

High-yield acyl anion trapping reactions. Nucleophilic acylation of dialkyl disulfides, S-alkyl thioesters and elemental sulfur

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Table I. Rate Constants for the Exchange Reaction of 0.1 M (*p*-Xylene)tricarbonylchromium with Benzene at 170 °C in Benzene Containing (Hexamethylbenzene)tricarbonylchromium^a

concn of HMBCr(CO) ₃ , M	10 ⁷ k _{obsd} , s ⁻¹			
	b	c	d	e
0.18	12.4 ± 0.3	11.5 ± 0.3	12.1 ± 0.5	12.9 ± 0.8
0.155	9.5 ± 1.3	8.8 ± 0.3	9.7 ± 1.2	9.7 ± 0.6
0.12	7.5 ± 1.0	8.5 ± 0.3	8.2 ± 1.3	10.0 ± 0.5
0.08	6.8 ± 0.7	6.5 ± 0.1	6.7 ± 0.7	7.2 ± 0.4
0.055	4.0 ± 0.9	4.4 ± 0.3	4.4 ± 0.6	4.4 ± 0.2
0.00	2.0 ± 0.1	1.8 ± 0.1	1.8 ± 0.1	2.0 ± 0.1

^a Cyclohexane was employed as internal standard. ^b Obtained from disappearance of *p*-xylene complex CH₃ protons. ^c Obtained from appearance of (benzene)tricarbonylchromium. ^d Obtained from disappearance of *p*-xylene complex ArH protons. ^e Obtained from appearance of free CH₃ protons (*p*-xylene and hexamethylbenzene).

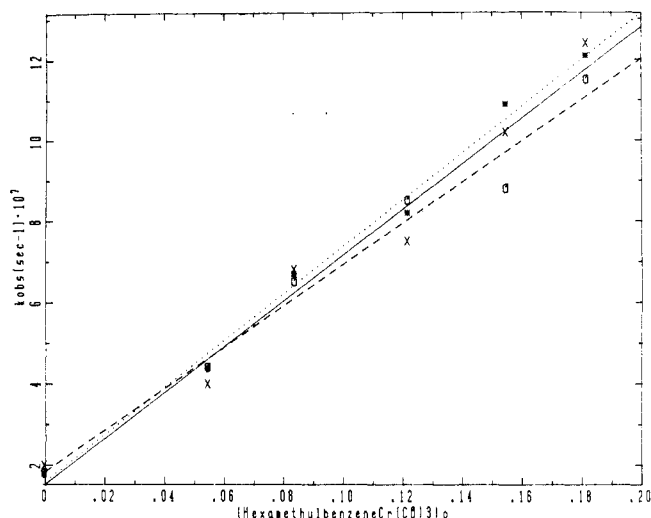


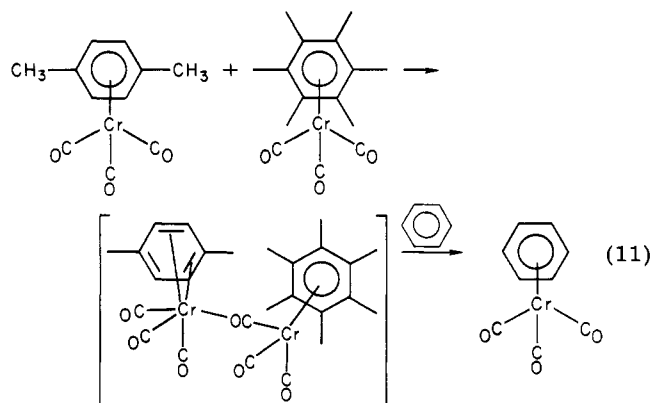
Figure 2. Plot of k_{obsd} vs. concentration of (hexamethylbenzene)tricarbonylchromium for arene exchange between (*p*-xylene)tricarbonylchromium and benzene in the presence of (hexamethylbenzene)tricarbonylchromium at 170 °C: × (—), k_{obsd} disappearance of (*p*-xylene)Cr(CO)₃-CH₃; ○ (---), k_{obsd} appearance of (benzene)Cr(CO)₃; * (···), k_{obsd} disappearance of (*p*-xylene)-Cr(CO)₃-ArH.

tricarbonylchromium, affords a mean second-order rate constant of $5.5 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ for the term

$$-\frac{d[\text{BZCr}(\text{CO})_3]}{dt} = k_2[(p\text{-xylene})\text{Cr}(\text{CO})_3][\text{HMBCr}(\text{CO})_3] + \dots \quad (10)$$

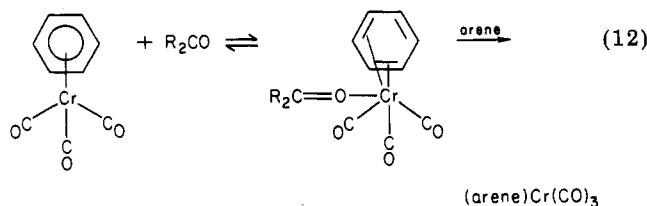
This value compares well with Strohmeier's values of $k_{\text{II}} = 1.5 \times 10^{-6}$ and $3 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ for the second-order terms in eq 1 for Ar = benzene and toluene, respectively.

We suggest a novel catalytic function of an (arene)tricarbonylchromium complex illustrated for our reaction shown in eq 11. Thus we have confirmed Strohmeier's

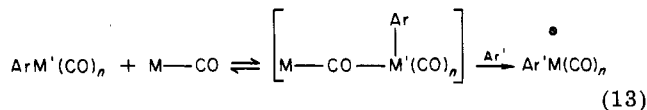


kinetic studies but eliminated both the proposed mecha-

nisms.⁷ In this catalysis the lone pairs on the bound CO are proposed to function in the manner suggested for the catalysis of these reactions by ketones, ethers, and nitriles (eq 12).^{3,8}



The increase of k_{II} in the order benzene complex < toluene complex < HMB complex accords with this proposal. It seems likely that such metal carbonyl catalysis is a general phenomenon.



Further details of catalyzed and uncatalyzed exchange reactions are discussed elsewhere.⁸

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE 81-20969) for financial support of this research.

Registry No. (*p*-Xylene)Cr(CO)₃, 12129-27-0; (hexamethylbenzene)Cr(CO)₃, 12082-08-5; (benzene)Cr(CO)₃, 12082-08-5; benzene, 71-43-2.

(7) We have shown that a labeled Cr(¹³CO)₃ group can be exchanged intact in the presence of ¹²CO, eliminating the mechanism of eq 4.⁸

(8) Traylor, T. G.; Stewart, K.; Goldberg, M., submitted for publication.

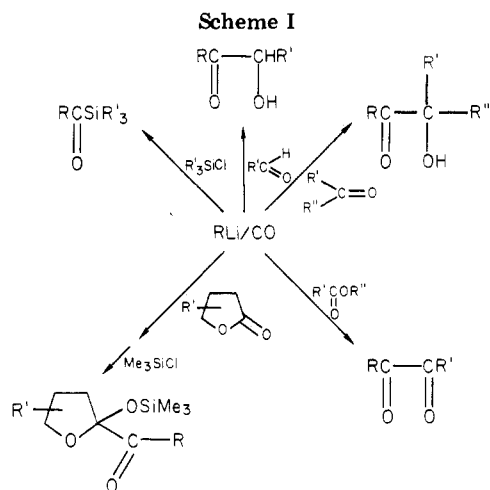
High-Yield Acyl Anion Trapping Reactions. Nucleophilic Acylation of Dialkyl Disulfides, *S*-Alkyl Thioesters, and Elemental Sulfur

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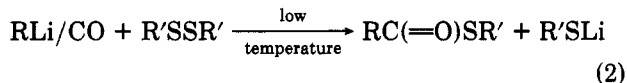
Summary: Organic disulfides may be acylated to give *S*-alkyl thioesters in good yield by the RLi/CO in situ procedure at very low temperatures. Similar nucleophilic acylation, at -78 °C, of elemental sulfur, followed by addition of iodomethane, gives RC(O)SMe.



In previous communications we have described the nucleophilic acylation of aldehydes,¹ ketones,^{1,2} esters,^{1,2} lactones,³ and trialkylchlorosilanes⁴ by means of the in situ RLi/CO system at very low temperature ($-110\text{ }^{\circ}\text{C} \rightarrow -135\text{ }^{\circ}\text{C}$) (Scheme I). The nucleophilic cleavage of organic disulfides by organolithium⁵ (eq 1) and organo-



magnesium^{5a,b,6} reagents is well-known, and thus the nucleophilic acylation of organic disulfides seemed an interesting possibility (eq 2). If successful, such reactions would provide a new route, based on readily available starting materials, to *S*-alkyl thioesters.



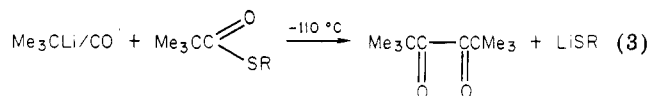
We have found that the reaction shown in eq 2 is easily effected. In a typical example, a 500-mL three-necked flask equipped with a mechanical stirrer, a Claisen adapter (fitted with a low-temperature thermometer and a gas outlet tube), and a no-air stopper which held a gas dispersion tube (which was connected to a carbon monoxide cylinder) was charged with 130 mL each of dry THF and diethyl ether, 40 mL of pentane, and 1.5 mL (9.55 mmol) of di-*n*-propyl disulfide. This solution was cooled to $-110\text{ }^{\circ}\text{C}$, and carbon monoxide was bubbled in for 30 min. Then a solution of *n*-butyllithium (2.54 M in hexane, 3.70 mL, 9.4 mmol) was added at a rate of 0.24 mL/min by means of a syringe pump (Orion Research, Inc., Model 341). After the addition had been completed, the now yellow reaction mixture was stirred at $-110\text{ }^{\circ}\text{C}$ under CO for 2 h and then was allowed to warm to room temperature while the CO stream was continued. After hydrolysis with saturated NH_4Cl solution, the organic layer was separated, dried, and concentrated (9-in. Vigreux column). GLC analysis of the

Table I. In Situ Nucleophilic Acylation of Disulfides and Elemental Sulfur^a

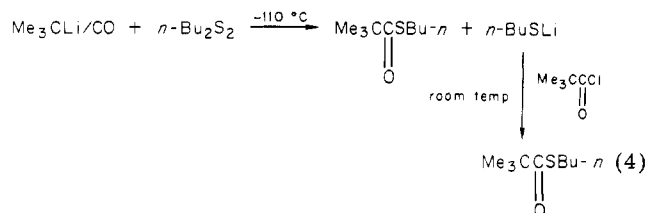
RLi	sulfur compds	product (% yield) ^b
<i>t</i> -BuLi	MeSSMe	<i>t</i> -BuC(O)SMe (66)
<i>n</i> -BuLi ^c	MeSSMe	<i>n</i> -BuC(O)SMe (78)
<i>t</i> -BuLi	<i>n</i> -PrSSPr- <i>n</i>	<i>t</i> -BuC(O)SPr- <i>n</i> (71)
<i>sec</i> -BuLi	<i>n</i> -PrSSPr- <i>n</i>	<i>sec</i> -BuC(O)SPr- <i>n</i> (74)
<i>n</i> -BuLi	<i>n</i> -PrSSPr- <i>n</i>	<i>n</i> -BuC(O)SPr- <i>n</i> (73)
<i>t</i> -BuLi	<i>n</i> -BuSSBu- <i>n</i>	<i>t</i> -BuC(O)SBu- <i>n</i> (73)
<i>sec</i> -BuLi	<i>n</i> -BuSSBu- <i>n</i>	<i>sec</i> -BuC(O)SBu- <i>n</i> (76)
<i>n</i> -BuLi	<i>n</i> -BuSSBu- <i>n</i>	<i>n</i> -BuC(O)SBu- <i>n</i> (81)
<i>t</i> -BuLi	<i>i</i> -PrSSPr- <i>i</i>	<i>t</i> -BuC(O)SPr- <i>i</i> (55)
<i>n</i> -BuLi	<i>i</i> -PrSSPr- <i>i</i>	<i>n</i> -BuC(O)SPr- <i>i</i> (63)
<i>t</i> -BuLi	(MeI)	<i>t</i> -BuC(O)S(CH ₂) ₄ SMe (63)
<i>n</i> -BuLi	(MeI)	<i>n</i> -BuC(O)S(CH ₂) ₄ SMe (55)
<i>t</i> -BuLi	(MeI)	<i>t</i> -BuC(O)S(CH ₂) ₅ SMe (68)
<i>n</i> -BuLi	(MeI)	<i>n</i> -BuC(O)S(CH ₂) ₅ SMe (62)
<i>t</i> -BuLi ^{d,e}	S ₈ (MeI)	<i>t</i> -BuC(O)SMe (57)
<i>t</i> -BuLi ^e	S ₈ (MeI)	<i>t</i> -BuC(O)SMe (45)
<i>sec</i> -BuLi ^{d,e}	S ₈ (MeI)	<i>sec</i> -BuC(O)SMe (51)

^a Using the procedure given in the text unless otherwise noted, reactions were carried out by using 1:1 $RLi/$ substrate stoichiometry at $-110\text{ }^{\circ}\text{C}$. ^b Yield based on RLi charged. ^c Reaction carried out at $-135\text{ }^{\circ}\text{C}$. ^d Reaction carried out at $-78\text{ }^{\circ}\text{C}$. ^e 1:2 RLi/S stoichiometry used.

residue showed the presence of *S*-*n*-propyl thiopentanoate, $n\text{-C}_4\text{H}_9\text{C(O)SC}_3\text{H}_7\text{-}n$, n^{20}_D 1.4597, in 73% yield.⁷ The other reactions that were carried out are summarized in Table I. A reaction temperature of $-110\text{ }^{\circ}\text{C}$ was found to be satisfactory; use of lower temperatures usually gave lower product yields. Lower yields of thioesters were obtained also at $-78\text{ }^{\circ}\text{C}$. In some reactions involving *tert*-butyllithium a 1,2-diketone, $t\text{-BuC(O)C(O)Bu-}t$, was a minor byproduct. This presumably was produced by the reaction of the $t\text{-BuLi/CO}$ reagent with the thioester (eq 3). Confirmation of such a process was given by a reaction of $\text{CH}_3\text{C(O)SC}_2\text{H}_5$ with the $t\text{-BuLi/CO}$ reagent at $-110\text{ }^{\circ}\text{C}$ (1:1 $t\text{-BuLi/}$ thioester stoichiometry) which gave $\text{Me}_3\text{CC(O)C(O)Me}$ in 67% yield.



If the acyl halide corresponding to the acyllithium used is available, then the yield of the thioester can be effectively more than doubled. Equation 4 illustrates this in



the case of the $t\text{-BuLi/CO}$ reagent. The yield of $\text{Me}_3\text{CC(O)SBu-}n$ obtained when pivaloyl chloride was added to the reaction mixture after it had warmed to room tem-

(1) D. Seyferth, R. M. Weinstein, W.-L. Wang, and R. C. Hui, *Tetrahedron Lett.* **1983**, 24, 4907.

(2) D. Seyferth, R. M. Weinstein, and W.-L. Wang, *J. Org. Chem.*, **48**, 1144 (1983).

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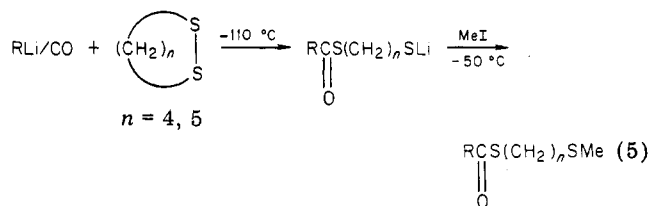
(5) (a) B. J. Wakefield, "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974; pp 192, 214. (b) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959). (c) L. Field in "Organic Chemistry of Sulfur", S. Oae, Ed., Plenum Press: New York, 1977; pp 356-7.

(6) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances"; Prentice-Hall: New York, 1954; p 1301.

(7) This and all other new compounds have been fully characterized (always C and H and sometimes S analysis; IR and ¹H NMR spectra).

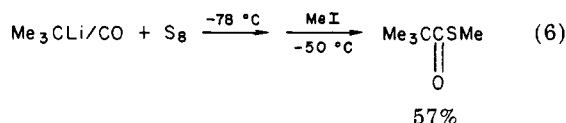
perature was 171% based on *t*-BuLi (or 85.5% based on both *n*-BuS units of the disulfide).

Such nucleophilic acylations of cyclic disulfides are of special interest in that the mercaptide leaving group (cf. eq 2) is retained in the acylation product (eq 5). In such



a reaction of the *t*-BuLi/CO reagent with 1,2-dithiane ($n = 4$) the methylated product $\text{Me}_3\text{CC}(\text{O})\text{S}(\text{CH}_2)_4\text{SMe}$ was obtained in 63% yield. Similar reactions are listed in Table I.

In view of this facile nucleophilic acylation of organic disulfides, it was of interest to see if the acylation of elemental sulfur, *cyclo*-S₈, also could be effected. (Elemental sulfur, it is known,⁶ reacts with alkylolithiums to give lithium alkyl mercaptides, RSLi.) Such a reaction does indeed occur (eq 6). The yield of thioester was lower (45%) when



the reaction was carried out at -110°C . In both reactions the 1,2-diketone, *t*-BuC(O)C(O)Bu-*t*, was a minor byproduct. The *sec*-BuLi/CO reagent reacted with elemental sulfur at -78°C , and after treatment of the reaction mixture with iodomethane the yield of *sec*-BuC(O)SMe was 51%. With *n*-butyllithium this chemistry was not successful in that at -78°C the yield of *n*-BuC(O)SMe was only 5%, while the *n*-BuC(O)C(O)Bu-*n* yield was 32%. The provenance of the latter has not yet been established.

Direct nucleophilic acylation with in situ generated acyllithium reagents thus seems to be a rather generally applicable procedure. As noted, we have been able to acylate aldehydes, ketones, esters, lactones, and trialkylchlorosilanes, and now, organic disulfides, thioesters, and elemental sulfur have been added to this list. Further work in progress is aimed at the in situ nucleophilic acylation of still other organic, organometallic and inorganic electrophiles.

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Synthesis, Crystal and Molecular Structure, and Reactions of the Bridging Vinylidenedicobalt Complex $(\mu\text{-CCH}_2)(\text{CpCoCO})_2$. Reaction with Molybdenum Hydrides To Give a Heteronuclear Cluster Complex

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Summary: The first unsubstituted dicobalt μ -vinylidene complex $(\mu\text{-CCH}_2)(\text{CpCoCO})_2$ (**1**) has been synthesized

and characterized by X-ray diffraction. **1** is readily protonated by HBF_4 at the β -carbon to yield an isolable μ -ethylidyne salt, **2**, which in turn is reduced by NaBH_4 to give the corresponding μ -ethylidene complex **3**. Complex **3** is also formed on treatment of **1** with H_2 at 60°C , but under these conditions competitive hydrogenolysis of **3** to ethane occurs. Reaction of **1** with $\text{CpMo}(\text{CO})_2(\text{L})\text{H}$ ($\text{L} = \text{CO}, \text{PPh}_3$) affords the mixed-metal cluster **4** in good yield, in a rational and potentially general route to μ -carbyne trinuclear systems. Possible mechanisms are briefly discussed.

As members of the important family of complexes containing a carbon bridging two or more metals, bridging vinylidene systems are particularly interesting in that the organic moiety is unsaturated. Therefore, in comparison with bridging alkylidene¹ and alkylidyne² complexes, they are expected to display unique reactivity at that site. Despite the fact that mono- and dinuclear vinylidene complexes of several transition-metal complexes are known,³ no simple cobalt vinylidene complex has yet been reported.⁴ In addition, aside from simple protonation reactions,^{3,10} the chemistry of bridging vinylidene complexes remains virtually unexplored.

We describe here the synthesis of a new μ -vinylidene system (**1**) by a route that exploits the versatile reactivity^{5,6} of the radical anion $[\text{CpCo}(\text{CO})]_2^-$, and the structural characterization of **1** by X-ray diffraction. Preliminary studies on the chemistry of **1** are also reported, including its reaction with mononuclear metal hydrides to afford a rational and potentially general route to μ -carbyne trinuclear cluster systems.

Addition of 1,1-dibromoethylene⁷ to a stirred suspension of $\text{Na}[\text{CpCo}(\text{CO})]_2$ at ambient temperature results in the appearance of new absorbances at 1796 (due to neutral dimer $[\text{CpCo}(\text{CO})]_2$) and at 1960 cm^{-1} in the IR spectrum of the solution. Purification by chromatography on neutral alumina II under air-free conditions affords the deep red (μ -vinylidene)bis($(\eta^5$ -cyclopentadienyl)carbonylcobalt] (**1**)⁸ in 40% of the theoretical yield (Scheme I). Only a single, presumably *trans* isomer could be detected by NMR and

(1) For reviews, see: (a) Herrmann, W. A. *Angew. Chem.* **1982**, *94*, 118. (b) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

(2) For reviews, see: (a) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97. (b) Dickson, R. S.; Fraser, P. J. *Ibid.* **1974**, *12*, 323.

(3) Dinuclear μ -vinylidene complexes have been reported for the following metals. (a) Mn: Foltling, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483. (b) Fe: Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911. Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499. (c) Ru: Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Taylor, G. E. *J. Organomet. Chem.* **1980**, *C43*, Cooke, M.; Davies, D. L.; Gherchais, J. E.; Knox, S. A. R.; Mead, K. A.; Roue, J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 862. (d) Rh: Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319. (e) Fe-Mn: Kolobova, N. E.; Ivanov, L. L.; Zhivanko, O. S.; Aleksandrov, G. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1982**, *228*, 265.

(4) To our knowledge the only cobalt complexes in the μ -vinylidene class are the monohalo- and dihalo-substituted (μ -butenolido)(μ -vinylidene)hexacarbonyldicobalt complexes reported by: Horvath, I. T.; Palyi, G.; Marko, L.; Andreotti, G. D. *Inorg. Chem.* **1983**, *22*, 1049.

(5) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 7436; **1977**, *99*, 1781.

(6) (a) White, M. A.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1979**, 1056. Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113. (b) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5694; *Organometallics* **1982**, *1*, 1571. (c) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464.

(7) Prepared by addition of $\text{CHBr}_2\text{CH}_2\text{Br}$ to a suspension of K_2CO_3 and KOAc in boiling ethanol. The dibromide is collected by distillation as an azeotrope with ethanol at 90°C . Verhulst, J.; van Hemelrijck, F.; Jungers, J. C. *Natuurwet. Tijdschr. (Ghent)* **1943**, *25*, 203.