom. out-of-plane deform.), 1259 m, 1367 st; 1451 st, 1461 m, 1490 m, 1598 w (arom. ring vibr.). ^{1}H NMR ($CDCl_3$, 80 MHz) of Isomer 1: δ 0.90, 1.19 (2s, 4Me), 1.22 (t, $^3J = 7.2$ Hz, Me of Et), 2.43 (q, $^3J = 7.2$ Hz, CH_2 of Et), 3.05 (s, 5-H), 7.13–7.37, 7.63–7.85 (2m, 10 arom. H); Isomer 2: δ 0.99, 1.04 (2s, 4Me), 1.19 (t, Me of Et), 2.40 (q, $^3J = 7.6$ Hz, CH_2 of Et), 3.05 (s, 5-H). ^{13}C NMR ($CDCl_3$, 20.2 MHz) of Isomer 1: δ 15.3 (q, Me of Et), 23.1, 32.2 (2q, 4Me), 27.1 (t, CH_2 of Et), 47.3 (s, C-4/C-6), 61.5 (d, C-5), 62.5 (s, C-3), 77.9 (s, C-2), 127.2, 130.8, 131.0 (3d, 4:4:2, 10 arom. CH), 140.1 (s, 2 arom. C_q); Isomer 2: δ 14.9 (q, Me of Et), 27.9 (t, CH_2 of Et), 30.3, 32.2 (2q, 4Me), 45.9 (s, C-4/C-6), 61.5 (d, C-5), 65.7 (s, C-3), 77.9 (s, C-2). MS (80°C), *m/z* (%): 368 (46) [M^+], 336 (13) [$M^+ -$ S], 307 (9) [$336^+ -$ Et], 282 (30), 259 (22) [$336^+ -$ Ph], 252 (14) [$M^+ - EtSC_4H_7$], 237 (45) [$252^+ -$ Me], 220 (45) [$252^+ -$ S], 205 (46) [$220^+ -$ Me], 165 (25) [$C_{13}H_9^+$, fluorenyl$^+$], 141 (23), 116 (100) [$EtS^+ = C_4H_7$], 91 (26) [$C_7H_7^+$], 87 (22), 77 (14) [$C_6H_5^+$]. Anal. calcd. for $C_{23}H_{28}S_2$ (368.59): C, 74.94; H, 7.66; S, 17.40; found: C, 74.89; H, 7.46; S, 17.47.

5,5-Bis(ethylsulfanyl)-4,4,6,6-tetramethyl-2,2-diphenyl-1-thiaspiro[2,3]hexane **9c**. Recrystallization of crude **9c** (74%) from MeOH gave pure thiirane as colorless crystals, m.p. 116°C. IR (KBr): ν 695 w, 706 st, 746 m, 779 m (arom. out-of-plane deform.), 1366 m, 1379 m, 1444 st, 1472 m, 1490 m, 1599 w. ^{1}H NMR ($CDCl_3$, Varian XR 400S, 400 MHz): δ 0.91, 1.47 (2s, 4Me), 1.21 (t, $^3J = 7.5$ Hz, 2Me of 2Et), 2.54, 2.58 (2q, $^3J = 7.5$ Hz, $2CH_2$ of 2Et), 7.09–7.18, 7.74–7.80 (2m, 6:4, 10 arom. H). ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ 13.74, 13.84 (4Me), 25.14, 26.15 (2Me of 2Et), 26.3, 28.5 ($2CH_2$ of 2Et), 53.1 (C-4/C-6), 69.9, 75.2, 76.5 (C-2, C-3, C-5), 127.16 (2 arom. *p*-CH), 127.23, 130.9 (8 aromat. *o*,*m*-CH), 140.4 (2 arom. C_q). Anal. calcd. for $C_{25}H_{32}S_3$ (428.70): C, 70.04; H, 7.52; S, 22.44; found: C, 70.15; H, 7.46; S, 22.60.

4,4,6,6-Tetramethyl-2,2-diphenyl-1-thiaspiro[2,3]-hexane-5-one **9d**. *Thione* **1d** *[46].* The ^{1}H NMR analysis was based on the singlets at δ 1.05 and 1.09: 82% of **9d**, m.p. 115°C (MeOH). IR (KBr): ν 694 w, 706 st, 750 m, 783 m, 1035 m, 1363 m, 1456 st, 1465 m, 1490 w, 1775 vst (C=O). ^{1}H NMR ($CDCl_3$, 80 MHz): δ1.05, 1.09 (2s, 4Me), 7.14–7.35 (m, 6 arom. H), 7.53–7.75 (m, 4 arom. H). ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ 23.5, 25.3 (2q, 4Me), 63.7 (s, C-4/C-6), 65.3 (s, C-3), 74.1 (s, C-2), 127.4 (d, 6 arom. CH), 130.6 (d, 4 arom. CH), 139.4 (s, 2 arom. C_q), 220.4 (s, C-5). MS (70°C), *m/z* (%): 322 (77) [M^+], 294 (9) [$M^+ -$ CO], 290 (10) [$M^+ -$ S], 262 (100) [$M^+ -$ S $-$ CO], 247 (61) [$262^+ -$ Me], 219 (90) [$290^+ - Me_2C{=}C{=}O - H$], 198 (46) [thiobenzophenone$^+$], 165 (33) [$C_{13}H_9^+$, fluorenyl$^+$], 91 (24) [$C_7H_7^+$], 77 (15) [$C_6H_5^+$]. Anal. calcd. for $C_{21}H_{22}OS$ (322.45): C, 78.22; H, 6.88; S, 9.94; found: C, 78.41; H, 6.98; S, 9.96.

4,4,6,6-Tetramethyl-2,2-diphenyl-1-thiaspiro[2,3]-hexane-5-thione **9e**. Dithione **1e** (10.0 mmol) [46] and **7** (5.61 mmol) were reacted in DMF (10 mL) for 1 h at 40°C. Work-up with H_2O (30 mL) and pentane (100 mL) gave an organic phase from which at 0°C a colorless powder (20 mg) precipitated, m.p. 235–237°C. The IR and ^{1}H NMR spectra corresponded

with the literature description of the 1:2-product, the diastereomeric mixture of bis-thiiranes [8] (m.p. 235–240°C); the MS (*m/z* 504, 3%) confirmed $C_{34}H_{32}S_2$. The monothiirane **9e** (1.81 g, 95%) was obtained from the mother liquor at −25°C in large crystals, m.p. 116–116.5°C. IR (KBr): ν 703 st, 744 m, 778 st; 865 m, 1091 st, 1312 st, 1360 st, 1444 st, 1462 m, 1492 m. ^{1}H NMR ($CDCl_3$, 80 MHz): δ 1.13, 1.16 (2s, 4Me), 7.13–7.39 (m, 6 arom. H), 7.55–7.83 (m, 4 arom. H). ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ 27.4, 29.4 (2q, 4Me), 65.7 (s, C-3), 67.2 (s, C-4/C-6), 77.3 (s, C-2), 127.4 (d, 6 arom. CH), 130.7 (d, 4 arom. CH), 139.5 (s, 2 arom. C_q), 194.9 (C=S). MS (70°C), *m/z* (%): 338 (80) [M^+], 323 (7) [M^+− Me], 306 (43) [M^+− S], 291 (9) [306$^+$− Me], 261 (6) [M^+− Ph], 251 (23), 237 (25), 220 (54) [306$^+$− Me_2C=C=S], 210 (100) [Ph_2C=C=S^+ ?], 205 (49) [220$^+$− Me], 165 (30) [$C_{13}H_9^+$, fluorenyl$^+$], 128 (16), 121 (10) [PhC≡S^+], 91 (13) [$C_7H_7^+$], 77 (12) [Ph^+]. Anal. calcd. for $C_{21}H_{22}S_2$ (338.52): C, 74.50; H, 6.55; S, 18.94; found: C, 74.60; H, 6.59; S, 18.96.

4,4,7,7-Tetramethyl-2,2-diphenyl-1-thiaspiro[2,4]-heptane **9f**. *Thione* **1f** [47,48]. ^{1}H NMR analysis with the singlets at δ 0.55, 1.27, 1.61: 83% of **9f**, m.p. 143°C (MeOH). IR (KBr): ν 695 m, 708 st, 750 m, 780 m (arom. out-of-plane deform.), 1365 m, 1381 w, 1444 st, 1462 m, 1488 m, 1598 w. ^{1}H NMR ($CDCl_3$, 80 MHz): δ 0.55, 1.27 (2s, 4Me), 1.61 (s, 5-H_2/6-H_2), 7.02–7.32 (m, 6 arom. H), 7.58–7.81 (m, 4 arom. H). ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ 29.2, 31.9 (2q, 4Me), 41.6 (m, C-5/C-6), 45.4 (s, C-4/C-7), 66.4 (s, C-3), 80.8 (s, C-2), 126.7 (d, 2 arom. *p*-CH), 127.1, 130.9 (2d, 8 arom. *o,m*-CH), 141.9 (s, 2 arom. C_q). MS (100°C), *m/z* (%): 322 (85) [M^+], 307 (6) [M^+−Me], 290 (9) [M^+− S], 251 (42) [M^+− C_5H_{11}], 219 (35) [251$^+$− S], 198 (100) [Ph_2C=S^+], 167 (33) [$C_{13}H_{11}^+$, benzhydryl$^+$], 165 (58) [$C_{13}H_9^+$, fluorenyl$^+$], 123 (33) [$C_9H_{15}^+$], 121 (13) [Ph–C≡S^+], 109 (64) [$C_8H_{13}^+$], 91 (15) [$C_7H_7^+$], 77 (8) [$C_6H_5^+$]. Anal. calcd. for $C_{22}H_{26}S$ (322.49): C, 81.93; H, 8.13; S, 9.94; found: C, 82.14; H, 8.01; S, 9.93.

2,3-Dihydro-1,1,3,3-tetramethyl-3′, 3′-diphenyl-spiro[1H-indene-2,2′-thiirane] **9g**. *Thione* **1g** [49]. In the quantitat. ^{1}H NMR analysis of the crude product, the singlets at δ 0.90 and 1.63 indicate 92% of **9g**, m.p. 215°C (MeOH). IR (KBr): δ 695 m, 714 st, 761 st br, 785 m, 1028 m, 1089 m, 1380 m, 1387 m, 1444 st, 1483 st, 1492 w. ^{1}H NMR ($CDCl_3$, 80 MHz): δ 0.90, 1.63 (2s, 4Me), 7.00–7.31 (m, 10 arom. H), 7.68–7.91 (m, 4 arom. H). ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ 29.3, 31.6 (2q, 4Me), 49.2 (s, C-1/C-3), 66.3 (s, C-2), 80.3 (s, C-3′), 121.5, 127.06, 127.24, 131.1 (4d, ratio 2:4:4:4, 14 arom. CH), 141.5, 150.0 (2s, 2 × 2 arom. C_q). MS (110°C), *m/z* (%): 370 (19) [M^+], 355 (1.5) [M^+− Me], 338 (4) [M^+− S], 323 (4) [M^+− S−Me], 293 (1) [M^+− Ph], 215 (3), 198 (1) [Ph_2C=S^+], 172 (100) [$C_{13}H_{16}^+$, tetramethylindene$^+$; ^{13}C calcd. 14.5/found 15.2], 165 (18) [$C_{13}H_9^+$, fluorenyl$^+$], 157 (44) [$C_{12}H_{13}^+$, trimethylindenyl$^+$], 142 (7) [$C_{11}H_{10}^+$, dimethylindenyl$^+$], 129 (6) [$C_{10}H_9^+$], 121 (5) [Ph–C≡S^+], 91 (8) [$C_7H_7^+$], 77 (4) [Ph^+]. Anal. calcd. for $C_{26}H_{26}S$ (370.53): C, 84.27; H, 7.07; S, 8.65; found; C, 84.21; H, 7.11; S, 8.63.

3′,3′-Diphenylspiro[adamantane-2,2′-thiirane] **9j**. Adamantanethione **1j** [50] (0.602 mmol) and **7** (0.619 mmol) in DMF (2 mL) were reacted at 45°C for 1 h and treated with H_2O (5 mL). Recrystallization of the powder from EtOH furnished **9j** (165 mg, 82%), m.p. 182–184°C. IR (KBr): ν 693 m, 705 st, 745 st, 775 st; 1348 m, 1444 st, 1467 w, 1490 m, 1596 w. ^{1}H NMR (CCl_4, 80 MHz): δ 1.25–2.33 (m, 14 H of $C_{10}H_{14}$), 6.95–7.28 (m, 6 arom. CH), 7.40–7.54 (m, 4 arom. CH). MS (90°C), *m/z* (%): 332 (77) [M^+], 300 (100) [M^+− S], 255 (2) [M^+− Ph], 211 (14), 198 (2) [Ph_2CS^+], 167 (15) [$C_{13}H_{11}^+$, benzhydryl$^+$], 165 (30) [$C_{13}H_9^+$, fluorenyl$^+$], 129 (5), 121 (5) [PhC≡S^+], 91 (80) [$C_7H_7^+$], 77 (4) [Ph^+]. Anal. calcd. for $C_{23}H_{24}S$ (332.49): C, 83.08; H, 7.28; S, 9.64; found: C, 83.05; H, 7.23; S, 9.66.

3′,3′-Diphenylspiro[fenchane-2,3′-thiirane] **9k**. (1*R*,4*S*)-Thiofenchone **1k** [51,52] (2.67 mmol) and **7** (2.70 mmol) in DMF (25 mL) were reacted at 40°C for 10 h. After work-up with H_2O/pentane (30 mL each), the crude product was ^{1}H NMR-analyzed with *sym*-$C_2Cl_4H_2$: the singlets at δ 0.39 + 0.42 for diastereomer 1 and δ 0.30 + 0.58 for diastereomer 2 indicated 97% of **9k**, 1/2 = 46:54. The crude product, twice recrystallized from EtOH, gave pure **9k**-1, m.p. 155–157°C. Fractional crystallization of the mother liquor afforded **9k**-2 (80 mg), which still contained 20% of **9k**-1; m.p. 90–93°C.

9k-1. IR (KBr): ν 692 st, 703 st, 729 m, 747 m, 779 m, 1097 m, 1375 m, 1443 st, 1462 m, 1487 m, 1592 w. ^{1}H NMR ($CDCl_3$, 80 MHz): δ 0.39, 0.42, 0.94 (3s, 3Me), 1.04–2.49 (m, 7H), 5.94–7.35 (m, 6 arom. H), 7.55–7.73 (m, 4 arom. H). ^{13}C NMR ($CDCl_3$, 20.2 MHz): δ 20.4, 27.05, 33.83 (3q, 3Me), 26.96, 32.77, 46.6 (3t, 3CH_2), 43.2, 53.7, 66.8 (3s, 3 alicycl. C_q), 50.6 (d, C-4), 126.61, 126.67, 127.3, 130.5 (4d, intensity ratio ~2:2:4:2, two diastereotopic Ph), 140.9, 144.0 (2s, 2 arom. C_q). MS (70°C), *m/z* (%): 334 (100) [M^+], 319 (10) [M^+− Me], 302 (100) [M^+− S; ^{13}C calcd. 25.6/found 24.7], 287 (9) [302$^+$− Me], 259 (41) [302$^+$ − *i*-Pr], 198 (24) [Ph_2C=S^+], 167 (48) [Ph_2CH^+], 165 (29) [$C_{13}H_9^+$, fluorenyl$^+$], 121 (24) [PhC≡S^+], 91 (49) [$C_7H_7^+$], 81 (22), 77 (10) [$C_6H_5^+$].

Anal. calcd. for $C_{23}H_{26}S$ (334.50): C, 82.58; H, 7.83; S, 9.59; found: C, 82.29; H, 7.81; S, 9.58.

9k-*2*. ^{1}H NMR ($CDCl_3$): δ 0.30, 0.58, 0.93. Anal. for $C_{23}H_{26}S$ (334.50); found: C, 82.68; H, 7.80; S, 9.56.

Ethenetetracarbonitrile (TCNE) and Diphenyldiazomethane

When rate measurements with TCNE (4.24 mmol L^{-1}) and **7** (2.65 mmol L^{-1}) in DMF were evaluated by Eqs. (1) and (2), no straight lines were obtained. However, the data of this and three further experiments fulfilled the first order in **7** up to 86–97% reaction and $r^2 \geq 0.998$; $10^3 k_1 = 4.94$, 4.20, 4.94, and 5.18 mol s^{-1} in four runs strayed more than usual. The combined reaction solutions were worked up with water/pentane, and separation by CC (pentane/CH_2Cl_2 10:2) gave the following fractions: tetraphenylethylene (17%), m.p. 200–212°C (MeOH), in IR spectrum and mixed m.p. identical with an authentic sample; benzophenone (40%), identified by TLC comparison and by mixed m.p. of the 2,4-dinitrophenylhydrazone, 227–230°C; diphenylcarbinol (29%) crystallized from petroleum ether in colorless needles, m.p. 66.5°C, without depression in mixed m.p.

ACKNOWLEDGMENTS

We express our thanks to Professor Heinz Langhals, Munich, who provided the computer program for the evaluation of the second-order rate measurements. We are grateful to Cand. Chem. Ulrich Pohl for his diligent and competent partaking in the kinetic measurements and the preparative work. We also thank Helmut Huber for many of the NMR recordings and Reinhard Seidl for the mass spectra. The elemental analyses were carried out by Helmut Schulz and Magdalena Schwarz. We are deeply grateful to the Fonds der Chemischen Industrie, Frankfurt, for supporting our research.

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