Kinetics of the [2^+ + 4]-Cycloaddition Reactions of 1,3-Dithian-2-ylium Ions with 1,3-Dienes

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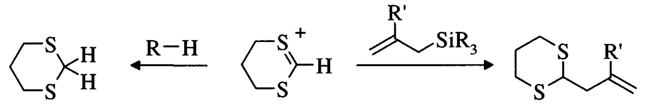
The kinetics of the [2^+ + 4] cycloadditions of 1,3-dithian-2-ylium ions (**1**) with 1,3-dienes was investigated photometrically in dichloromethane. The second-order rate constants determined for the reactions of **1** with 2,3-dimethyl-1,3-butadiene (**2a**) and isoprene (**2b**) were identical to those calculated for the first step of a stepwise cycloaddition pathway by the correlation lg $k = s\,(E + N)$. Though a concerted cycloaddition pathway is not excluded by this finding, it is obvious that the transition states of these reactions are not noticeably stabilized by the simultaneous formation of two new σ bonds.

Introduction

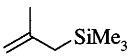
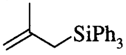
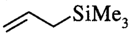
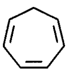
1,3-Dithian-2-ylium ions are useful acylium equivalents. Their synthetic potential has been specified by the determination of their electrophilicity parameters E[1], which can be used to estimate the rate constants k of their reactions with uncharged nucleophiles (with known nucleophilicity parameter N and slope parameter s)[2] by Equation 1 (Table 1).

$$\lg k = s\,(E + N) \qquad (1)$$

Table 1. Comparison of calculated and observed rate constants for the reactions of the 1,3-dithian-2-ylium tetrafluoroborate ($1-BF_4^-$) with nucleophiles at 20°C



$E(\mathbf{1}) = -2.17$

nucleophile	N[a]	s[a]	$k_{calcd.}$ (Eq.1) [l mol^{-1} s^{-1}]	$k_{obsd.}$ [l mol^{-1} s^{-1}]
	4.90	0.89	2.69×10^2	1.82×10^2[b]
	3.68	0.92	2.45×10^1	2.57×10^1[b]
	1.62	1.01	2.78×10^{-1}	4.04×10^{-1}[b]
$HSiMe_2Ph$	3.39	0.72	7.56×10^0	1.07×10^0[b]
	0.5[c]	1.0[c]	2.1×10^{-2}	2.1×10^{-2}[d]

[a] Ref.[2]. – [b] Ref.[1]. – [c] Ref.[3]. – [d] The measured rate constant $k = 3.8 \times 10^{-2}$ l mol^{-1} s^{-1} (CD_3CN, 28°C)[4] was converted to 20°C by assuming an activation entropy of −100 J mol^{-1} K^{-1}.

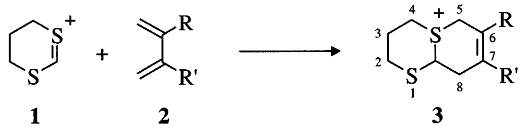
As discussed previously, Equation 1 holds for reactions of cationic electrophiles with neutral nucleophiles when *one* new bond is formed in the rate-determining step[2]. Pericyclic reactions in which the transition state profits from the simultaneous formation of more than one new bond, can be expected to proceed faster than predicted by Equation 1[5].

Corey and Walinsky[6] described hetero Diels–Alder reactions of 1,3-dithian-2-ylium tetrafluoroborate ($\mathbf{1}-BF_4^-$) with 1,3-dienes (**2**). We have now determined the kinetics of these reactions and compared the rate constants with those calculated from Equation 1 in order to obtain information on the concertedness of these cycloadditions.

Results

Suspensions of the 1,3-dithian-2-ylium tetrafluoroborate ($\mathbf{1}-BF_4^-$) in dichloromethane react with 2,3-dimethyl-1,3-butadiene (**2a**), isoprene (**2b**), and 1,3-butadiene (**2c**) to give the 3,4,8,8a-tetrahydro-2*H*,5*H*-1-thia-4a-thionianaphthalene tetrafluoroborates ($\mathbf{3}-BF_4^-$, Scheme 1). Since the spectral data of these compounds have not been published by Corey

Scheme 1. Reactions of the 1,3-dithian-2-ylium tetrafluoroborate ($\mathbf{1}-BF_4^-$) with the 1,3-dienes **2a–c**



1 **2** **3**

diene	R	R′	T [°C]	time	yield (%)
2a	Me	Me	25	15 min	82
2b	H	Me	25	60 min	64
2c	H	H	−17 to 25	6 d	84

1434–193X/98/0909–1919 $ 17.50+.50/0

Table 2. ^{13}C-NMR chemical shifts of compounds (**3a**−**c**)−BF_4^- in CD_3CN (75.5 MHz)[a]

compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-8a	CH_3
3a	25.40	21.19	34.57	33.60[b]	115.86	127.19	33.46[b]	43.69	19.39, 20.03
3b	25.19	21.84	33.19	31.62	109.60	135.65	31.87	43.99	24.20
3c	25.26	21.84	33.60	31.61	115.67	127.12	27.39	43.80	–

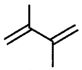
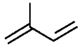
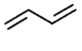
[a] Assignments corroborated by (H,H)-COSY-45 and INV-(C,H)-correlated 2D-NMR experiments. – [b] Assignments may be reverse.

and Walinsky[6], a complete characterization of the compounds **3**−BF_4^- will be given in this article (Table 2 and Experimental). Though complex ^{1}H-NMR resonances for all ring hydrogen atoms can be expected, triplets were observed for 8a-H in all compounds **3** and for 4-H in **3a** and **3b**.

The Diels−Alder adducts **3** do not show any absorption at λ_{max} of the 1,3-dithian-2-ylium ion (**1**) (311 nm). It was possible, therefore, to monitor the rates of the reactions by UV spectroscopy using a workstation as described previously[7]. In analogy to other reactions of carbocations with π nucleophiles, the reactions of the carbenium ion **1** with 2,3-dimethyl-1,3-butadiene (**2a**) and isoprene (**2b**) follow second-order kinetics, first-order with respect to the nucleophile and first-order with respect to the carbocation (Table 3).

The second-order rate law is not exactly obeyed in the reaction with 1,3-butadiene (**2c**). Since the formal second-order rate constant appears to be larger in the initial phase of the reaction than at higher degree of conversion, one can only determine an approximate value of k (Table 3).

Table 3. Kinetics of the reactions of the 1,3-dithian-2-ylium ion (**1**) with 1,3-butadienes (**2**) in CH_2Cl_2

diene		T [°C]	$k_{obsd.}$ [l mol^{-1} s^{-1}]	$k_{calcd.}$[c] (**1** + **2** → **4**)
	**2a**	20	$(3.10 \pm 0.12) \times 10^{-1}$	1.6×10^{-1}
	**2b**	20	$(1.23 \pm 0.05) \times 10^{-1}$ [a]	9.4×10^{-2}
	**2c**	0	(2 to 13) $\times 10^{-3}$ [b]	7.4×10^{-5}[d]

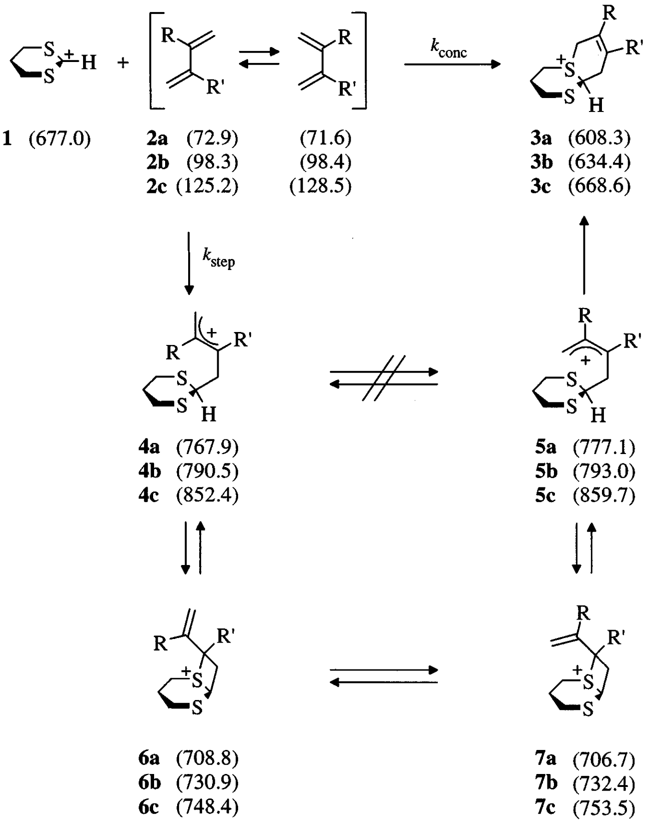
[a] $\Delta H^{\neq} = 46.32 \pm 0.81$ kJ mol^{-1}; $\Delta S^{\neq} = -104.2 \pm 2.9$ J mol^{-1} K^{-1}. – [b] The second-order rate law is not exactly obeyed (see text). – [c] From Eq. (1) with $E(\mathbf{1}) = -2.17$[1], $N(\mathbf{2a}) = 1.37$, $s(\mathbf{2a}) \approx 1$, $N(\mathbf{2b}) = 1.12$, $s(\mathbf{2b}) = 0.98$, $N(\mathbf{2c}) = -1.15$, $s(\mathbf{2c}) \approx 1$[2]. – [d] From $k_{calcd.}$ (20°C) = 4.79×10^{-4} l mol^{-1} s^{-1} with estimated $\Delta S^{\neq} = -104$ J mol^{-1} K^{-1}.

Discussion

For the Diels−Alder reactions of **1** with the butadienes **2**, which are exothermic by −133.6 to −140.9 kJ mol^{-1} according to AM1 calculations[8] (Scheme 2), a concerted or a stepwise mechanism has to be considered. While the less stable s-*cis* conformer of the dienes **2** [the calculated higher stability of s-*cis* compared to s-*trans*-**2a** (Scheme 2) is an artifact of the AM1 method] is required for the concerted [4 + 2] cycloaddition, the stepwise process can proceed by attack of **1** at the s-*trans* conformers of **2a**−**c** to yield the allyl cations **4a**−**c**.

Since attempts to optimize the structures **4a**−**c** with the AM1 method sometimes immediately yielded the bicyclic cations **6a**−**c**, one can conclude that the barrier for the cyclization **4** → **6** is negligible. Rotation of a C−C single bond may yield **7a**−**c**, which may undergo a [1,3]-shift of sulfur to give the cycloadducts **3a**−**c** probably via the allyl cations **5a**−**c**.

Scheme 2. Concerted and stepwise cycloaddition of the 1,3-dithian-2-ylium cation (**1**) with the 1,3-dienes **2a**−**c** ($\Delta H_f°$ [kJ mol^{-1}] calculated by the semiempirical AM1 method)[8]

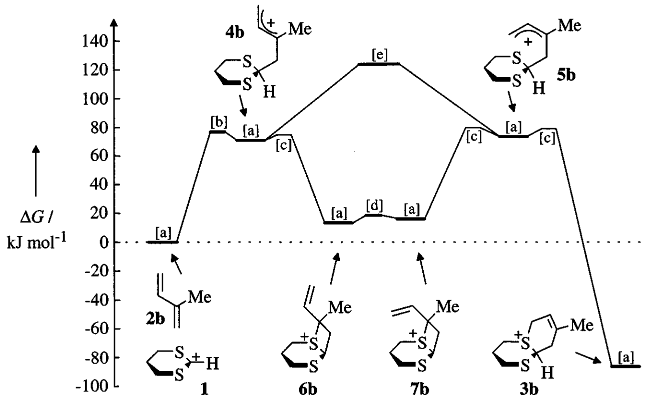


Because of the favorable pathway **4** → **6** → **7** → **5**, the direct isomerizations of **4** to **5**, for which rotational barriers of 45.6 (**4a**), 53.4 (**4b**), and 78.5 (**4c**) kJ mol^{-1} can be assumed (Eq. 19 in ref.[9]), do not play a role.

These considerations which are summarized in the free-enthalpy profile of Scheme 3 suggest that in case of a stepwise cycloaddition the formation of the allyl cation **4** can be assumed to be rate-determining. Since the formation of

4 from **1** and **2** is mechanistically analogous to the rate-determining step of the reactions described in Table 1, Equation 1 should be applicable to calculate its rate.

Scheme 3. Free-enthalpy profile (20 °C) for the stepwise Diels−Alder reaction of the 1,3-dithian-2-ylium cation (**1**) with isoprene (**2b**)



[a] From Mopac−Thermo (AM1) calculations[10]: $\Delta G°$(20 °C)/kJ mol^{-1} = 580.8 (**1**), 4.0 (**2b**), 501.5 (**3b**), 655.2 (**4b**), 658.2 (**5b**), 598.3 (**6b**), 600.5 (**7b**). − [b] Barrier derived from Eq. 1 (see Table 3). − [c] Unknown barrier assumed to be very small (see text). − [d] Barrier of interconversion of 1-butene conformers[11]. − [e] Rotational barrier of the 1,1-dimethylallyl cation in superacid solution (Eq. 19 in ref.[9]).

According to Table 3, the observed cycloaddition rate constants for 2,3-dimethyl-butadiene (**2a**) and isoprene (**2b**) and those calculated for the rate-determining steps of the stepwise processes are almost identical. This coincidence suggests stepwise cycloaddition mechanisms. Though one cannot exclude concerted pathways on this basis, it is obvious that the transition states are not noticeably stabilized by the simultaneous formation of two new σ bonds.

The cycloaddition of **1** with 1,3-butadiene (**2c**) was observed to be 10^2 times faster than calculated for the formation of the intermediate **4c**. Though a small degree of concertedness is suggested by this deviation of $k_{\text{obsd.}}$ and $k_{\text{calcd.}}$, the poor quality of the observed rate constants prevents definite conclusions.

The failure to unequivocally assign the mechanism of these reactions illuminates an important feature of this mechanistic tool. In principle, the comparison of observed cycloaddition rate constants with those calculated for stepwise processes by Equation 1 provides a means to estimate the degree of concertedness, i.e., the energetic preference of the concerted over a (hypothetical) stepwise process. However, in this way, we can neither differentiate borderline cases nor exclude concerted mechanisms with highly unsymmetrical transition states. It should furthermore be noted that this method of determining the degree of concertedness is not applicable to cycloadditions of two non-charged components, since one cannot presently predict the rates of formation of dipolar or diradical intermediates which might be involved in such reactions. In cycloadditions of closed-shell ions with neutral reaction partners, on the other hand, the potential intermediates are closed-shell ions like one of the reactants and like the cycloadduct, which greatly facilitates the mechanistic analysis.

The observation that in none of the cycloadditions studied in this work a large difference between $k_{\text{obsd.}}$ and $k_{\text{calcd.}}$ was observed, implies that Equation 1, which has been parametrized for reactions of carbocations with non-charged nucleophiles, may also be used to estimate the rates of the $[2^+ + 4]$ cycloadditions of **1** with conjugated dienes. It is thus for the first time possible to predict absolute rate constants of such cycloadditions with reasonable accuracy.

Generous support by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged. We thank *Nathalie Hampel* for experimental assistance.

Experimental Section

General: NMR: Bruker WM 300 or Bruker ARX 300. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) refer to [D$_3$]acetonitrile (δ_H = 1.93 and δ_C = 1.30) as internal standard. − IR: IR spectrophotometer 325 (Perkin−Elmer). − MS: Varian MAT 311A. − Melting points (uncorrected): Büchi 530. − All reactions were carried out under dry nitrogen. Dichloromethane was freshly distilled from CaH$_2$ before use. The 1,3-butadienes **2a**−**c** are commercially available. **2a**,**b** were freshly distilled before use. 1,3-Dithian-2-ylium tetrafluoroborate (**1**−BF$_4^-$) was prepared from 1,3-propanedithiol, ethyl orthoformate and HBF$_4$ as described in ref.[12].

General Procedure: The 1,3-butadienes **2** were added dropwise to (or condensed into) a suspension of 1,3-dithian-2-ylium tetrafluoroborate (**1**−BF$_4^-$) in dry CH$_2$Cl$_2$. The mixture was stirred until the solid component had disappeared (except for the reaction with **2c** because **3c** is also poorly soluble in CH$_2$Cl$_2$). The solvent and the excess of the dienes were removed in vacuo to yield the solid products which were purified by recrystallization.

6,7-Dimethyl-3,4,8,8a-tetrahydro-2H,5H-1-thia-4a-thionianaphthalene Tetrafluoroborate (**3a**−BF$_4^-$): Reaction of **1**−BF$_4^-$ (0.13 g, 0.63 mmol) with **2a** (0.28 g, 3.4 mmol) at ambient temperature for

Table 4. Kinetics of the reactions of 1,3-dithian-2-ylium tetrafluoroborate (**1**−BF$_4^-$) with 2,3-dimethyl-1,3-butadiene (**2a**)

T [°C]	[**1**]$_o$ [mol l^{-1}]	[**2a**]$_o$ [mol l^{-1}]	conversion (%)	k[a] [l mol^{-1} s^{-1}]
20.0	2.82×10^{-4}	1.46×10^{-2}	51	3.25×10^{-1}
19.9	2.49×10^{-4}	7.70×10^{-3}	82	3.03×10^{-1}
20.0	2.52×10^{-4}	1.04×10^{-2}	70	3.18×10^{-1}
20.0	2.81×10^{-4}	5.70×10^{-3}	71	2.94×10^{-1}

[a] k(20 °C) = $(3.10 \pm 0.12) \times 10^{-1}$ l mol^{-1} s^{-1}.

Table 5. Kinetics of the reactions of 1,3-dithian-2-ylium tetrafluoroborate (**1**−BF$_4^-$) with isoprene (**2b**)

T [°C]	[**1**]$_o$ [mol l^{-1}]	[**2b**]$_o$ [mol l^{-1}]	conversion (%)	k[a] [l mol^{-1} s^{-1}]
20.0	2.33×10^{-4}	1.45×10^{-2}	90	1.19×10^{-1}
20.0	1.91×10^{-4}	1.98×10^{-2}	80	1.19×10^{-1}
19.9	2.06×10^{-4}	1.09×10^{-2}	83	1.25×10^{-1}
20.0	3.80×10^{-4}	4.03×10^{-3}	83	1.23×10^{-1}
0.0	1.90×10^{-4}	1.95×10^{-2}	84	2.97×10^{-2}
−9.9	2.29×10^{-4}	2.66×10^{-2}	87	1.42×10^{-2}
−28.5	4.31×10^{-4}	5.01×10^{-2}	52	2.22×10^{-3}

[a] k(20 °C) = $(1.23 \pm 0.05) \times 10^{-1}$ l mol^{-1} s^{-1}; $\Delta H^{\neq} = 46.32 \pm 0.81$ kJ mol^{-1}; $\Delta S^{\neq} = -104.23 \pm 2.92$ J mol^{-1} K^{-1}.

Table 6. Kinetics of the reactions of 1,3-dithian-2-ylium tetrafluoroborate (**1**$-BF_4^-$) with 1,3-butadiene (**2c**)

T [°C]	[**1**]$_o$ [mol l^{-1}]	[**2c**]$_o$ [mol l^{-1}]	conversion 1 (%)	k_{max}[a] [l mol^{-1} s^{-1}]	conversion 2 (%)	k_{min}[a] [l mol^{-1} s^{-1}]
−0.1	6.82×10^{-4}	1.41×10^{-2}	0 to 5	1.27×10^{-2}	21 to 50	3.76×10^{-3}
0.1	3.04×10^{-4}	1.26×10^{-2}	0 to 7	7.14×10^{-3}	9 to 43	3.74×10^{-3}
0.1	5.90×10^{-4}	2.44×10^{-2}	0 to 7	3.28×10^{-3}	7 to 56	1.91×10^{-3}
0.4	4.10×10^{-4}	9.86×10^{-3}	0 to 4	4.19×10^{-3}	11 to 33	2.20×10^{-3}
0.1	1.84×10^{-4}	3.55×10^{-2}	0 to 11	8.45×10^{-3}	41 to 81	1.91×10^{-3}

[a] $k(0°C) = (2 \text{ to } 13) \times 10^{-3}$ l mol^{-1} s^{-1}; the second-order rate law is not exactly obeyed in this reaction; k_{max} is determined from the regression line in the initial phase of the reaction (range evaluated for the determination of k_{max}: conversion 1), k_{min} is determined from the regression line in a latter phase of the reaction (range evaluated for the determination of k_{min}: conversion 2).

15 min and recrystallization of the product from butanone/diethyl ether yielded 0.15 g (0.52 mmol, 83%) of **3a** as colorless needles with m.p. 79.5−81°C (ref.[6]: 96%, 85−86°C). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 1.72, 1.76 (2 s, 2 × 3 H, 6-CH_3, 7-CH_3), 2.05−2.35 (m, 2 H, 3-H_2), 2.62−3.01 (m, 4 H, 8-H_2 and 2-H_2), 3.40 (t, ^3J = 5.9 Hz, 2 H, 4-H_2), 3.73, 3.94 (2 d, ^2J = 16.8 Hz, 2 H, 5-H_2), 4.80 (t, ^3J = 6.2 Hz, 1 H, 8a-H). − ^{13}C NMR: Table 2. − MS (FD, 0−12 mA); *m/z* (%): 204, 203, 202, 201 (2, 12, 11, 100) [$M^+ - BF_4^-$]. − $C_{10}H_{17}BF_4S_2$ (288.2): calcd. C 41.68, H 5.95; found C 41.84, H 5.95.

7-Methyl-3,4,8,8a-tetrahydro-2H,5H-1-thia-4a-thionianaphthalene Tetrafluoroborate (**3b**$-BF_4^-$): Reaction of **1**$-BF_4^-$ (0.41 g, 2.0 mmol) with **2b** (0.27 g, 4.0 mmol) at ambient temperature for 1 h and recrystallization of the product from butanone/ethyl acetate yielded 0.35 g (1.3 mmol, 64%) of **3b** as colorless prisms with m.p. 134−135°C (ref.[6]: 95%, 131−132°C). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 1.79 (m_c, 3 H, 7-CH_3), 2.07−2.36 (m, 2 H, 3-H_2), 2.63−2.92 (m, partly superimposed, 2 H, 8-H_2), 2.83−3.04 (m, partly superimposed, 2 H, 2-H_2), 3.27−3.45 (m, 2 H, 4-H_2), 3.81−3.98 (m, 2 H, 5-H_2), 4.82 (t, ^3J = 6.4 Hz, 1 H, 8a-H), 5.49 (m_C, 1 H, 6-H). − ^{13}C NMR: Table 2. − IR (KBr): $\tilde{\nu}$ = 1680 cm^{-1}. − MS (FD, 0−12 mA); *m/z* (%): 189, 188, 187 (10, 27, 100) [$M^+ - BF_4^-$]. − $C_9H_{15}BF_4S_2$ (274.2): calcd. C 39.43, H 5.52; found C 39.65, H 5.57.

3,4,8,8a-Tetrahydro-2H,5H-1-thia-4a-thionianaphthalene Tetrafluoroborate (**3c**$-BF_4^-$): Reaction of **1**$-BF_4^-$ (1.50 g, 7.50 mmol) with **2c** (2.36 g, 43.6 mmol) at −17°C for 2 d and at ambient temperature for 4 d and recrystallization of the product from butanone yielded 1.59 g (6.11 mmol, 82%) of **3c** in colorless prisms with m.p. 114.0−114.5°C (ref.[6]: 85%, 118−119°C). − ^{1}H NMR (CD_3CN, 300 MHz): δ = 2.10−2.38 (m, 2 H, 3-H_2), 2.71−3.03 (m, 4 H, 8-H_2 and 2-H_2), 3.33−3.47 (m, 2 H, 4-H_2), 3.85−4.00 (m, 2 H, 5-H_2), 4.82 (t, ^3J = 6.4 Hz, 1 H, 8a-H), 5.71−5.79 (m, 1 H, 6-H), 5.94−6.01 (m, 1 H, 7-H). − ^{13}C NMR(CD_3CN, 75.5 MHz): Table 2. − MS (FD, 0−15 mA); *m/z* (%): 435, 434, 433, 432 (1, 1, 11, 2) [2 $M^+ - BF_4^-$], 175, 174, 173 (10, 27, 100) [$M^+ - BF_4^-$]. − $C_8H_{13}BF_4S_2$ (260.1): calcd. C 36.94, H 5.04; found C 36.98, H 4.98.

Kinetic Investigations: The reactions were monitored with a workstation as described in ref.[7]. The spectrometric measurements were performed with a fiber optic system: The light of a deuterium lamp (CLD 300, Fa. Zeiss) was conducted in a quartz fiber to a probe (Hellma GmbH and Co. Müllheim) and was led back to the spectrometer (MCS 220, Fa. LOT).

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