Reactivity of Triplet Diphenylcarbene towards the Sulphur Atom of 1,2,3-Benzothiadiazole

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Thermal decomposition of diphenyldiazomethane (1) at 87 °C in chlorobenzene in the presence of 1,2,3-benzothiadiazole (2) afforded 9-phenylthioxanthen (3), 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (4), 6-benzhydryl-6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (5) and thianthren (6). Reaction products are explained in terms of attack on the sulphur atom of (2) by triplet diphenylcarbene, leading to decomposition of the heterocyclic nucleus with loss of nitrogen and formation of a diradical intermediate (7), from which products (3)—(6) can arise. Some evidence is presented that benzothidiazole (2) may act as an an effective spin-trap for triplet diphenylcarbene, thus preventing reversible interconversion of singlet and triplet states.

STRONGLY electrophilic carbenes substituted by electron-withdrawing substituents are known to attack the non-bonding electron pair of the sulphur atom of alkyl and aryl sulphides to give stable sulphur ylides.[1,2] Vinyl sulphides, thiophen, and dibenzothiophen, in which the sulphur lone pair is highly delocalized, have also been found to be efficient traps for such carbenes and to form stable sulphur ylides.[1]

As for less electrophilic carbenes, such as aryl- and diaryl-carbenes, reactions with alkyl and allylic sulphides have been found to lead to products which presumably arise from rearrangement of the unstable sulphur ylides first formed.[3]

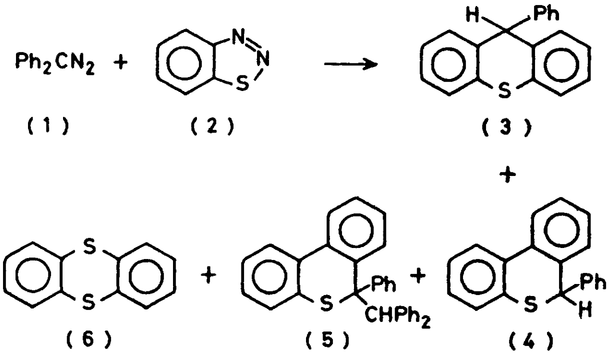
Reactions are all assumed to occur by electrophilic attack of singlet carbenes on the sulphur atom; no evidence of radical attack by triplet carbenes has been so far reported. In this paper we wish to report the first definite example of radical attack on the sulphur atom by triplet carbenes, obtained from a study of the reactivity of diphenyldiazomethane (1) with 1,2,3-benzothiadiazole (2) (BTD). This substrate was selected in view of its great reactivity towards radical species which attack the sulphur bringing about decomposition of the heterocyclic nucleus with loss of nitrogen;[4] moreover, there is some very recent evidence that triplet arylnitrenes[5] are also capable of adding to the sulphur atom of BTD.

RESULTS AND DISCUSSION

Thermal decomposition of diphenyldiazomethane (1) (0.4M) at 87 °C in chlorobenzene containing a two-fold excess of BTD for *ca.* 12 h (until disappearance of the diazo-band at 2 100 cm^{-1} was observed in the i.r. spectrum) gave, after column chromatography; (*i*) 9-phenylthioxanthen (3) (5%); (*ii*) 6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (4) (8%); (*iii*) 5-benzhydryl-5-phenyl-6*H*-dibenzo[*b,d*]thiopyran (5) (15%); and (*iv*) thianthren (6) (5%), as well as trace amounts of an unidentified product (Scheme 1).

Benzophenone (5%), benzophenone azine (20%), and traces of tetraphenylethylene and 1,1,2,2-tetraphenylethane were also isolated.

The structures of the hitherto unknown dibenzothiopyrans (4) and (5) were assigned on the basis of elemental analysis and spectral data, and by spectral comparison with specimens prepared by other routes. Compound (4) could also be prepared by treatment of an ether suspension of dibenzothiopyrylium perchlorate with an excess of phenylmagnesium bromide; metallation of (4) with n-butyl-lithium in dry tetrahydrofuran at 0 °C followed by reaction of the resulting lithium derivative with benzhydryl chloride led to the dibenzothiopyran (5)



SCHEME 1

Kinetic studies of the thermal decomposition of diphenyldiazomethane (1) in chlorobenzene at 87 °C showed the reaction to be first-order in diazo-compound (1) both in the absence and in the presence of BTD (rate constants are reported in Table 1).

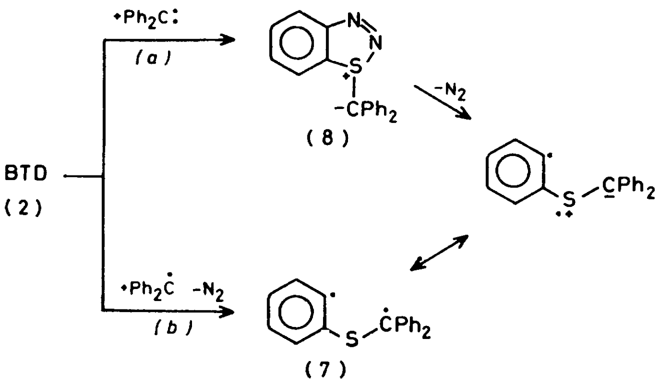
TABLE 1

Thermal decomposition of diphenyldiazomethane (1) in chlorobenzene at 87 °C in the presence of BTD

[Ph$_2$CN$_2$]/M	[BTD]/M	Rate constant/min^{-1}
0.20	0.00	1.2×10^{-2}
0.20	0.40	1.7×10^{-2}
0.20	2.00	2.3×10^{-2}

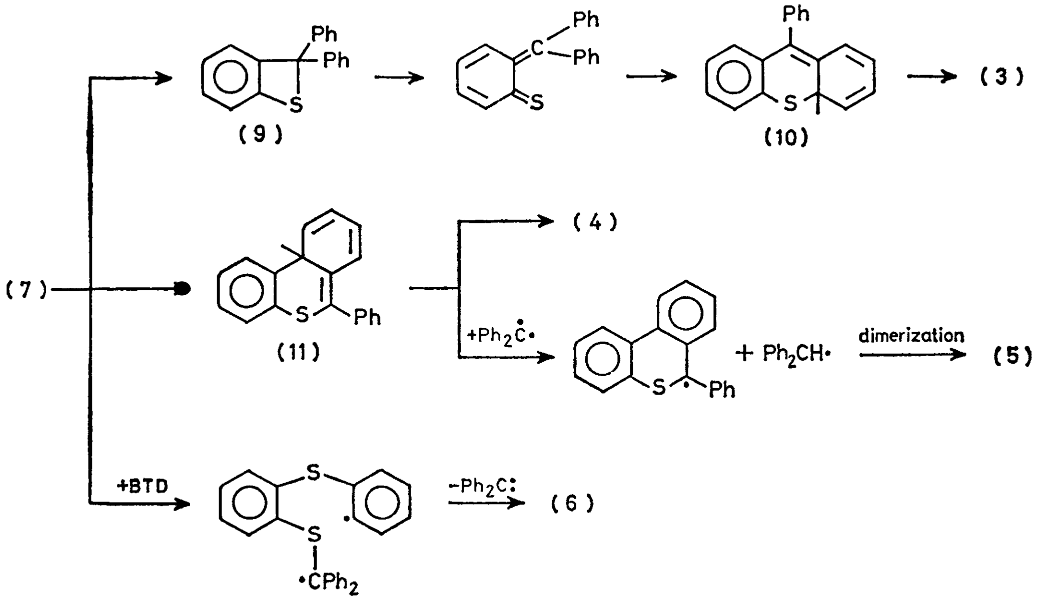
These findings would appear to indicate intermediate formation of diphenylcarbene in the decomposition of (1) in the presence of BTD, thus suggesting that diphenylcarbene (singlet or triplet) is the species reacting with BTD to give products (3)—(6). On the other hand some intervention of benzhydryl radicals, unlikely to be formed in such conditions, in the formation of products

(3)—(6) appears to be definitely ruled out by our observation that benzhydryl radicals, produced by thermolysis of azobis(diphenylmethane)[6] in refluxing benzene, are not capable of reacting with BTD.



Scheme 2

Reaction products (3)—(6) can be rationalized by assuming intermediate formation of diradical (7), arising from attack of diphenylcarbene (singlet or triplet) on the sulphur atom of BTD. In fact electrophilic attack by a singlet carbene might lead to ylide (8) and then to (7) by loss of nitrogen; on the other hand radical attack by a triplet carbene would afford (7) by a mechanism analogous to that by which BTD traps radicals[4] (Scheme 2).



Scheme 3

1,4-Cyclization of the diradical (7) would give benzothiete (9), from which 9-phenyl-4a*H*-thioxanthen (10) might be formed through ring-opening followed by electrocyclic closure;[7] aromatization of (10) would lead to 9-phenylthioxanthen (3).

1,6-Cyclization of (7) would afford (11), from which 6-phenyl-6*H*-dibenzo[*b*,*d*]thiopyran (4) would arise by aromatization. The small amounts of thianthren (6) can be ascribed to radical attack on the sulphur of BTD by diradical (7), by analogy with that exhibited by *ortho*-thio-substituted aryl radicals[4] (Scheme 3).

Formation of the dibenzothiopyran (5) might be attributed to further reaction of dibenzothiopyran (4) with diphenylcarbene. However this possibility appears to be ruled out by our independent experiments, which showed the reaction of diphenylcarbene with (4) to produce dibenzothiopyran (5) as well as a major product, which was assigned the structure of 6,6,7-triphenyl-6,7-dihydrodibenzo[*b*,*d*]thiepin (12).* Compound (12) was shown not to be formed from decomposition of diphenyldiazomethane (1) in the presence of BTD, and was found to be quite stable under the reaction conditions.

An alternative reasonable route leading to (5) might be hydrogen abstraction from (11) by triplet diphenylcarbene and dimerization of the resulting radicals.

From reactions carried out in more dilute chlorobenzene solutions of (1) (0.05M) containing BTD (0.1—1.2M) we observed that compound (5) was formed only in trace amounts and, more interestingly, that yields of (3) and (4) were independent of BTD concentration at BTD concentrations $\geqslant$0.2M, thus suggesting that BTD may be an effective diphenylcarbene (singlet or triplet) trap. The gradual increase in thianthren (6) yield observed with increasing BTD concentration appears to support the reaction pathway previously suggested for formation of (6), since intermolecular reaction of diradical intermediate (7) with BTD is expected to be favoured by increasing BTD concentration. These findings are collected in Table 2.

In order to throw light on the nature of the carbene species attacking the sulphur atom of BTD, we carried

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* Chemical and spectral evidence for compound (12), as well as a study of the mechanism of its formation, will be reported elsewhere.

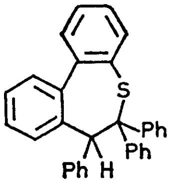
TABLE 2

Product yields * for thermal decomposition of diphenyldiazomethane (1) (0.05M) in chlorobenzene at 87 °C in the presence of BTD

[BTD]/M	Products (%) (3)	(4)	(6)
0.1	4.5	18	1
0.2	7	28	2
0.4	9	29	3
0.6	10	28	4
0.8	10	28	5
1.2	11	28	9

* Yields are based on starting diphenyldiazomethane; in all experiments benzophenone azine (10—20%), benzophenone (3—5%), and trace amounts of 6-benzhydryl-6-phenyl-6*H*-dibenzo[*b,d*]thiopyran (5) were also observed.

out a study of the decomposition of diphenyldiazomethane (1) (0.05M) both in toluene and in a suitable mixture of n-butyl alcohol–toluene in the presence of varying amounts of BTD. Thermal decomposition of (1) in toluene has been reported[8] to afford 1,1,2-triphenylethane (13), 1,1,2,2-tetraphenylethane (14), and 1,2-diphenylethane (15); these arise from hydrogen abstraction from the solvent by triplet diphenylcarbenes and couplings of the resulting benzhydryl and benzyl radicals formed; we observed that in the presence of BTD (0.4—0.8M), decomposition of (1) in toluene led to suppression of coupling products (13)—(15) with formation of compounds (3) and (4) in yields which were found to be independent of the BTD concentrations employed, analogous to the results from the corresponding reactions carried out in chlorobenzene solution. Results are reported in Table 3.



(12)

On the other hand n-butyl benzhydryl ether (16) was found to be formed in 65% yield from thermolysis of diphenyldiazomethane (1) in n-butyl alcohol solution; the formation of this product (16) is most reasonably ascribed to attack of singlet diphenylcarbene on the solvent, in line with the mechanism suggested for ether formation from diarylmethylenes and alcohols.[9]

TABLE 3

Product yields for thermal decomposition of diphenyldiazomethane (1) (0.05M) in toluene at 87 °C in the presence of BTD

[BTD]/M	Products (%) * (3)	(4)	(13)	(14)	(15)
0.0			25	12	12
0.4	6	28			
0.8	6	28			

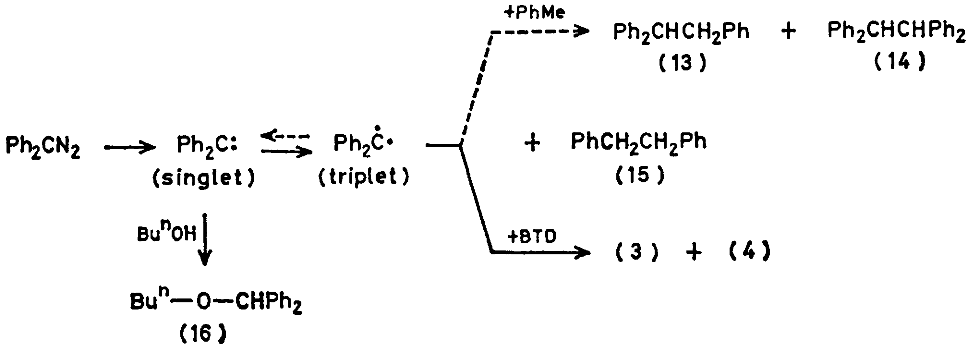
* Thianthren (6) was also formed; yields were not calculated.

Decomposition of phenyldiazomethane (1) in suitable solutions of n-butyl alcohol in toluene was found to afford mixtures of products arising from reaction of diphenylcarbene both with toluene and with n-butyl alcohol; in particular n-butyl benzhydryl ether (16) was obtained in 40% yield, together with products (13)—(15) in 20% overall yield, from decomposition of a toluene solution of (1) in the presence of n-butyl alcohol (0.1M). Thus thermal decomposition of (1) in toluene containing n-butyl alcohol (0.1M) and BTD (0.4M) would be expected to show suppression of triplet products with toluene [(13)—(15)] and little variation in the yield of ether (16), if triplet diphenylcarbenes were the species attacking the sulphur of BTD, whereas a drastic decrease in the yield of ether (16) would be expected if attack on the sulphur of BTD occurred by singlet carbenes. The data in Table 4 indicate that suppression of products (13)—(15) was accompanied by a noticeable decrease in the yield of (16); however, yields of (16), and of (3) and (4), were found to be

TABLE 4

Product yields for the thermal decomposition of diphenyldiazomethane (1) (0.05M) and n-butyl alcohol (0.1M) in toluene at 87 °C in the presence of BTD.

[BTD]/M	Products (%) (3)	(4)	(13)	(14)	(15)	(16)
0.0			10	5	5	40
0.4	4	15				19
0.8	4	17				22
1.2	4	16				19



SCHEME 4

practically unchanged over the range of BTD concentrations investigated (0.4—1.2M). These findings are consistent with triplet attack on the sulphur of BTD; singlet attack would reasonably lead to a decrease in the yield of ether (16) and an increase in the yields of (3) and (4) with increasing BTD concentrations.

Moreover, the lack of any appreciable variation in the yields of (16), (3), and (4) appears to indicate that BTD, acting as an effective spin-trap for triplet diphenylcarbenes, prevents a reversible interconversion of singlet and triplet states, at least for concentrations $\geqslant$0.4M. Such reversible interconversion, which has been previously suggested[10] for diphenylcarbene, appears to be occurring in the absence of BTD, as evidenced by the increased yield of the ether (8) obtained in this case.

EXPERIMENTAL

Diphenyldiazomethane (1)[11] and 1,2,3-benzothiadiazole (2)[12] were prepared as described in the literature. The reaction products 9-phenylthioxanthen (3),[13] thianthren (6), 1,1,2-triphenylethane (13),[8] 1,1,2,2-tetraphenylethane (14),[6] 1,2-diphenylethane (15),[5] benzhydryl n-butyl ether (16),[14] benzophenone, and benzophenone azine[15] were identified by mixed m.p. and spectral comparison (i.r. and n.m.r.) with authentic specimens, which were prepared according to the literature or were commercially available. G.l.c. analyses were performed on a Varian 1440 instrument (5% SP 2250 on Supelcoport column).

*6-Phenyl-*6H*-dibenzo*[b,d]*thiopyran* (4).—To a suspension of dibenzothiopyrylium perchlorate[16] (2.3 g) in dry ether (100 ml) was added an ether solution of phenylmagnesium bromide [from Mg (2.1 g) and bromobenzene (14 g) in dry ether (100 ml)]. The reaction mixture was stirred at room temperature for 1 h and then treated with an aqueous solution of ammonium chloride. The organic layer was dried and the solvent evaporated to give an oily residue which was chromatographed on a silica gel column. Elution with n-pentane gave *6-phenyl-*6H*-dibenzo*[b,d]*thiopyran* (1.2 g, 60%), m.p. 83—85 °C; *m/e* 274 (M^+), 273, 197, and 165; δ($CDCl_3$), 5.20 (1 H, s), 6.95—7.45 (11 H, m), and 7.72—7.90 (2 H, m) (Found: C, 82.7; H, 5.1; S, 11.5. $C_{19}H_{14}S$ requires C, 83.15; H, 5.15; S, 11.7%).

*6-Benzhydryl-6-phenyl-*6H*-dibenzo*[b,d]*thiopyran* (5).—A solution of (4) (0.27 g) in dry tetrahydrofuran (10 ml) was treated with 1.5N n-butyl-lithium (0.8 ml) at 0 °C. The resulting reddish mixture was stirred for 15 min, and then a solution of benzhydryl chloride (0.35 g) in tetrahydrofuran (5 ml) was added dropwise. The reaction mixture was stirred for 2 h, the solvent evaporated, and the crude product chromatographed on silica gel. Elution with n-pentane afforded the *title compound* (0.25 g, 57%), m.p. 208—210 °C; *m/e* 440 (M^+), 273, 242, 241, 197, and 165; δ($CDCl_3$) 5.24 (1 H, s), 6.64—6.80 (2 H, m), and 6.92—7.84 (21 H, m) (Found: C, 86.6; H, 5.5; S, 7.45. $C_{32}H_{24}S$ requires C, 87.25; H, 5.5; S, 7.3%).

Kinetic Experiments.—Kinetic measurements of the thermal decomposition of diphenyldiazomethane (1) were carried out at 87 °C in chlorobenzene solutions of (1) (0.20M) containing BTD (0.0, 0.4, and 2.0M). During the thermolyses portions were removed at regular intervals, diluted twenty-fold with chlorobenzene, and assayed by measuring the area of the diazo-band at 2 040 cm^{-1} in the i.r. spectrum. Concentrations of diphenyldiazomethane (1) were obtained from a previously prepared calibration curve. Disappearance of the diazo-compound (1) was followed over at least two half-lives and first-order kinetic plots of log [diphenyldiazomethane (1) concentration] *vs.* time were obtained, and the rate constants reported in Table 2 were determined from the slopes of the graphs.

Thermal Decomposition of Diphenyldiazomethane (1). *General Procedure.*—Solutions of diphenyldiazomethane (1) in the appropriate solvent were de-gassed by bubbling through a stream of nitrogen for 3 h and then kept at 87 °C for 12—14 h under nitrogen until disappearance of the diazo-band at 2 040 cm^{-1} in the i.r. spectrum was observed.

(*A*) *In chlorobenzene.* A solution of (1) (1.55 g) in chlorobenzene (20 ml) containing BTD (2.18 g) was allowed to react as described above. Column chromatography on silica gel (n-pentane as eluant) afforded (in order of elution): thianthren (6) (5%), tetraphenylethane (1—2%), 9-phenylthioxanthen (3) (5%), 6-phenyl-6*H*-dibenzo[*b*,*d*]thiopyran (4) (15%), small amounts (2%) of an unidentified product [m.p. 175 °C, *m/e* 440 (M^+)], and 6-benzhydryl-6-phenyl-6*H*-dibenzo[*b*,*d*]thiopyran (5) (15%). Elution with 20% ether–n-pentane gave benzophenone (5%) and benzophenone azine (13%).

Quantitative determination of reaction products was carried out by g.l.c. analysis of mixtures obtained from thermolysis of diphenyldiazomethane (1) (0.05M) in chlorobenzene containing BTD (0.1, 0.2, 0.4, 0.6, 0.8, and 1.2M). Results collected in Table 1 are the average of at least two independent experiments. Product (5) was not detectable by g.l.c., due to its thermal instability; however, t.l.c. analyses of these reaction mixtures showed (5) to be present only in trace amounts.

(*B*) *In toluene.* Thermal decompositions of (1) (0.05M) in toluene solution (10 ml) were carried out in the absence and in the presence of BTD (0.4 and 0.8M); the reaction mixtures were directly analysed by g.l.c. without manipulation. Results reported in Table 3 are the average of at least two independent experiments.

(*C*) *In n-butyl alcohol.* Column chromatography on silica gel (n-pentane as eluant) of the reaction mixture from decomposition of diphenyldiazomethane (1) (1.55 g) in n-butyl alcohol (20 ml) gave benzophenone (5%), benzophenone azine (5%), and benzhydryl n-butyl ether (16) (65%).

(*D*) *In n-butyl alcohol* (0.1M)*–toluene.* Reactions were carried out in solutions of diphenyldiazomethane (1) (0.05 M) in n-butyl alcohol (0.1M)–toluene solutions (10 ml) containing BTD (0.0, 0.4, 0.8, and 1.2M). Quantitative determination of the reaction products was effected by g.l.c. analysis of the reaction mixtures without manipulation. At least three independent experiments were performed in each case and the averaged results are collected in Table 4.

Thermal Decomposition of Azobis(diphenylmethane).—A solution of azobis(diphenylmethane)[6] (1.52 g, 4.2 mmol) and BTD (0.57 g, 4.2 mmol) in benzene (20 ml) was refluxed for 5 h. On filtration of the cooled reaction mixture, 1,1,2,2-tetraphenylethane (14) (1.40 g, 100%) was isolated; evaporation of the filtrate gave undecomposed BTD. No evidence of other products was found.

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REFERENCES

[1] W. Ando, *Acc. Chem. Res.*, 1977, **10**, 179.

[2] J. Dieckmann, *J. Org. Chem.*, 1965, **30**, 2272.

[3] W. Ando, M. Yamada, E. Matsozaki, and T. Migita, *J. Org. Chem.*, 1972, **37**, 3791.

[4] L. Benati, P. C. Montevecchi, A. Tundo, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1276; *J. Org. Chem.*, 1976, **41**, 1331.

[5] L. Benati, P. C. Montevecchi, and P. Spagnolo, *J. Chem. Soc. Chem. Commun.*, 1980, 715.

[6] S. Cohen and C. W. Wang, *J. Am. Chem. Soc.*, 1955, **77**, 2457.

[7] J. Nasielski and G. Jacquin, *Tetrahedron*, 1972, **28**, 597.

[8] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, 1969, **91**, 4549.

[9] D. Bethell, A. R. Hewall, and D. Whittaker, *J. Chem. Soc. B*, 1971, 23.

[10] D. Bethell, G. Stevens, and P. Tickle, *J. Chem. Soc., Chem. Commun.*, 1970, 792; D. Bethell, J. Hayes, and A. R. Newall, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1307; Carbenes,' eds. M. Jones and R. A. Moss, John Wiley and Sons, New York, 1973, vol. 1, pp. 76—77.

[11] L. I. Smith and K. L. Howard, *Org. Synth.*, Coll. vol. 3, 351.

[12] J. Jacobson and H. Jansen, *Liebigs Ann. Chem. Soc.*, 1893, **277**, 219.

[13] G. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, 1963, **85**, 2278.

[14] E. F. Pratt and J. D. Draper, *J. Am. Chem. Soc.*, 1949, **71**, 2846.

[15] S. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, 1957, **79**, 1924.

[16] A. Luttringhans and A. Kolb, *Z. Naturforsch.*, 1961, **166**, 762.