

- [14] Vgl. Zusammenfassung *A. Albert*, *Angew. Chem.* **79**, 913 (1967).  
[15] *A. Albert, D. J. Brown & H. C. S. Wood*, *J. chem. Soc.* **1956**, 2066; *D. D. Perrin*, *J. chem. Soc.* **1962**, 645.  
[16] *C. Grundmann & A. Kreuzberger*, *J. Amer. chem. Soc.* **76**, 5646 (1954).  
[17] *H. C. van der Plas, B. Haase, B. Zuurdeeg & M. C. Voltering*, *Rec. Trav. chim. Pays-Bas* **85**, 1101 (1966); *J. B. Gullivan, J. S. Brinen & J. G. Koren*, *J. molecular Spectroscopy* **26**, 24 (1968).  
[18] *P. Caveng & H. Zollinger*, *Helv.* **50**, 861 (1967).  
[19] *P. Caveng, P. B. Fischer, E. Heilbronner, A. L. Miller & H. Zollinger*, *Helv.* **50**, 848 (1967).  
[20] *R. Foster & C. A. Fyfe*, *Rev. pure and appl. Chemistry* **16**, 61 (1966).  
[21] *G. Illuminati & F. Stegel*, *Tetrahedron Letters* **1968**, 4169; *P. Bemporad, G. Illuminati & F. Stegel*, *J. Amer. chem. Soc.* **91**, 6742, 6746 (1969).  
[22] *B. Bitter & H. Zollinger*, *Helv.* **44**, 812 (1961).

## 15. The $^{35}\text{Cl}$ Nuclear Quadrupole Resonance Frequencies of Complexes of Boron Trichloride

by **S. Ardjomand** and **E.A.C. Lucken**

Département de Chimie Physique. Section de Chimie, de l'Université de Genève, Sciences II, 30, Quai de l'Ecole de Médecine, 1211 Genève 4

(24 XI 70)

*Résumé.* Les fréquences de résonance quadripolaire du noyau  $^{35}\text{Cl}$  dans les complexes du trichlorure de bore avec une variété de donneurs organiques ont été mesurées à 77 K. Quoique ces fréquences dans l'accepteur soient assez peu sensibles à la nature du ligand, la tendance observée est en accord avec d'autres mesures du pouvoir donneur des ligands. Certains des ligands étudiés ici contiennent un atome de chlore et les changements de fréquence amenés par la complexation sont également en accord avec les résultats prévus. Le trichloroacétonitrile et le dichloroacétonitrile réagissent avec le trichlorure de bore pour donner un composé d'addition sur la triple liaison du groupement  $-\text{C}\equiv\text{N}$  plutôt qu'un complexe donneur-accepteur. Ce comportement est clairement mis en évidence par la spectroscopie de résonance quadripolaire.

**Introduction.** – The nature of the dative link between an electron-pair donor (D) and an electron-pair acceptor (A) has been the subject of much investigation. The strength of the bond varies with the nature of D and A, a great variety of methods having been employed to measure this quantity. Purely thermochemical measurements of equilibrium constants are of course open to the objection that no account is taken of the various intermolecular energies such as solvation energy which, in going from possibly rather non-polar reactants to a highly polar product, may be of considerable importance, so that of recent date attention has mostly been given to spectroscopic data of one sort or another. Most of these spectroscopic methods are indirect and the data rather tenuously related to the parameter under study, for example changes in an infra-red stretching frequency or in a nuclear magnetic resonance chemical shift.

Nuclear quadrupole coupling constants provide in principle a measure of the electron distribution at the particular nucleus studied and are thus a tool of choice for the study when the immediate environment of such a nucleus is maintained relatively constant, so that the unavoidable approximations which have to be made in

going from the observed coupling constants to the more loosely-defined 'chemically significant' quantities, such as ionic character, remain relatively constant. This latter condition is fulfilled when the nuclear quadrupole coupling constants of nuclei in a fixed donor or acceptor are measured for a variety of complexes and thus should provide a scale for measuring the relative donor or acceptor powers for various molecules interacting with a particular partner. In the light of these considerations we are investigating such systems and report here the results of the measurements of the  $^{35}\text{Cl}$  nuclear quadrupole resonance frequencies of complexes of the acceptor, boron trichloride, with a variety of electron-donating ligands.

**Experimental.** – *The complexes* were in general prepared by the dropwise addition under dry nitrogen of a cold, approximately 6.0M solution of the ligand in methylene chloride to a slight excess of a well stirred solution of a similar concentration of boron trichloride in methylene chloride cooled in a bath of acetone/solid carbon dioxide. Light petroleum ether (40–60°) previously cooled in acetone/solid carbon dioxide was then added and the whole stirred for several hours under a slight vacuum, the temperature being allowed to rise gradually to room temperature. The resultant solid complex was then filtered, washed with a 10:1 mixture of light petrol/methylene chloride and dried under vacuum.

*Tetramethylammonium tetrachloroborate* was prepared by a published method [1] and the complex with 4-chloropyridine was prepared by leaving 4-chloropyridinium tetrachloroborate, prepared as in [1], at room temperature under vacuum when it lost hydrogen chloride to give the desired product.

The complexes which have not previously been reported have the following characteristics:

*3,5-dichloropyridine · BCl<sub>3</sub>*: M.p. 172.5–175°. NMR. spectrum in methylene chloride: Free ligand:  $\delta_x = 8.41$  ppm,  $\delta_y = 7.67$  ppm; Complex:  $\delta_x = 9.22$  ppm,  $\delta_y = 8.24$  ppm.

$\text{C}_5\text{H}_3\text{BCl}_5\text{N}$  Calc. C 22.65 H 1.14 N 5.28% Found C 22.8 H 1.24 N 5.32%

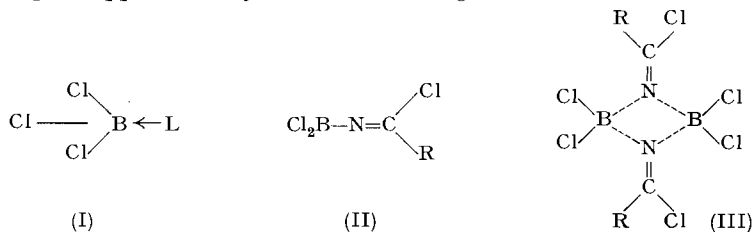
*Thioanisole · BCl<sub>3</sub>*: NMR. spectrum: Free ligand:  $\delta_{\text{CH}_3} = 2.48$  ppm; Complex:  $\delta_{\text{CH}_3} = 2.84$  ppm.

$\text{C}_7\text{H}_8\text{BCl}_3\text{S}$  Calc. C 34.8 H 3.3 S 13.3% Found C 35.1 H 3.4 S 13.2%

*Pure quadrupole resonance spectra* were observed on a self-quenched superregenerative oscillator constructed in this laboratory, employing frequency modulation and phase-sensitive detection. Frequencies were measured with a heterodyne BC221 frequency meter.

*Infra-red spectra* were observed on a Perkin-Elmer 521 grating spectrometer, and *nuclear magnetic resonance spectra* at 60 MHz on a Perkin-Elmer R12 spectrometer<sup>1)</sup>. Chemical shifts are reported with respect to tetramethylsilane (TMS):  $\delta = \text{H}_{\text{TMS}} - \text{H}_{\text{obs}}/14092 \times 10^6$ .

**Results and discussion.** – *The structure of the adducts.* As far as we can ascertain, none of the complexes studied here, and indeed no complexes of boron trichloride, have been the object of a structural determination. However in the complexes  $(\text{CH}_3)_3\text{N} \cdot \text{BF}_3$  [2] [3],  $(\text{CH}_3)_3\text{N} \cdot \text{B}(\text{CH}_3)_3$  [4], and  $\text{H}_3\text{N} \cdot \text{BF}_3$  [2], where the free boron compound has the trigonal planar structure [5], the  $\text{BR}_3$  fragment in the complex has taken up an approximately tetrahedral configuration.



<sup>1)</sup> Purchased with funds provided by the *Fonds National Suisse de la Recherche Scientifique*, Requête No 5202, whom we thank for their support.

Solution studies of many of these complexes have, however, established that they are monomeric 1:1 adducts [6], and it will be assumed in what follows that all the complexes have a structure in which the boron trichloride fragment remains intact and has a tetrahedral configuration, the fourth co-ordination position being taken up by the donor atom of the organic ligand I. One exception to this arises in complexes of certain nitriles, where it has been established that addition of boron trichloride across the  $-C\equiv N$  triple bond takes place to yield II or the dimeric form III.

Adducts with nitriles of both types have been studied here, and indeed the quadrupole resonance spectrum shows clearly which type of adduct has been formed.

A similar adduct across the double bond of the carbonyl group in certain ketones has also been occasionally suggested [7], but the infra-red spectrum of the only ketone complex studied here, namely benzophenone-boron trichloride, shows a strong absorption at  $1480\text{ cm}^{-1}$ , characteristic of a complexed carbonyl group [8], and no other  $^{35}\text{Cl}$  resonance than those given in Table 1. (The resonance frequency of the chlorine atom attached to the carbon atom in the compound  $\Phi_2\text{C}(\text{Cl})\cdot\text{OBCl}_2$  would, by analogy with the  $\alpha$ -chloroethers, probably be in the region of 30 MHz.)

*The interpretation of quadrupole resonance frequencies.* The  $^{35}\text{Cl}$  isotope has a nuclear spin quantum number of  $3/2$  and the pure quadrupole resonance frequencies,  $\nu_Q$ , are given by the relationship

$$\nu_Q = \frac{1}{2} e^2 Qq \left(1 + \frac{\eta}{3}\right)^{1/2} \quad (1)$$

where  $e^2 Qq$  is the nuclear quadrupole coupling constant and  $\eta$  is the asymmetry parameter.

Further studies, usually involving the application of a small magnetic field to the sample, are required to separate  $e^2 Qq$  and  $\eta$ . However if  $\eta$  is not too large ( $\sim 0.1$ ) the resonance frequency differs very little from  $1/2 e^2 Qq$ . At least for the resonances of the chlorine nuclei in the complexed  $\text{BCl}_3$  fragment, where little double-bond character of the B-Cl bond is to be expected, this condition is likely to be fulfilled, but this limitation should be born in mind throughout the discussion which follows.

The interpretation of these results will be based on the *Townes-Dailey* theory which ascribes the field gradients to the  $3p$  electrons of the chlorine atom. This theory and its limitations are discussed in detail in [9]. For the present purposes it will suffice to quote the approximate relationship between on the one hand the populations of the 'lone-pair' chlorine  $3p$  orbitals ( $a_x$  and  $a_y$ ) and of the bonding  $3p_z$  orbital,  $a_z$ , and on the other the quadrupole coupling parameters:

$$\frac{a_x + a_y}{2} - a_z = - \frac{e^2 Qq}{e^2 Qq_{\text{atomic}}}, \quad (2)$$

$$a_x - a_y = \eta \frac{2}{3} \frac{e^2 Qq}{e^2 Qq_{\text{atomic}}}, \quad (3)$$

where  $e^2 Qq_{\text{atomic}}$  is the coupling constant of the isolated chlorine atom (109.8 MHz). Although the sign of the coupling constant is not determined experimentally here, there is little doubt that all the coupling constants reported are negative, and this will be assumed henceforward.

*Frequencies of the chlorine atoms in the  $BCl_3$  fragment.* The resonance frequencies (MHz at 77K) of the complexes studied here are shown in Table 1. In most cases the only  $^{35}Cl$  nuclei are those belonging to the  $BCl_3$  group and the resonance frequencies all fall in the region of 21–22 MHz. For those compounds in which one or more chlorine atoms form part of the donor molecule there is no reasonable doubt that the frequencies in the 21–22 MHz region belong to the  $BCl_3$  group, while those at markedly higher frequencies arise from the chlorine atoms in the organic portion of the complex.

Table 1.  $^{35}Cl$  NQR. frequencies in boron trichloride complexes (MHz at 77 K)

Compound	Frequencies (MHz)
Boron trichloride [11]	21,580 21,585
Tetramethylammonium tetrachloroborate	20,76 21,24
4-Chloropyridine · $BCl_3$ <sup>a)</sup>	21,05 21,57 21,68 36,59
Tetrahydrofuran · $BCl_3$	21,04 21,76 21,91
$\gamma$ -Picoline · $BCl_3$	21,35 21,65 21,74
Benzophenone · $BCl_3$	21,46 21,82
Pyridine · $BCl_3$	21,55 21,82 21,87
Triphenylphosphine · $BCl_3$	21,72 21,79 21,85
3,5-Dichloropyridine · $BCl_3$ <sup>b)</sup>	21,88 21,96 22,27 37,47 37,92
Thioanisole · $BCl_3$	21,95 22,05 22,16
Nitrobenzene · $BCl_3$	22,08 22,20
Triethylamine · $BCl_3$	21,97 22,38
4-Chlorobenzonitrile · $BCl_3$ <sup>c)</sup>	22,16 22,27 22,39 35,86
Acetonitrile · $BCl_3$	22,30

a) 4-chloropyridine:  $\nu_Q = 34,739; 34,748; 35,031; 35,042$  MHz [12].

b) 3,5-dichloropyridine:  $\nu_Q = 35,601$  MHz [12].

c) 4-chlorobenzonitrile:  $\nu_Q = 35,17$  MHz.

For such complexes the resonance frequencies for the free donor are also shown. Two or three of these complexes have previously been studied by *Whitehead* [10]; our frequencies and his are in agreement within experimental error.

The obvious reference compound for the  $^{35}\text{Cl}$  quadrupole coupling constant of the chlorine atoms of the coordinated  $\text{BCl}_3$  group is the  $\text{BCl}_4^-$  anion. The isolated ion has undoubtedly tetrahedral symmetry and is isoelectronic with carbon tetrachloride. The tetrahedral symmetry imposes an asymmetry parameter identical with zero, and as a first approximation we may suppose that the  $3p$  lone-pair populations  $a_x$  and  $a_y$  are numerically equal to 2.0. The populations of the chlorine atom  $p\sigma$ -orbital is thus, according to Equation 1, 1.62, and hence the net charge on the boron atom is + 1.46. For the isoelectronic  $\text{CCl}_4$ , where the  $^{35}\text{Cl}$  coupling constant is 40.6 MHz, the  $p\sigma$ -population is 1.26 and the charge on the carbon atom + 1.04. This trend is to be expected from the relative electronegativities of boron and carbon.

It is of interest to compare the charge distribution in the  $\text{BCl}_4^-$  ion with that in the trigonal planar  $\text{BCl}_3$  molecule, whose pure quadrupole resonance frequencies are also given in Table 1. The field gradients in this molecule are undoubtedly highly asymmetric; for  $\text{BBr}_3$  and  $\text{BI}_3$   $\eta$  is  $0,45 \pm 0,05$  and 0.456 respectively [11] [13], and almost certainly is somewhat greater for  $\text{BCl}_3$ . If a value of  $\eta = 0,5$  is assumed, then according to Equation (1) the coupling constant in  $\text{BCl}_3$  is 41.46 MHz. If the chlorine atom  $3p$  population in the plane of the molecule is assumed to be 2.0, then the population of the  $3p\pi$  orbital is, according to Equation 3, 1.87 and hence, from Equation 2, the population of the  $3p\pi$  orbital is 1.56. The total charge on the boron atom is then  $3 - 3(2 - 1.56) - 3(2 - 1.87) = +1.29$ . This paradoxical result, implying that the central atom increases its positive charge on changing from a neutral molecule to an anion may well only reflect the inadequacies of the simple *Townes-Dailey* theory used here; but in the case of the tetrahedral anion it must not be forgotten that in a tetrahedral molecule (Symmetry  $T_d$ ) the lone-pair  $p$ -orbitals of the ligand atoms (belonging to the irreducible representations  $e + t_1 + t_2$ ) can also interact with the central atom  $p$ -orbitals (irreducible representation  $t_2$ ) and that some, albeit small, degree of electron transfer from these orbitals can take place. If 0.06 electrons from each  $3p_x$  and  $3p_y$  orbital are transferred in this way, the population of the  $3p_z$  orbitals yielded by Equation 2 rises to 1.68 and the charge on the boron atom drops to + 1.24, a result much more in agreement with expectation. This interaction is essentially one of hyperconjugation and we will return to this point below.

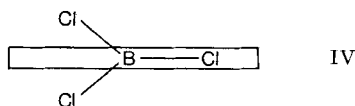
The most noticeable thing about the resonance frequencies of the complexed  $\text{BCl}_3$  group is their constancy over the wide variety of complexes prepared here. Thus the spread from the  $\text{BCl}_4^-$  ion to that of a weak complex such as that formed by nitrobenzene is only 1.0 MHz or 4.8% of the frequency of the  $\text{BCl}_4^-$  ion. This is in marked contrast to the results for the analogous  $\text{GaCl}_3$  complexes [14] where the corresponding spread is 2.3 MHz or 14.3% of the value of the frequency of the  $\text{GaCl}_4^-$  ion (16.1 MHz), or in the *trans* square-planar complexes of platinum or palladium dichloride where the spread of frequencies is as much as 20% [15]. One might conceivably suggest that this is due to the greater polarizability of heavy metals; however in compounds of the general formula  $\text{RCCl}_3$  the spread in resonance frequencies ( $\text{CH}_3\text{CCl}_3 = 37,829$  and  $38,052$ , MHz;  $\text{NC}\cdot\text{CCl}_3$ : 41.729, 41.666, 41.534 MHz) is some 3.4 MHz or 8.7%. The only other  $\text{MCl}_3$  group where such a low sensitivity to the nature of the substituent

has been observed is found in  $\text{RSiCl}_3$  compounds and in this case the anomalously high asymmetry parameter observed in  $\text{SiCl}_4$  [16] makes it possible that some sort of intermolecular bonding is occurring in the solid state, so that the results are not truly representative of the isolated  $-\text{SiCl}_3$  group. Further comment on this point—both the complexes described here and the silicon derivatives—must await the result of the determination of the asymmetry parameters and the detailed structures of the crystalline complexes.

Despite the comparative lack of sensitivity of the  $^{35}\text{Cl}$  resonance frequency of the chlorine atoms of the  $\text{BCl}_3$  group to the nature of the fourth ligand, the relative order of electron donor ability of these ligands which the results provide is similar to that observed for the  $\text{GaCl}_3$  complexes [13]. Thus the  $\text{BCl}_4^-$  ion has the lowest frequency and hence the highest ionic character of the B-Cl bond, while the much higher frequency of, say, the nitrile complexes indicates that here the electron donor ability of the nitrile group is much less than that of the  $\text{Cl}^-$  ion. Likewise triethylamine is, as expected, a better donor than tetrahydrofuran.

On the assumption that all these complexes are essentially monomeric 1:1 adducts in which the  $\text{BCl}_3$  fragment retains its identity, then there will be in general three distinct resonances in the 21 MHz region. Certain of the compounds in which the organic ligand has a three-fold or potentially three-fold symmetry axis (triphenylphosphine, triethylamine and acetonitrile) could conceivably show only one  $^{35}\text{Cl}$  resonance. This would however require that the three-fold axis be retained in the solid state, and only in acetonitrile is this phenomenon observed.

Some of the compounds of planar ligands in which the boron atom would be expected to reside also in the molecular plane (benzophenone, nitrobenzene) show only two resonances of unequal intensity. Unless it is accidental, this implies that two of the chlorine atoms are equivalent in the complex and hence that one of the chlorine atoms also lies in the molecular plane (IV).



This point is of interest in connection with the possible 'hyperconjugation' referred to above. The chlorine-boron bond in the molecular plane is necessarily unaffected by hyperconjugation with the organic ligand so that the difference between the two frequencies is a measure of the hyperconjugative interaction which, for the above compounds, thus appears to be rather small. It must be concluded therefore that the *Townes-Dailey* theory cannot cope well with the considerable change in environment of the chlorine atoms going from planar  $\text{BCl}_3$  to tetrahedral  $\text{BCl}_4^-$ . The fault probably lies in assuming that the field gradient produced by the  $3p_x$  and  $3p_y$  electrons is both constant and equal to the field gradient produced by the  $3p_z$  electrons [9].

*The chlorine atoms in the ligand molecules.* The expected effect of complexation on chlorine atom on a ligand would be to decrease the ionic character of the C-Cl bond owing to the partial positive charge built up on the donor atom.

This general expectation is fulfilled in the compounds investigated here, although when the chlorine atom is attached to an aromatic ring, change in conjugative interactions can also take place. A more detailed discussion must thus await the determination of asymmetry parameters.

*The adducts of BCl<sub>3</sub> with trichloroacetonitrile and dichloroacetonitrile.* The <sup>35</sup>Cl pure quadrupole resonance of these two compounds are given in Table 2. They show at once that the adducts cannot have the structure I since, for example, for the trichloroacetonitrile adduct there are four separate frequencies in the high frequency region, three in the neighbourhood of 40 MHz, corresponding to the three chlorine atoms of the trichloromethyl group and a fourth resonance at a much lower point. The resonances in the 21 MHz region are, on the other hand, composed of a closely spaced doublet. Thus one of the chlorine atoms originally attached to boron has changed its position and is bonded to a more electronegative atom. This conclusion that the structure is not simply an adduct with the type I structure is confirmed by the absence in the infra-red spectrum of an absorption in the region of 2200 cm<sup>-1</sup>, typical of a complexed nitrile group [17] (2248 cm<sup>-1</sup> in the free nitrile) and structure II or III is indicated by the presence of a band at 1617 cm<sup>-1</sup>, typical of a carbon-nitrogen double bond.

Table 2. <sup>35</sup>Cl NQR. frequencies in boron trichloride adducts with the chloroacetonitriles (MHz at 77 K)

Compound	Frequencies (MHz)
Chloroacetonitrile · BCl <sub>3</sub> <sup>a)</sup>	22,12
	22,32
	22,53
	22,66
	41,32
	41,59
Dichloroacetonitrile · BCl <sub>3</sub> <sup>b)</sup>	22,12
	22,22
	36,85
	37,01
	38,59
	38,81
Trichloroacetonitrile · BCl <sub>3</sub> <sup>c)</sup>	39,23
	23,08
	23,16
	37,82
	40,26
	41,16
	41,68

a) Chloroacetonitrile:  $\nu_Q = 38,125$  MHz [18].

b) Dichloroacetonitrile:  $\nu_Q = 39,443; 39,754; 39,923; 40,048$  MHz [18].

c) Trichloroacetonitrile:  $\nu_Q = 41,553; 41,666; 41,730$  MHz [18].

Up to this point we are in complete agreement with a recent extensive investigation of complexes of this kind [19]. However the molecular weight of this compound, determined by cryoscopy in benzene, was  $260 \pm 11$  (3 determinations) (C<sub>2</sub>BC<sub>6</sub>N

requires 261.6) and we thus formulate it as II, whereas in [19] the compound is formulated as III. A further important difference concerns the monochloroacetonitrile adduct. The resonance frequencies in Table 2 show clearly that the compound we have prepared has the structure I, as does the infra-red spectrum ( $\nu_{C\equiv N} = 2338 \text{ cm}^{-1}$ ); however *Meller & Ossko* formulated this compound as III [20]. It is possible that all three forms of these complexes can exist in some cases and that the product obtained depends critically on the reaction conditions. Further investigations of this point are under way.

## BIBLIOGRAPHY

- [1] *W. Kynaston, B. E. Larcombe & H. S. Turner*, J. chem. Soc. 1960, 1772.  
 [2] *A. M. Prokhorov & G. P. Shipulov*, Optics and Spectroscopy 8, 218 (1960).  
 [3] *S. Geller & J. L. Hoard*, Acta crystallogr. 4, 399 (1951).  
 [4] *D. R. Lide, R. W. Taft & P. Love*, J. chem. Physics 31, 561 (1969).  
 [5] *H. A. Levy & L. O. Brockway*, J. Amer. chem. Soc. 59, 2085 (1937).  
 [6] *F. G. A. Stone*, Chem. Reviews 58, 101 (1958).  
 [7] *R. J. Gillespie & J. S. Hartman*, Canad. J. Chemistry 46, 2147 (1968).  
 [8] *P. N. Gates, E. J. McLauchlan & E. F. Mooney*, Spectrochim. Acta 21, 1445 (1965).  
 [9] *E. A. C. Lucken*, Nuclear Quadrupole Coupling Constants, Chap. 7, Academic Press Inc., New York 1969.  
 [10] *M. Kaplansky & M. A. Whitehead*, Canad. J. Chemistry 48, 697 (1970).  
 [11] *T. Chiba*, J. physic. Soc. Japan 13, 860 (1958).  
 [12] *J. P. Bray, S. Moskowitz & H. O. Hooper*, J. chem. Physics 28, 99 (1958).  
 [13] *W. G. Saurita & W. S. Kooki*, J. Amer. chem. Soc. 81, 3179 (1959).  
 [14] *D. A. Tong*, Chem. Commun. 1969, 790.  
 [15] *C. W. Fryer & J. A. S. Smith*, J. organometall. Chemistry 18, P35 (1969).  
 [16] *J. D. Greybeal & P. J. Green*, J. physic. Chemistry 73, 2947 (1969).  
 [17] *W. Gerrard, M. F. Lappert, H. Physzora & J. W. Wallis*, J. chem. Soc. 1960, 2182.  
 [18] *J. Graybeal*, J. chem. Physics 62, 483 (1958).  
 [19] *A. Meller & W. Maringgele*, Mh. Chem. 99, 2504 (1968).  
 [20] *A. Meller & A. Ossko*, Mh. Chem. 100, 1187 (1969).

## 16. Pyrolysen- und Hydrierungsversuche in der Elemol- und Dihydrogeijeren-Reihe

von **C. Ganter** und **Frau B. Keller-Wojtkiewicz** [1]

Laboratorium für Organische Chemie der Eidg. Technischen Hochschule, Zürich

(27. XI. 70)

*Summary.* 1. The pyrolysis of elemol (**1**) in the presence of benzoic or *p*-nitrobenzoic acid, and of elemyl-*p*-nitrobenzoate (**3**) was studied. From the many products formed, the compounds **6**, **7**, **8**, **10**, **11**, **14**, **15**, and **18** were isolated and identified. On the basis of systematic experiments in the elemol (**1**) and dihydrogeijerene (**26**) series the sequence of the formation of these products could be determined. Several factors influencing the compositions of the pyrolysis mixtures are discussed.

2. The products of pyrolysis of both series [elemol (**1**) and dihydrogeijerene (**26**), respectively] were catalytically hydrogenated, yielding the saturated hydrocarbons **34**, **35–37**, and **38–40**, respectively.

3. The synthesis of racemic dihydrogeijerene (**26**) was achieved starting from germacrone (**41**).