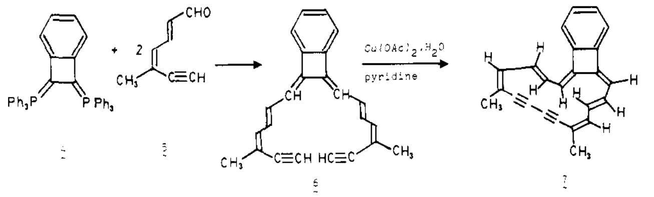
Scheme I



over 20 min gave annulene 7 in an isolated yield of less than 20% whereas a 51% yield was obtained when the addition was carried out over a period of 21.5 h.

The assignment of structure 7 to the cyclization product follows from the molecular model studies discussed earlier and was confirmed by proton NMR spectroscopy. The three inner olefinic protons resonate at low field (δ 10.00–9.20) whereas the five outer olefinic protons resonate at relatively high field (δ 6.40–5.52). These values are consistent with the magnetically induced paramagnetic ring current associated with [16]annulenes,[12] and as the phenyl protons resonate at similar chemical shifts in 6 and 7, it appears that the two ring systems in 7 are independent and that peripheral delocalization does not occur.[13]

Experimental Section

Melting points were determined on a Kofler hot-stage apparatus. Infrared (IR) spectra were recorded on a Unicam SP200 spectrophotometer in chloroform solution. Proton magnetic resonance spectra were recorded on a Varian T-60 or Varian HA-100 spectrometer with CDCl$_3$ as the solvent and tetramethylsilane as an internal standard. Mass spectra were determined with an AEI MS-9 or MS-12 spectrometer. Merck alumina (neutral, activity III) was used for column chromatography.

Bis-Wittig Reaction. 1,2-Dihydro-1,2-bis(triphenylphosphonio)benzocyclobutene dibromide[6] (1.34 g, 1.70 mmol) was suspended in dry THF (100 mL) and stirred at 0 °C under nitrogen. *n*-Butyllithium (1.97 M, 1.73 mL, 3.4 mmol) was added in one portion, and the mixture was stirred at 0 °C for 1 h to complete the formation of 1,2-dihydro-1,2-bis(triphenylphosphoranylidene)benzocyclobutene (4). (*E*,*Z*)-6-Methylhepta-2,4-dien-6-ynal (5; 0.4 g, 3.33 mmol) in THF (10 mL) was then added dropwise over 30 min to the red solution of the diylide, and the mixture was stirred at 0 °C for 1 h and then boiled under reflux for 2 h. After cooling, the reaction mixture was poured into water (100 mL) and extracted with three portions of ether (100 mL each). The organic extracts were combined and dried (MgSO$_4$), and the solvent was then removed under reduced pressure. The resulting oil was chromatographed on alumina, elution with ether–hexane (1:19) giving the *diacetylene* 6 (200 mg, 38%) as yellow-orange crystals from ether–hexane: IR ν_{max} 3300, 2100, 980 cm^{-1}; NMR δ 7.38–7.10 (4 H, m, aromatic), 7.00–6.16 (8 H, m, olefinic), 3.38 (2 H, s, 2C≡CH), 2.00 (6 H, s, 2Me).

Coupling Reaction. A solution of the diacetylene 6 (100 mg, 0.36 mmol) in pyridine (25 mL) was added dropwise over 21.5 h with a syringe pump to a rapidly stirred solution of copper(II) acetate monohydrate (3 g, 15.0 mmol) in pyridine (100 mL) at 50–60 °C under nitrogen. The reaction mixture was then stirred for another hour at 50 °C, cooled, poured into ice-cold 5% hydrochloric acid, and extracted with three portions of ether (50 mL each). The organic extracts were combined, washed with water, and dried (MgSO$_4$), and the solvent was then removed under reduced pressure. The resulting oil was purified by chromatography on alumina. Elution with ether–hexane (1:19) gave the *conjugated tricyclic product* 7 (51 mg, 51%) as purple needles (decomposing at 150 °C) from ether–hexane: IR ν_{max}(soln) 2200, 980 cm^{-1}; δ NMR 10.00–9.20 (3 H, m, olefinic), 7.22 (4 H, s, aromatic), 6.40–5.52 (5 H, m, olefinic), 1.68 (3 H, s, Me), 1.62 (3 H, s, Me): mass spectrum calcd for $C_{24}H_{18}$ *m*/*e* 306.1409, found *m*/*e* 306.1411.

Registry No. 4, 1820-39-9; 5, 55304-70-6; 6, 78871-08-6; 7, 78871-09-7; 1,2-dihydro-1,2-bis(triphenylphosphonio)benzocyclobutene dibromide, 78871-10-0.

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[12] Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811. Calder, I. C.; Gaoni, Y.; Garratt, P. J.; Sondheimer, F. *J. Am. Chem. Soc.* **1968**, *90*, 4954.

[13] Reprints of this paper will not be available.

A Caveat on the Use of Linear Free Energy Correlations with σ or σ^+ To Distinguish Transition-State Types. A Useful Graphic for the Selection of Substituents for a Linear Free Energy Study

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For nearly 50 years, the use of linear free energy relationships (LFER's) had dominated mechanistic organic chemistry[1] to the point that LFER's have become "fundamental" to the science.[2] The addition in 1958 of Brown's σ^+ substituent constants for electrophilic reactions[1c] "extended the validity range of the Hammet equation and allowed one to draw conclusions about conjugation in the transition state".[3] Thus, a data set which correlates with σ^+ but not with σ is thought to possess an electron-deficient site in the transition state which is in conjugation with an electron-donating substituent. In this paper we (a) demonstrate the importance of substituent selection in order to make a valid judgement regarding transition states and (b) present a graphic model to facilitate appropriate substituent selection.

We began to notice some time ago that certain data presented in the literature correlated with both σ and σ^+ to a reasonable degree.[4] An example from the recent literature[5] will suffice as an example: The rates of HCl-catalyzed *E*–*Z* isomerization of substituted *O*-methylbenzohydroximoyl chlorides were correlated in an LFER plot against σ, with $\rho = -0.65$ and $r = 0.993$ (the substrates utilized were *p*-OMe, *p*-Cl, H, *m*-Cl, and *p*-NO$_2$).[6] Against σ^+, the same five substituents afford $\rho = -0.47$ and $r = 0.980$. Thus an excellent[4] correlation is achieved with σ

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[1] (a) L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937); (b) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953); (c) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958); (d) L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963); (e) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963; (f) S. Ehrenson, *Prog. Phys. Org. Chem.*, **2**, 195 (1964); (g) C. D. Ritchie and W. F. Sager, *ibid.*, **2**, 323 (1964); (h) P. R. Wells, "Linear Free Energy Relationships", Academic Press, New York, 1968; (i) J. Shorter, *Q. Rev., Chem. Soc.*, **24**, 433 (1970); (j) N. B. Chapman and J. Shorter, Eds., "Advances in Linear Free Energy Relationships", Plenum, London, 1972; (k) K. F. Johnson, "The Hammett Equation", Cambridge University Press, New York, 1973; (l) M. Charton, *Prog. Phys. Org. Chem.*, **10**, 81 (1973); (m) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *ibid.*, **10**, 1 (1973); (n) J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley, New York, 1975; (o) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc., Jpn.*, **48**, 3356 (1975); (p) R. D. Topsom, *Prog. Phys. Org. Chem.*, **12**, 1 (1976); (p) S. H. Unger and C. Hansch, *ibid*, **12**, 91 (1976); (q) L. S. Levitt and H. F. Widing, *ibid.*, **12**, 119 (1976).

[2] T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", 2nd ed., Harper and Row, New York, 1981, pp 130–144.

[3] O. Exner, in ref 1j., p 33.

[4] Jaffe[1b] suggested the following terminology for describing the degree of correlation as measured by the correlation coefficient: $r > 0.99$, excellent; $r > 0.95$, satisfactory; $r > 0.90$, fair.

[5] J. E. Johnson, N. M. Silk, E. A. Nalley, and M. Arfan, *J. Org. Chem.*, **46**, 546 (1981).

[6] All values of r and ρ mentioned in this paper were calculated by using the σ and σ^+ values listed in ref 1c,d.

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Table I. Statistical Data for the Indicated Reaction of Substituted Benzenes

entry	reaction	n[a]	r (σ vs. σ^+)[b]	r (vs. σ)	ρ[c]	r (vs. σ^+)	ρ^+[d]	Δr[e]	ref
1	bromination (HOBr catal)	7[f]	0.835	0.819	−7.5	0.997	−5.8	0.178	9a
2	bromination (HOBr catal)	6[g]	0.952	0.962	−8.9	0.998	−5.7	0.036	9a
3	bromination (HOBr catal)	9[h]	0.970	0.973	−6.4	0.997	−6.1	0.024	9a
4	bromination (HOBr catal)	8[i]	0.982	0.987	−6.3	0.997	−6.1	0.010	9a
5	protodesilylation (H_2SO_4 catal)	12[j]	0.952	0.971	−6.0	0.991	−4.4	0.020	9b
6	protodesilylation (H_2SO_4 catal)	11[k]	0.975	0.989	−5.4	0.989	−4.6	0	9b
7	protodesilylation ($HClO_4$ catal)	14[l]	0.951	0.974	−8.3	0.994	−4.5	0.020	9c
8	protodesilylation ($HClO_4$ catal)	12[m]	0.969	0.981	−8.3	0.998	−4.5	0.017	9c
9	Beckmann rearrangement	6[n]	0.951	0.983	−1.9	0.969	−1.4	−0.014	9d
10	Beckmann rearrangement	5[o]	0.992	0.983	−1.9	0.987	−1.7	0.004	9d
11	ethylation ($GaBr_3$ catal)	11[p]	0.952	0.963	−2.9	0.982	−2.4	0.019	1d
12	bromination (uncatalyzed)	8[q]	0.830	0.733	−19.5	0.984	−12.2	0.251	1c
13	bromination (uncatalyzed)	15[r]	0.783	0.704	−19.8	0.980	−13.1	0.276	1d
14	bromination (uncatalyzed)	9[s]	0.950	0.942	−37.5	0.996	−13.6	0.054	1d

[a] Number of data points used in correlations. Selection of points to be deleted was accomplished by using Figure 1 and a straight edge. [b] Correlation coefficient (σ^+ vs. σ) using values for σ and σ^+ from ref 1c, d. [c] Reaction constant for rate data correlated against σ. [d] Reaction constant for rate data correlated against σ^+. [e] $\Delta r = r$ (vs. σ^+) − r (vs. σ). [f] *p*-Ph, *m*-Ph, *p*-*t*-Bu, *m*-*t*-Bu, *p*-Me, *m*-Me, and H. [g] Same as entry 1, with *p*-Ph deleted. [h] Same as entry 1, with *m*-CO_2H and *m*-NO_2 added. [i] Same as entry 3, with *p*-Ph deleted. [j] *p*-NO_2, *m*-Cl, *p*-Br, *p*-I, *p*-Cl, *m*-Ph, *m*-OMe, *p*-F, H, *p*-Ph, *p*-Me, and *p*-OMe. [k] Same as entry 5, with *p*-OMe deleted. [l] *p*-NMe_2, *p*-OH, *p*-OMe, *p*-Me, *p*-Et, *p*-*i*-Pr, *p*-*t*-Bu, *p*-Ph, *p*-$SiMe_3$, *m*-Me, H, *p*-F, *p*-Cl, and *p*-Br. [m] Same as entry 7, with *p*-*t*-Bu and *p*-$SiMe_3$ deleted. [n] *p*-Me, *p*-*t*-Bu, H, *p*-Cl, *p*-OMe, and *p*-NO_2. [o] Same as entry 9, with *p*-OMe deleted. [p] *p*-Me, *m*-Me, *p*-Ph, *m*-Ph, *p*-F, *m*-F, *p*-Cl, *m*-Cl, *p*-Br, *m*-Br, and H. [q] *p*-Me, *m*-Me, *p*-OMe, *m*-OMe, *p*-Ph, *m*-*t*-Bu, *p*-*t*-Bu, and H. [r] Same as entry 12, plus *p*-NHAc, *p*-OH, *p*-OPh, *m*-Ph, 2-naphthyl, *p*-Et, and *p*-*i*-Pr. [s] *p*-Me, *m*-Me, *p*-OH, *p*-OMe, *p*-Et, *p*-*i*-Pr, *m*-*t*-Bu, *p*-*t*-Bu, and H.

and a satisfactory[4] one with σ^+. It is not obvious that a difference in correlation coefficients (Δr) of 0.013 is significant for only five data points.[7]

The fact that the rate data correlates well with both σ and σ^+ suggests that *σ and σ^+ must therefore correlate with each other.* In fact, the correlation of σ with σ^+ for the five substituents used is good: $r = 0.960$.

To assess the degree of correlation between values of σ and σ^+, we have constructed the graphic in Figure 1 which presents values of σ^+ relative to values of σ for some 40 substituents. It can be seen that there is a rough correlation ($r = 0.947$) for the whole data set but very high correlations for selected subsets located with a straight edge. For example, a correlation of σ^+ vs. σ for *p*-CO_2Et, *m*-Br, *m*-F, *m*-OH, H, and *m*-Et affords $r = 1.000$. For the substituents *p*-Me, *m*-Br, *p*-CO_2Et, *p*-CF_3, *m*-CO_2Et, *m*-Cl, and *m*-Br, $r = 1.00$. Addition of the substituents *p*-OPh, *p*-CN, and *m*-NO_2 gives a correlation coefficient, r, of 0.994. The three substituent sets described possess linear correlations of σ^+ and σ values, even though a significant mixture of meta and para substitution is present. *A distinction between conjugated and nonconjugated transition states could not be made by using these sets of substituents.* Exner[8] has suggested the set *p*-OMe, *m*-Me, H, *p*-Cl, *m*-Cl, *m*-NO_2, and *p*-NO_2 (the *p*-OMe substituent is included to decide between σ or σ^+). For these seven substituents, σ^+ vs. σ affords $r = 0.955$; deleting *p*-OMe gives $r = 0.990$.

Table I lists correlation data for several reactions whose rate data[9] were used in the early analyses[1c,d] of the σ^+ constants. In the hypobromous acid catalyzed bromination of substituted benzenes[9a] for the substituents studied (Table I, entry 1), examination of Figure 1 provides a data set (Table I, entry 2) whose σ and σ^+ constants have an approximately linear relationship. Correlation of the rate data gives an excellent[4] correlation against σ^+ and a satisfactory[4] correlation against σ. Inclusion of *p*-Ph in the regression analysis (Table I, entry 1) lowers the σ/σ^+ correlation constant and destroys the correlation against σ, while the correlation against σ^+ remains excellent.[4] In a review article[1d] appearing some years after the original work,[1c] Brown presented the same data again, with points added for the *m*-CO_2H and *m*-NO_2 substituents (Table I, entry 3). An excellent[4] correlation was achieved against σ^+, while a satisfactory[4] one ensued against σ. Deletion of *p*-Ph from the data set (Table I, entry 4) affords ex-

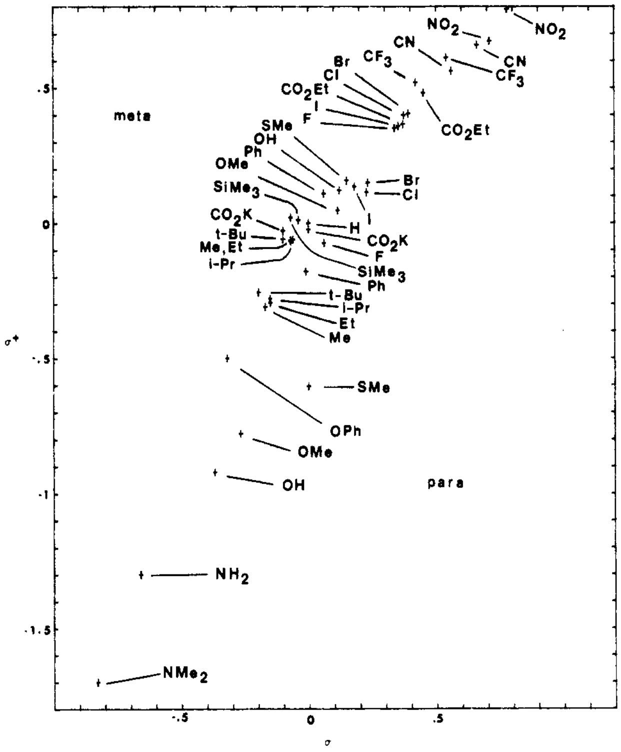

Figure 1. Relationship between σ^+ and σ values. Points for meta substituents are labeled to the left of the data set with para (and unsubstituted, H) substituents labeled to the right. Values of σ and σ^+ were taken from ref 1c,d.

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[7] We do not wish to challenge the conclusions drawn by the authors of ref 5, since their other evidence corroborates a transition state in which there is little or no conjugation in the rate-determining step.

[8] O. Exner, in ref 1j, p 50.

[9] (a) P. B. D. de la Mare and I. C. Hilton, *J. Chem. Soc.*, 997 (1962); (b) F. B. Deans and C. Eaborn, *ibid.*, 2299 (1959); (c) C. Eaborn, *ibid.*, 4858 (1956); (d) D. E. Pearson, J. F. Baxter, and J. C. Martin, *J. Org. Chem.*, 17, 1511 (1952).

cellent[4] correlation against σ^+ and satisfactory (but improved) correlation against σ. *Thus, mere inclusion of meta substituents may not always provide an easy distinction between valid correlations with σ or σ^+.*

Another interesting example of the problem is seen in the sulfuric acid catalyzed protodesilylation reaction of substituted benzenes[9b] (Table I, entries 5 and 6). Deletion of one substituent (identified by use of Figure 1 and a straight edge) affords a data set of 11 points (3 meta) which provide equally excellent[4] correlations with either σ or σ^+. Similar but less dramatic trends are seen for the perchloric acid catalyzed reaction[9c] (Table I, entries 7 and 8).

The Beckmann rearrangement of substituted acetophenones[9d] was shown by Brown[10] to correlate with σ^+. In fact, the data correlate better with σ than with σ^+ (Table I, entry 9). Deletion of one data point (located with Figure 1 and a straight-edge) improves the correlation against σ^+ to approximately the same level as σ. Interestingly, the point deleted is *p*-OMe, the very one which Exner[8] indicated should be included to decide on a correlation with σ^+. The poor showing of the Beckmann rearrangement data against σ^+ was explained by Pearson to be a result of incorrect σ^+ constants for alkyl groups.[11] He had earlier defined a set of constants for electrophilic reactions, which differ from the σ^+ constants most markedly for the alkyl groups.[9d] Brown ascribed the absence of large deviations from the regression line against σ as being due to the absence of any meta substituents in the data set.[10]

Two reactions which appear to be at the extremes for the magnitude of ρ are $GaBr_3$-catalyzed Friedel–Crafts ethylation and uncatalyzed bromination of substituted benzenes[1d] (Table I, entries 11–14). The reaction constant for the ethylation reaction of -2.4 (vs. σ^+) indicates a small substituent effect. The 11 substrates studied (Table I, entry 11) give a σ/σ^+ correlation coefficient of 0.952, and the rate data correlate satisfactorily[4] against both σ and σ^+. At the other end of the reaction constant scale is the uncatalyzed bromination, the textbook[2] example of differentiating correlations with σ and σ^+. In both articles presenting the σ^+ correlation,[1c,d] large differences in correlation coefficient were observed (Table I, entries 12 and 13). However, from the data a set of nine substituents may be selected (including two meta) with the use of Figure 1 and a straight edge, which afford a reasonably good σ/σ^+ correlation (Table I, entry 14). The correlation of rates against σ^+ improves from satisfactory[4] to excellent, while the correlation against σ improves from no correlation to fair.[4]

The importance of substituent selection appears to increase as the reaction, constant, ρ, decreases. The σ/σ^+ correlations for several entries in Table I are the same (0.951 ± 0.001 for entries 2, 5, 7, 9, 11, and 14). For these entries, Δr increases approximately with ρ and ρ^+ through the series (entry number) 9, 11, 5, 7, 2, 14.

In conclusion, the graphic presented in Figure 1 is a valuable tool in selecting appropriate substituents for an LFER study in which discernment of an electron-deficient conjugated transition state is desired. Substituents should be selected which provide poor σ/σ^+ correlations, especially if a small reaction constant is expected.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the University of Miami Research Council for support of this work.

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[10] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[11] P. J. McNulty and D. E. Pearson, *J. Am. Chem. Soc.*, 81, 612 (1959).

Preparation of 1,3,5-Triaminobenzene by Reduction of Phloroglucinol Trioxime

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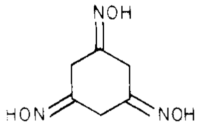
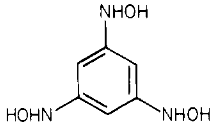
1,3,5-Triaminobenzene or its triacyl derivatives (**5**) have been prepared by catalytic hydrogenation of 1,3,5-trinitrobenzene with palladium on carbon[1] or Raney nickel[2] as catalysts. Since phloroglucinol trioxime (**1**) is nonexplosive and readily available, we have explored the reduction of **1** as a route to 1,3,5-triaminobenzene. Catalytic hydrogenation of **1** with Raney Ni in *n*-butyl acetate is a convenient method for preparing 1,3,5-triaminobenzene in high yield. Pd/C also catalyzes the hydrogenation of **1** in the presence of acetic anhydride to give **5**, in somewhat lower yield. Zinc in acetic acid/acetic anhydride converts **1** to **5** in good yield. The results are summarized in Table I.

Although Pd/C can be used for the hydrogenation of 1,3,5-trinitrobenzene,[1] it is not effective for the hydrogenation of **1** itself. The ^1H NMR spectrum of **1** in Me_2SO indicates that **1** exists as **1a** rather than **1b** (see Experimental Section), which may explain why **1** is not hydrogenated over Pd/C. On the other hand, acyl derivatives of **1** appear to exist in the aromatic form, and Pd/C catalyzes the hydrogenation of **1** in the presence of acetic anhydride. Excess acetic anhydride (6 molar equiv/mol of trioxime) is necessary to obtain good yields of **5**.



1a



1b

n-Butyl acetate is a good solvent for this reduction, whereas the more polar solvent acetic acid gives a low yield of **5**. The differences between the two solvents were revealed by following the reductions with TLC. In *n*-butyl acetate, the reduction proceeded slowly to give **4**–**6**; in acetic acid, hydrogen uptake occurred at the beginning of the reduction but gradually stopped, and TLC analysis showed the formation of **6**–**8** and only a small amount of **5**. All of these compounds were isolated, and their structures were assigned on the basis of their chemical and spectral properties. *n*-Butyl acetate is not a very good solvent for the reduction products, which precipitate on the catalyst and stop the hydrogenation; addition of a small amount of acetic acid to the initial reaction mixture gives better yields of **5**. The reaction sequence of eq 1 appears reasonable for the hydrogenation in *n*-butyl acetate. It appears that, in acetic acid, the hydroxy groups of the oxime are readily acetylated and that these acetoxy derivatives are not reduced. This surmise is supported by our observation that the triacetoxy derivative **8** is essentially unchanged by treatment with hydrogen and Pd/C in acetic acid at 80 °C.

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[1] H. Stetter, D. Theise, and G. J. Steffens, *Chem. Ber.*, **103**, 200 (1970).

[2] J. E. Gill, R. MacGillivray, and J. Munro, *J. Chem. Soc.*, 1753 (1949).

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