Cycloadditions. XIII. Kinetics of the Reactions of *exo*-3-Phenyl-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-4-ene with Aryl Isocyanates[1,2]

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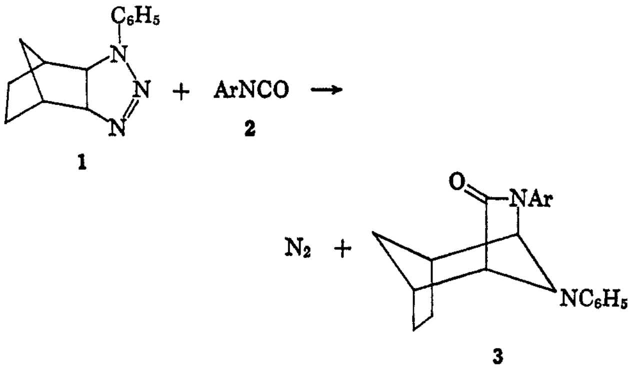
The reactions of *exo*-3-phenyl-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-4-ene with aryl isocyanates give nitrogen and cycloadducts, 3-aryl-10-phenyl-3,10-diazatricyclo[4.2.1.$1^{2,5}$]decan-4-ones having the one-atom bridges *trans*. The observed dependence of the rates of nitrogen evolution in these reactions at 154° on the concentrations of phenyl, α-naphthyl, or *p*-bromophenyl isocyanates is consistent with kinetic schemes involving either reversible formation of a triazoline–aryl isocyanate complex and a triazoline–aryl isocyanate bimolecular process or reversible formation of the complex and its unimolecular decomposition to give nitrogen and the cycloadduct. With *p*-nitrophenyl isocyanate, the observed pseudo-first-order rate constants for nitrogen evolution from the triazoline are approximately proportional to the isocyanate concentration. The triazoline–phenyl isocyanate complex has been detected through nmr spectroscopy.

The reactions of the norbornene–phenyl azide adduct, *exo*-3-phenyl-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-4-ene (1), with aryl isocyanates (2) have occasioned recent mechanistic and structural controversy;[4,5] the structural uncertainties have been rigorously settled through a complete X-ray single crystal structure determination of the adduct derived from *p*-bromophenyl isocyanate (3, Ar = *p*-bromophenyl).[6,7]



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The mechanistic course of the reactions has remained unclarified. Only qualitative indications of the kinetic characteristics of the reactions have appeared. A dependence of the rate of nitrogen evolution from 1 on the phenyl isocyanate concentration has been noted.[8] At 150° the rate of nitrogen evolution from 1 in *p*-cymene was increased twofold by adding 10% phenyl isocyanate to the solvent; in neat phenyl isocyanate, the rate was three to four times faster.[5]

We now report kinetic data for nitrogen evolution from 1 in four aryl isocyanate α-chloronaphthalene solvent systems. They have provided a determination of the kinetic form of these reactions, thus limiting possible mechanistic formulations.

Kinetic Results and Discussion

Earlier attempts[8] to secure useful rate data for the reaction of triazoline 1 with phenyl isocyanate employed conventional apparatus; the nitrogen evolved was collected in a water-jacketed buret and its volume as a function of time was estimated visually. The data obtained did serve to establish that the rate of nitrogen evolution from 1 depended on the concentration of phenyl isocyanate, thus precluding a simple unimolecular rate-determining decomposition of the triazoline to give nitrogen and a 1,3-dipolar species or some other reactive intermediate.[8] These data, however, were too imprecise to establish with certainty the functional form of the dependence of rates on phenyl isocyanate concentrations. Hence, an improved experimental procedure had to be adopted.

The equipment developed and utilized in the present study involved a constant pressure–variable volume system. As nitrogen was evolved from a reaction, the slight pressure increase in the closed system was detected by a photocell located at the meniscus of a mercury U-tube; the signal from the photocell activated a servomotor which drove a syringe, increasing the volume of the system enough to maintain a constant pressure. A recorder plotted a signal proportional to the increased volume of the system as a function of time.

In trial runs with this equipment, the kinetics of the thermal decomposition of 2,5-diphenyltetrazole[9,10] were followed. The decomposition is known to be first order and can be conducted conveniently at the same temperature and in the same solvent systems used for the triazoline decompositions. The rate data obtained (Table I) both confirmed the earlier report[10] and indicated the precision associated with the constant pressure–variable volume apparatus used. A least-squares calculation for the rates in Table I against the volume per cent phenyl isocyanate gave a slope of zero within the estimated probable error.

The observed pseudo-first-order rate constants for nitrogen evolution from the triazoline 1 as a function of the phenyl, α-naphthyl, or *p*-bromophenyl isocyanate volume or weight per cent in the solvent α-chloronaphthalene showed dependences of the form given in eq 1

$$k_{\mathrm{obsd}} = \frac{A + B(I)}{1 + C(I)} \qquad (1)$$

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(2) Paper XII in this series: J. E. Baldwin and R. A. Smith, *J. Am. Chem. Soc.*, **89**, 1886 (1967).

(3) Alfred P. Sloan Research Fellow.

(4) J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *ibid.*, **87**, 4114 (1965).

(5) R. Huisgen, R. Grashey, J. M. Vernon, and R. Kunz, *Tetrahedron*, **21**, 3311 (1965); **22**, 2400 (1966).

(6) J. E. Baldwin, J. A. Kapecki, M. G. Newton, and I. C. Paul, *Chem. Commun.*, 352 (1966).

(7) M. G. Newton, J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc., Sect. B*, 189 (1967).

(8) J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *J. Am. Chem. Soc.*, **86**, 4509 (1964).

(9) O. Dimroth and S. Merzbacher, *Chem. Ber.*, **40**, 2402 (1907).

(10) R. Huisgen, J. Sauer, and M. Seidel, *ibid.*, **94**, 2503 (1961).

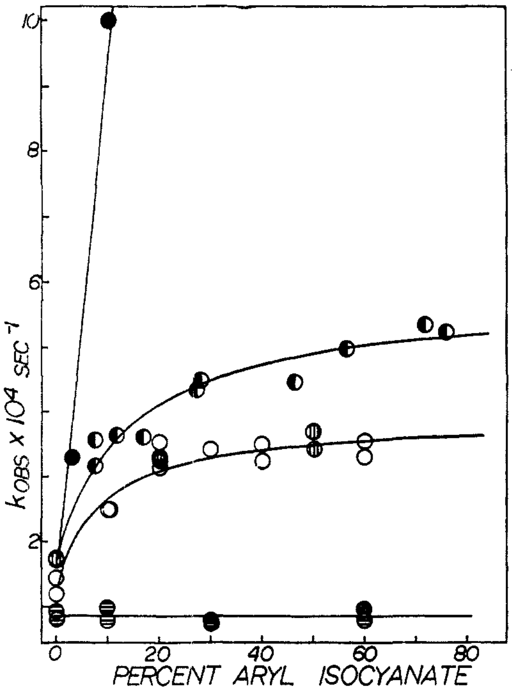

Figure 1.—Dependence of pseudo-first-order rate constants for nitrogen evolution at 154° on the per cent aryl isocyanate in the α-chloronaphthalene solvent: horizontally lined circles, 2,5-diphenyltetrazole decomposition with phenyl isocyanate; other points are for triazoline 1 with phenyl isocyanate (○), α-naphthyl isocyanate (vertically lined circles), *p*-bromophenyl isocyanate (◐), and *p*-nitrophenyl isocyanate (●).

TABLE I
FIRST-ORDER RATE CONSTANTS FOR NITROGEN EVOLUTION FROM 2,5-DIPHENYLTETRAZOLE IN α-CHLORONAPHTHALENE–PHENYL ISOCYANATE AT 154.0°

Point	$k \times 10^4$, sec^{-1}	Isocyanate, vol, %
1	0.815	0
2	0.916	0
3	0.983	10
4	0.786	10
5	0.773	30
6	0.785	30
7	0.962	60
8	0.777	60

where I represents the weight or volume fraction of aryl isocyanate and A, B, and C are constants (Table II and Figure 1).

These kinetic results are equally compatible with two kinetic schemes involving formation of a triazoline–aryl isocyanate complex. In the first, the triazoline decomposes unimolecularly to nitrogen and other products, such as the corresponding aziridine or anil, and it reversibly forms a 1:1 complex with aryl isocyanate. This complex decomposes unimolecularly to form the adduct and nitrogen (eq 2–4). These equations lead to eq 5, the observed pseudo-first-order rate constant for nitrogen evolution.

$$1 \xrightarrow{k_1} N_2 + \text{products} \tag{2}$$

$$1 + 2 \underset{}{\overset{K}{\rightleftharpoons}} 12 \tag{3}$$

$$12 \xrightarrow{k} N_2 + 3 \tag{4}$$

$$k_{\text{obsd}} = \frac{k_1 + kK(2)}{1 + K(2)} \tag{5}$$

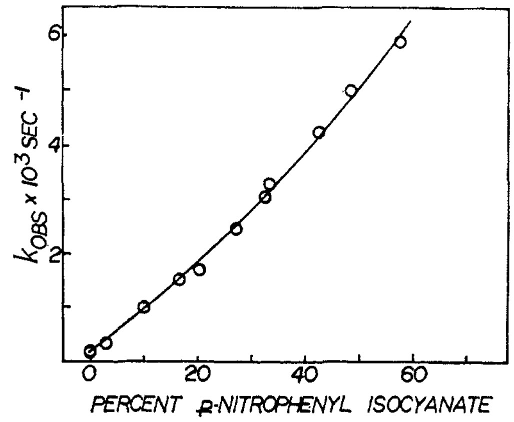

Figure 2.—Dependence of pseudo-first-order rate constants for nitrogen evolution from triazoline 1 at 154° on the weight per cent *p*-nitrophenyl isocyanate in the α-chloronaphthalene solvent.

In the second kinetic scheme, triazoline–aryl isocyanate complex formation reduces the concentration of free triazoline, but is not an intermediate along the reaction coordinate (eq 6–8). The derived expression

$$1 \xrightarrow{k_1} N_2 + \text{products} \tag{6}$$

$$1 + 2 \overset{K}{\rightleftharpoons} 12 \tag{7}$$

$$1 + 2 \xrightarrow{k_2} N_2 + 3 \tag{8}$$

for k_{obsd} is shown in eq 9.

$$k_{\text{obsd}} = \frac{k_1 + k_2(2)}{1 + K(2)} \tag{9}$$

The method of least squares[11] was applied to the data of Table II to find the best values for the constants in eq 1. The calculations were performed by computer, giving the curves drawn in Figures 1 and 2 and the numerical results listed in Table III.

The rate constants for the reactions with *p*-nitrophenyl isocyanate do not show any tendency to level off at high concentrations of the isocyanate; in fact they show a dependency slightly higher than first order on the *p*-nitrophenyl isocyanate weight per cent. This anomaly may be a mere artifact caused by, for instance, a corresponding nonlinear relationship between weight per cent and concentration in solutions of *p*-nitrophenyl isocyanate and α-chloronaphthalene over the wide composition range used (0–57.6% isocyanate).

Spectroscopic Results

Ultraviolet spectra of the triazoline 1 in *n*-decane determined between 28 and 152° did not show an appreciable temperature dependence.[12] More positive evidence was secured through temperature-dependent nmr spectroscopic scrutiny of the triazoline dissolved in phenyl isocyanate.[13] At 40°, absorptions at 60 Mc associated with the two protons on carbons bearing nitrogen appeared as a four-line pattern at

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[11] H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1956, p 517.

[12] *Cf.* P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Am. Chem. Soc.*, **87**, 306 (1965).

[13] The nmr spectrum of triazoline 1 in deuteriochloroform has been published by R. Huisgen, L. Möbius, G. Müller, H. Stangel, G. Szeimies, and J. M. Vernon, *Chem. Ber.*, **98**, 3992 (1965).

TABLE II

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR NITROGEN EVOLUTION FROM *exo*-3-PHENYL-3,4,5-TRIAZATRICYCLO[5.2.1.$0^{2,6}$]DEC-4-ENE IN α-CHLORONAPHTHALENE–ARYL ISOCYANATES

Point	$k \times 10_3$,[a] sec^{-1}	Phenyl isocyanate[b]	$k \times 10^3$,[c] sec^{-1}	α-Naphthyl isocyanate[b]	$k \times 10^3$,[c] sec^{-1}	*p*-Bromophenyl isocyanate[d]	$k \times 10^2$,[c] sec^{-1}	*p*-Nitrophenyl isocyanate[d]
1	0.119	0	0.168	0				
2	0.143	0	0.182	0				
3	0.251	10	0.321	20	0.357	7.5	0.033	2.9
4	0.250	10	0.331	20	0.314	7.5	0.100	10.1
5	0.318	20	0.367	50	0.361	12.2	0.151	16.5
6	0.353	20	0.342	50	0.359	16.9	0.169	20.3
7	0.341	30	0.312	100	0.434	27.3	0.245	27.1
8	0.350	40	0.338	100	0.467	27.8	0.306	32.5
9	0.322	40			0.442	46.3	0.331	23.3
10	0.330	60			0.394	56.1	0.425	42.4
11	0.357	60			0.535	71.9	0.501	48.5
12					0.522	75.9	0.589	57.6

[a] At 154.0°. [b] Volume per cent. [c] At 154.1°. [d] Weight per cent.

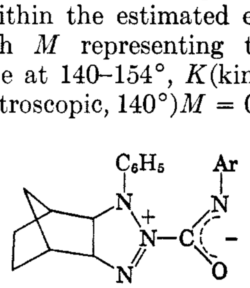
TABLE III

KINETIC PARAMETERS FOR NITROGEN EVOLUTION FROM *exo*-3-PHENYL-3,4,5-TRIAZATRICYCLO[5.2.1.$0^{2,6}$]DEC-4-ENE IN α-CHLORONAPHTHALENE–ARYL ISOCYANATES AT 154°

	Constants[a]		
Isocyanate	$A \times 10^3$, sec^{-1}	$B \times 10^2$ [b]	C[c]
Phenyl	0.129	0.465	12.1
p-Bromophenyl	0.179	0.412	7.18
p-Nitrophenyl	0.121	0.800	−0.37

[a] Calculated for the dependence $k_{obsd} = [A + B(I)]/[1 + C(I)]$, where I is the weight or volume fraction of aryl isocyanate in the solvent. [b] Units, sec^{-1} (weight or volume fraction)$^{-1}$. [c] Units, (weight or volume fraction)$^{-1}$.

265, 256, 207, and 198 cps below the internal standard, tetramethylsilane. At 140°, these four lines had shifted to 266, 257, 210, and 201 and a new four-line pattern, with absorptions at 283, 274, 227, and 218, had grown so that its integrated intensity was about half as great as that of the other four-line pattern. The formation of the species responsible for the four new lines located in an unobstructed region of the spectrum was reversible; after the sample cooled to room temperature, the original spectrum was observed. One plausible but obviously speculative formulation for the complex responsible for the nmr and kinetic observations would be structure **4**. The kinetically and spectroscopically derived equilibrium constants were identical within the estimated experimental uncertainties. With M representing the molarity of phenyl isocyanate at 140–154°, K(kinetic, 154°)M = 0.465 and K(spectroscopic, 140°)M = 0.5.



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Definitions of Cycloaddition Reactions

This seems an appropriate context for comment on possible definitions for cycloaddition reactions, since other workers no longer consider the reactions in question to be cycloadditions.[5,14] When judged by the defined characteristics of cycloadditions proposed by Huisgen, Grashey, and Sauer,[15] the reaction of triazoline **1** with an aryl isocyanate to give nitrogen and an adduct **3** is not a cycloaddition; it violates the defined requirement that "the product of a cycloaddition corresponds to the sum of the components. Cycloadditions are not accompanied by the elimination of small molecules." We, in contrast, favor a more liberal working definition: cycloadditions are chemical transformations giving at least one product having at least two new bonds as constituents of a new ring. By this standard, the formation of product **3** clearly qualifies as a cycloaddition.

It would be as idle to argue the merits of one definition against the other as it is important to recognize that they are quite different. Many reactions that may be considered cycloadditions by the second may not be so classified by the first. Thus, in the triazoline decomposition investigated kinetically in this paper, or in other systems where elimination of a molecular fragment may precede or accompany the formation of a new compound having at least two new bonds as constituents of a new ring, the process is termed a cycloaddition from the second viewpoint; it merits the designation "cycloaddition" according to the first only if the elimination precedes, and kinetic data demonstrate that the elimination precedes, the product-determining stage of the reaction. Such reactions as the combination of two cyclopropanes to give a cyclohexane[16] or the 1:1 additions of dienophiles with quadracyclanes[17] contradict the rules "the number of σ bonds is increased in cycloadditions," and "cycloadditions do not involve the breaking of σ bonds" yet could be considered as cycloadditions by the alternative definition. The second definition has no rule comparable to this limiting statement in the first: "cycloadditions of more than two reactants are multistep processes; only the last step, leading to the ring structure, is strictly speaking a cycloaddition."

The two definitions group sets of reactions differently, suggest alternative relationships among reactions, and inevitably contribute to the evolution of

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(14) R. Huisgen, private communication.

(15) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 741–746.

(16) *Cf.* R. A. Baylouny and R. Jaret, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 24P.

(17) C. D. Smith, *J. Am. Chem. Soc.*, **88**, 4273 (1966).

distinct priorities for experimental work. Whether one considers both definitions, or merely selects one arbitrarily and views it as approximately equivalent to the other, is not immaterial; they have different powers of connotation and reflect different conceptions of the interplay between definitions and mechanisms.

Conclusion

The kinetic results and the nmr spectroscopic detection of a triazoline–phenyl isocyanate complex serve to identify the main outlines of the reactions leading to the adducts **3**. Although many details of these cycloadditions remain unelucidated, their prime characteristics are now known and planning for the other types of experimentation required for a more complete understanding of the reactions has become feasible.

Experimental Section

Materials.—Reagent-grade phenyl isocyanate, α-naphthyl isocyanate, *p*-bromphenyl isocyanate, and α-chloronaphthalene were used without further purification. *p*-Nitrophenyl isocyanate was recrystallized from carbon tetrachloride and had mp 56.5–58° (lit.[18] mp 56–57°). The triazoline **1** after recrystallization from methanol had mp 98.4–100.2°.

Kinetic Method.—A battery jar suspended in a marine plywood framework and insulated with glass wool served as the constant-temperature bath. A magnetic stirrer was positioned under the framework about 3 cm below the bottom of the bell jar. The mineral oil in the bath was maintained to ±0.03° with two knife-blade heaters, one controlled by a Variac, the other by a proportional controller using a thermistor as a sensor.[19] Reaction flasks for the kinetic runs were flattened 15–20-ml bulbs connected to a 10-cm stem of 7-mm tubing sealed with a rubber septum, secured to the threaded-glass stem with a suitable screwcap.

For each run the connection between the reaction bulb and the pressure-sensing apparatus was made by inserting a hypodermic needle sealed to 1-mm polyethylene tubing through the rubber septum, the bulb containing a magnetic stirring bar was inserted into the kinetic bath with all but 1–2 cm of the stem submerged, the triazoline-aryl isocyanate-α-chloronaphthalene solution (approximately 0.01 *M* in triazoline) was injected through the septum, and, after a delay of a few minutes, the valve on the pressure bridge was closed and data collection commenced.

The polyethylene tube coming from the reaction bulb connected with a four-way junction of 1-mm capillary tubing; one route led through a stopcock to the atmosphere, another led to a 10-ml bulb surrounded by circulating water at 25 ± 0.01°, and the other branch led to a U-tube of 3-mm capillary tubing partially filled with mercury. A photocell was mounted on the U-tube and connected to a relay so that, as nitrogen was evolved in the reaction, the mercury level dropped in the U-tube and the photocell activated a servomotor, driving a syringe which withdrew di-*n*-butyl phthalate from the 10-ml bulb until the original pressure was reattained. A system of gears connected the servomotor to a potentiometer which in turn gave a signal proportional to the increase in volume in the system required to maintain a constant pressure; this signal was plotted against time on a strip-chart recorder.

Analog to digital conversion was accomplished by hand and the resulting data were used to calculate with a least-squares program and an IBM 7094 the best pseudo-first-order rate constants for each run. The precision of the experimental method can be gauged from the summaries of data in Table I and II and the Figures 1 and 2.

Registry No.—1, 4928-90-9.

Acknowledgment.—We thank Professors J. F. Bunnett and S. G. Smith for helpful suggestions pertinent to this investigation.

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[18] P. P. T. Sah, *Rec. Trav. Chim.*, **59**, 232 (1940).

[19] R. Anderson, *J. Chem. Educ.*, in press.

The Chemistry of Indenothiophenes. I. 8H-Indeno[2,1-*b*]thiophene

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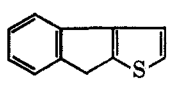
The synthesis of the title compound (I) has been achieved by the following route: conversion of 3-phenyl-2,5-thiophenedicarboxylic acid (VIII) into the diacid chloride (IX) and subsequent cyclization affords 8-oxo-8H-indeno[2,1-*b*]thiophene-2-carboxylic acid (X). Decarboxylation of X affords the corresponding ketone XIII, while Wolff–Kishner reduction of X affords the title compound I. Metalation of I with *n*-butyllithium followed by carbonation yields exclusively 8-H-indeno[2,1-*b*]thiophene-8-carboxylic acid (XV). In contrast to this, 2-benzylthiophene under the same conditions yields only 2-benzylthiophene-5-carboxylic acid.

There are three possible indenothiophenes, namely, 8H-indeno[2,1-*b*]thiophene (I), 4H-indeno[1,2-*b*]thiophene (II), and 8H-indeno[1,2-*c*]thiophene (III).



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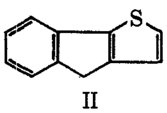

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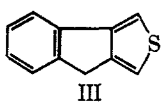
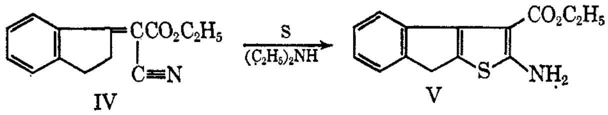


III

Compounds I, II, and III have not been reported in the literature and very little work has been recorded pertaining to derivatives of these compounds. The only known derivatives of I are 8H-indeno[2,1-*b*]thiophen-8-one[1,2] (XIII), prepared as a low-yield by-product from the diazotization of 2-aminophenyl 2′-thienyl ketone, and 8H-indeno[2,1-*b*]thiophen-8-ol[2] (XIV) for which satisfactory analytical data were not reported. Poirier[3] has recently described some substituted keto derivatives of II and III. The present work describes the synthesis of I and its metalation reaction with *n*-butyllithium.

Our first attempt to prepare I was by projected removal of the amine and ester functions of ethyl 2-amino-8H-indeno[2,1-*b*]thiophene-3-carboxylate (V), prepared in 95% yield by treating ethyl (1-indanylidene)-cyanoacetate (IV) with sulfur in the presence of di-



IV V

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[1] W. Steinkopf and E. Gunter, *Ann. Chem.*, **522**, 28 (1936).

[2] C. L. Arcus and E. C. Barrett, *J. Chem. Soc.*, 2098 (1960).

[3] Y. Poirier and N. Lozac'h, *Bull. Soc. Chim. France*, 1062 (1966).