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THE LOCATION OF DOUBLE BONDS IN ALKYLPYRENES

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Abstract—The syntheses of 1,6-dimethyl-3,4,5,8,9,10-hexahydropyrene, 3,8-dimethylpyrene, 3,5,8-trimethylpyrene, 3,5,8,10-tetramethylpyrene, 3,8-dicarboxymethly-pyrene, 3,5,8-tricarboxymethyl-pyrene, 3,5,8,10-tetracarboxymethyl-pyrene are described. The NMR spectra of the above hydrocarbons and of 4,9-di-t-butylpyrene are recorded. The multiplicity of the alkyl signals and decoupling experiments allow one to ascertain the location of double bonds.

UNLIKE the NMR spectra of perylene,1,12-benzoperylene, 1,12,*o*-phenyleneperylene[1] and fluoranthene,[2] that produced by the two 3-proton systems of pyrene is different and more complex.[3]

A contribution to the problem can be made using methylpyrenes and other alkylpyrenes and determining the spin-spin coupling of the Me protons with the neighbouring aromatic protons. This makes it possible to record the true double bond character of aromatic bonds next to the Me group. This double bond character is different from the purely nominal double bond character calculated by the VB method. In addition it has been found useful in this paper to apply the principle, which has been stated recently,[4] that only one true double bond can be present in any aromatic hexagonal ring.

The NMR spectrum of 1,6-dimethylpyrene[5] is shown in Fig. 1. The Me resonance is so strongly split into a doublet with a separation of 1 c/s that the 1,2- and 6,7-bonds must be true double bonds* like the 9,10-bond in phenanthrene.[5] The doublet remains intact if the protons in 5,10- and 3,4,8,9-positions are irradiated (marked with points), but it goes over to a sharp singlet if the protons in 2- and 7-positions are irradiated. Decoupling of the Me protons sharpens the ill-defined quartet at 773 c/s (the difference is marked in black). There is also a sharpening of the low field double doublet (marked in black) centered at 809 c/s and originating from the protons $H_{5,10}$. If this group is irradiated the Me doublet (second from the left in Fig. 1) also sharpens a little. There must be some interaction with the protons in peri-position.

Spin-spin interaction between Me protons and aromatic protons is completely absent in the hexahydro derivative of 1,6-dimethylpyrene (Fig. 2). The aromatic singlet at 681 c/s and the Me singlet show no observable splitting even at the highest expansion. No splitting occurs if the spectrum is recorded at 220 mc/s.† Therefore it must be concluded that there is no true double bond between the β-β-positions in the central naphthalene complex (marked black) and that these two middle rings in 1,6-dimethylpyrene do not have the character of a naphthalene complex. In accordance with this we have found that in 1,5-dibromo-2,6-dimethylnaphthalene and in

* In the formulae we have indicated only those double bonds which can be demonstrated by spin-spin interaction with the Me group.

Thanks are due to the staff of Petrochemical and Petroleum Laboratories, I.C.I., Runcorn for the recording of the 220 mc/s spectrum.

1,2,5,6-tetramethylnaphthalene there is no measurable coupling of the 2,6-Me protons with the neighbouring aromatic protons in 3,7-position.

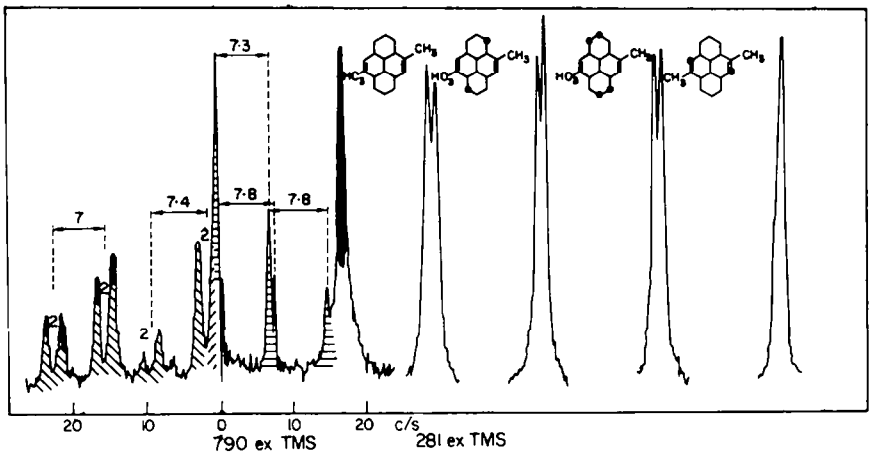


FIG. 1. NMR spectrum of 1,6-dimethylpyrene in CS_2 at 100 mc/sH_{CH_3}, 280·6 (Doublet, separation 1 c/s); $H_{2,7}$, 773·0; $H_{3,8}$, 794·0; $H_{5,10}$, 809·0; $H_{4,9}$, 783·8. $J_{3,4} = J_{8,9} = 7{\cdot}6$; $J_{4,5} = J_{9,10} = 7$; $J_{3,5} = J_{8,10} = 1{\cdot}8$. Decoupling of protons marked with points in the formulae. Black area after decoupling H_{Me}.

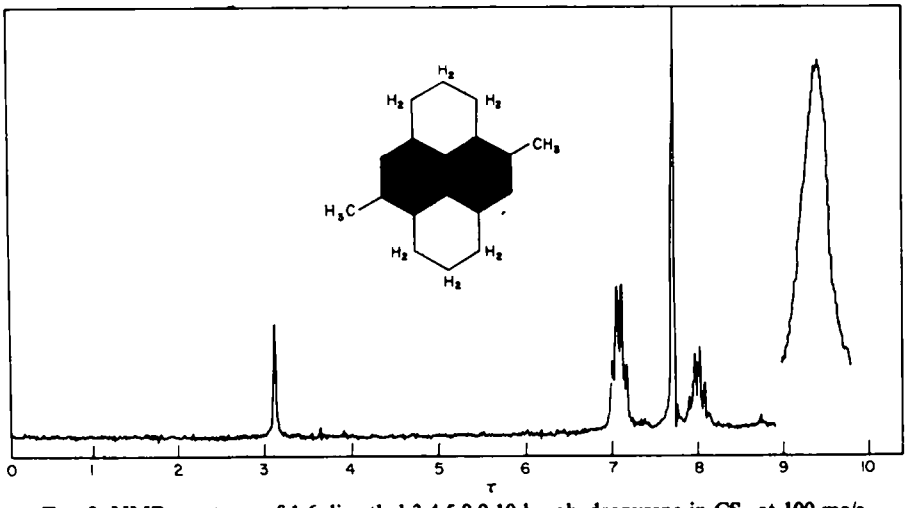


FIG. 2. NMR spectrum of 1,6-dimethyl-3,4,5,8,9,10-hexahydropyrene in CS_2 at 100 mc/s. H_{Me}, 226·0 (singlet); $H_{2,7}$, 681·0; $H_{3,5,8,10}$, 288·0 (multiplet); $H_{4,9}$, 199·0 (multiplet).

The Me resonance of 4,9-dimethylpyrene* (Fig. 3) is clearly split into a triplet with a separation of 2 × 0·55 c/s. This indicates that the two adjacent bonds to the Me groups have true double bond character and that they are in fact three centre π-bonds. The four aromatic protons $H_{3,5,8,10}$ form an ill-defined quartet at 778·2 c/s which becomes a sharp singlet after irradiation of the Me protons. This singlet

* The spectrum at 60 mc/s in $CDCl_3$ was recorded by E. Clar *et al.*

becomes equal in intensity to the singlet originating from the positions 1,2,6,7. The Me absorption also appears as a triplet in 4-methylpyrene *

The NMR spectrum of 4,6-di-t-butylpyrene† shows only two sharp signals at 807·6 and 784·5 c/s caused by the protons $H_{1,2,6,7}$ and $H_{3,5,8,10}$ resp. There is no indication of any meta- or peri-coupling between these aromatic protons.

From the above results a distribution of double bonds as presented in formula I is the most likely one. There is a 3-centre π-bond between the positions 3,4,5 and 8,9,10 and there are also two fixed double bonds in the positions 1,2 and 6,7. All other π-electrons are not symbolized in formula I.

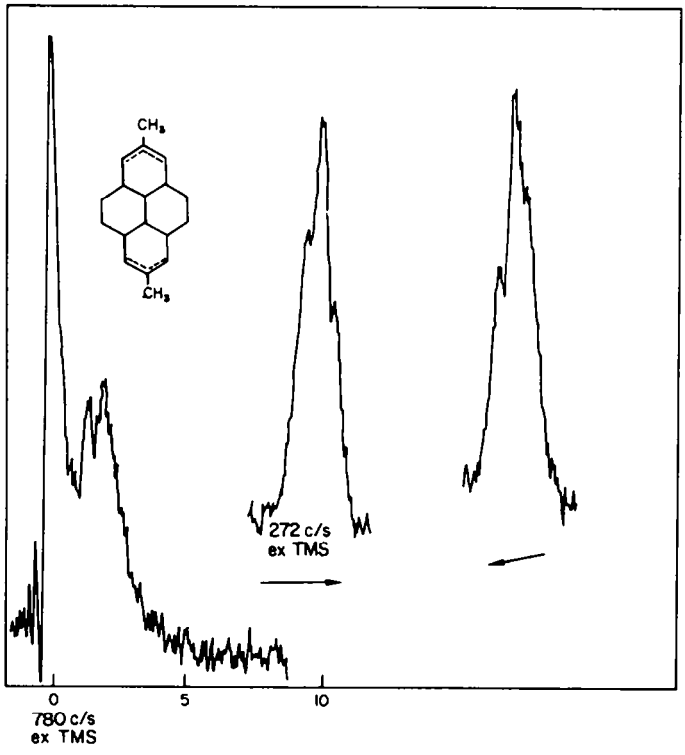


FIG. 3. NMR spectrum of 4,9-dimethylpyrene in CS_2 at 100 mc/s. H_{Me}, 272·0 (triplet, separation 0·55 c/s); $H_{1,2,6,7}$, 780·0; $H_{3,5,8,10}$, 778·2 (quartet).

This formula is supported by the NMR spectrum of 3,5,8,10-tetramethylpyrene (Fig. 4). The Me protons form a doublet which is little affected by irradiation of $H_{1,2,6,7}$ (marked with points), but form a sharp singlet when H_4 and H_9 are irradiated. These protons form a rather broad band at 758 c/s, indicating coupling with the Me protons. This is in agreement with the structure I.

The NMR spectrum of 3,5,8,10-tetraisopropylpyrene‡ consists of two sharp

† The spectrum at 60 mc/s in $CDCl_3$ was recorded by E. Clar *et al.* It does not show a distinct splitting of the Me band.

‡ This was recorded at 60 mc/s by Prof. A. Berg, private communication.

* A sample was kindly supplied by Prof. A. Berg, who showed us also the NMR spectrum at 60 mc/s.

aromatic singlets at 819 and 780 c/s. There is also a septet at 399 and a doublet at 148·4 c/s, originating from the isopropyl-groups. Irradiation of the Me protons causes the collapse of the septet into a sharp singlet, which shows no indication of a doublet. Other decouplings of the aromatic protons and the methine protons cause little effect. This may be due to hindered rotation of the isopropyl groups.

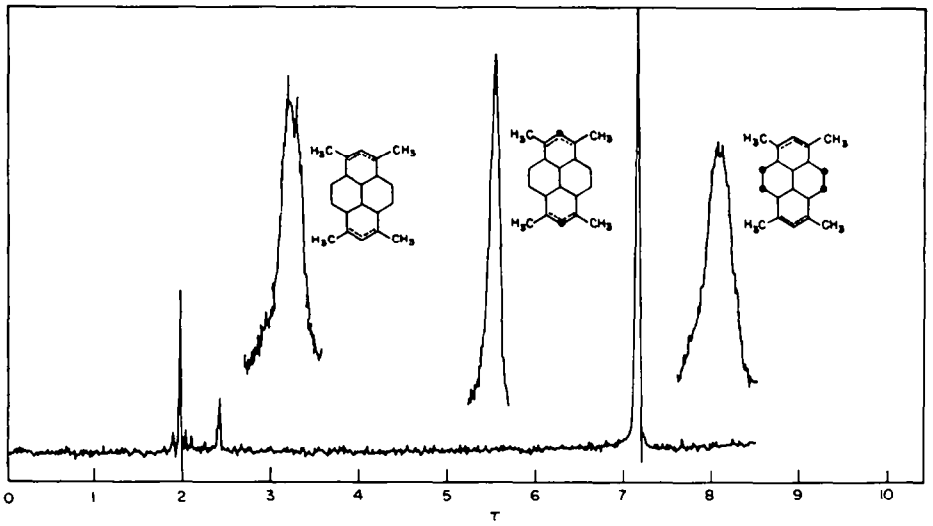


FIG. 4. NMR spectrum of 3,5,8,10-tetramethylpyrene in CS_2 at 100 mc/s. H_{Me}, 286·0 (doublet, separation 0·5 c/s); $H_{1,2,6,7}$, 803·0; $H_{4,9}$, 758·0 c/s.

The Me absorption in 3,8-dimethylpyrene (Fig. 5) shows no tendency of splitting. The Me band sharpens if the aromatic protons (marked with points) are irradiated. Decoupling the Me protons sharpens the signals of all the aromatic protons as marked by the black area in Fig. 5. This effect is strongest for the protons in *peri*- and *o*-position, i.e., the doublets at lowest and highest field resp. These facts cannot be explained by formula I for the pyrene complex. The possibility must be considered that in 3,8-dimethylpyrene the three centre π-bonds are partly or completely replaced by fixed double bonds as presented in formula II. This formula would also account for the remarkable fact that 3-methylpyrene yields 3-methylpyrene-5-aldehyde when submitted to a Vilsmeier synthesis[6] and does not result in the usual substitution in the position 8 or 10.

The three Me groups in 3,5,8-trimethylpyrene form two bands with an intensity of 3 H and 6 H resp. The two Me groups at 285 c/s form a band which seems to be a singlet. However, it is very unlikely that they coincide exactly. Any small difference would transform a doublet into a broad singlet. For this reason no conclusion can be drawn from the shape of the Me bands at 285 c/s and 289 c/s.

In this context it is worthwhile to draw attention to some experimental facts reported by Vollmann *et al.*,[7] which have not been explained by theory. 4-Hydroxypyrene (III) couples readily with diazo-compounds in *o*-position as indicated by the

arrow in III. This is in line with the appearance of a Me triplet in 4-methyl- and 4,9-dimethylpyrene which we have correlated to the 3-centre π-bonds.

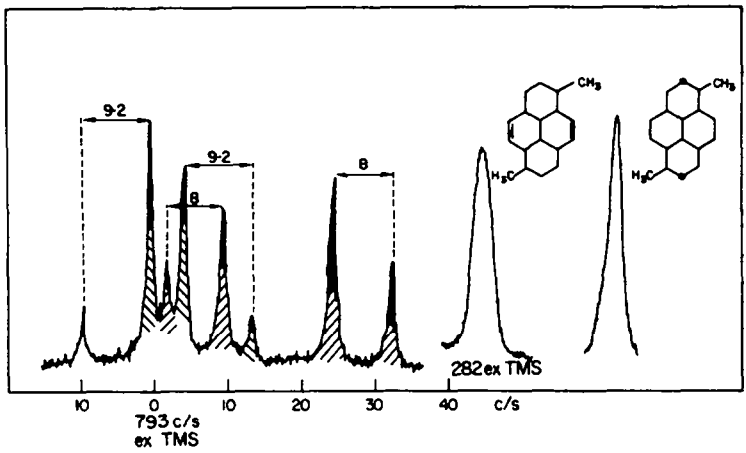
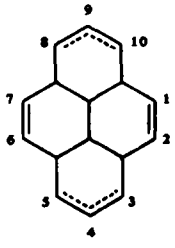
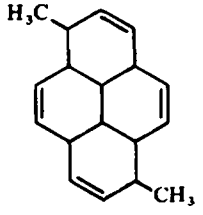


FIG. 5. NMR spectrum of 3,8-dimethylpyrene in CS_2 at 100 mc/s. H_{Me}, 282·0; $H_{2,7}$, 791·9; $H_{1,6}$, 781·4; $H_{5,10}$, 782·3; $H_{4,9}$, 760·7 c/s. $J_{4,5} = J_{9,10} = 8$ c/s; $J_{1,2} = J_{6,7} = 9{\cdot}2$ c/s.

1-Hydroxypyrene (IV) also couples readily with diazo compounds. In agreement with this fixed double bonds were found in 1-methylpyrene and 1,6-dimethylpyrene (Fig. 1). No diazo coupling can be observed with 3-hydroxypyrene (V). In accordance with this the Me group in 3-methylpyrene and 3,8-dimethylpyrene do not form doublets in their NMR spectra because there appears to be no true double bond between Me and the *o*-positions (Fig. 5). There is thus a complete analogy between doublet formation in methylpyrenes and diazo coupling with hydroxypyrenes.

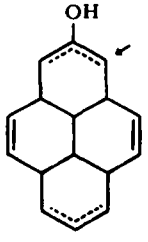


I

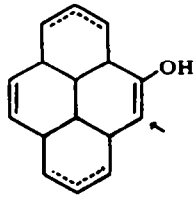


II

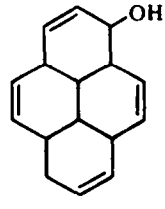
All hexagons symbolize aromatic rings. Double bonds are only marked were they can be proved. All other electrons are unmarked.



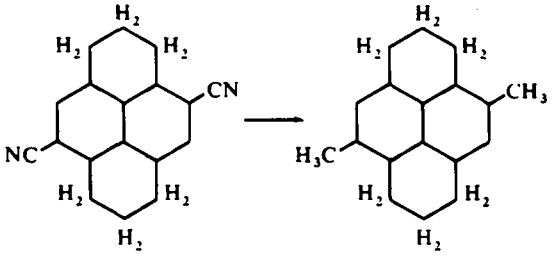
III
couples easily



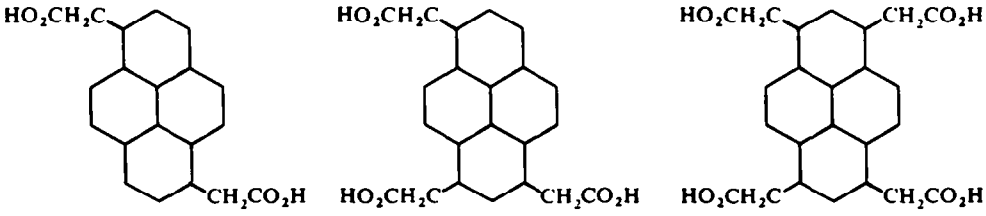
IV
couples easily



V
does not couple



VI VII



VIII IX X

EXPERIMENTAL*

The synthesis of the compounds. The preparation of 1,6-dimethylpyrene has been reported before.[5] 1,6-Dimethyl-3,4,5,8,9,10-hexahydropyrene (VII) was prepared by reduction of the dinitril (VI) with hydrazine-hydrate under pressure at 200°. 3,8-Dimethylpyrene, 3,5,8-trimethylpyrene and 3,5,8,10-tetramethylpyrene were prepared by decarboxylation of the corresponding carboxymethylpyrenes. A mixture of the acids (VIII, IX and X) was obtained by prolonged reaction of pyrene with chloroacetic acid. They were separated using their different acidities.

1,6-*Dimethyl*-3,4,5,8,9,10-*hexahydropyrene* (VII). Compound VI[7] (0·4 g), hydrazine hydrate (80%, 7 ml) and xylene (15 ml) were heated in a sealed tube at 200–220° for 28 hr. The solid was filtered from the xylene–hydrazine mixture which was then diluted with water. The xylene layer was separated and combined with a hot xylene extract of the solid residue. The soln was concentrated and chromatographed on alumina. The hydrocarbon was eluted from the column with light petroleum (100–120°) and yielded colourless crystals which after two crystallizations from light petroleum formed colourless needles, m.p. 183°, (12 mg). The UV absorption spectrum was that of a pure naphthalene derivative. (Found: C, 91·4; H, 8·6. $C_{18}H_{20}$ requires: C, 91·5; H, 8·5%).

Condensation of pyrene with chloroacetic acid. Powdered pyrene (300 g) was heated with chloroacetic acid (500 g) at 190–200° for 200 hr. The mixture was poured into water, the residue filtered off, washed with water and extracted with 5% Na_2CO_3 aq. The soln of the Na salts was acidified with conc HCl filtered, washed and dried (420 g). 320 g of this ppt were extracted with AcOH (2 l), filtered hot and the residue washed with AcOH and then with ether, yield 83 g.

3,8-*Dicarboxymethylpyrene* (VIII). The crystals (78 g) from the above cooled AcOH extract were filtered off, washed with water and ether. 70 g of this ppt were dissolved in dil ammonia and acidified with AcOH (pH 5–6). The ppt (31·5 g) was filtered off and washed with water and ether. The filtrate was acidified with conc HCl (pH 1), the ppt filtered off hot and dissolved in dil ammonia. Acidification (pH 5) with AcOH gave a further quantity (11·5 g) of 3,8-dicarboxymethylpyrene. The filtrate of this ppt was used for the preparation of tricarboxymethylpyrene. 3,8-Dicarboxymethylpyrene (VIII) gave, after two crystallizations from AcOH, small crystals, m.p. 306–312° dec. (Found: C, 75·3; H, 4·4. $C_{20}H_{14}O_4$ requires: C, 75·5; H, 4·4%).

* M.ps are uncorrected and were taken in evacuated capillaries.

3,8-*Dimethylpyrene*. The above acid (0·6 g) and soda–lime (1 g) were heated with a free flame. The distillate (0·29 g) was dissolved in light petroleum (100–120°) and chromatographed on alumina. Concentration of the eluate gave crystals, m.p. 160–162°. This product could possibly contain some of the isomeric 3,10-dimethylpyrene. A purer hydrocarbon was obtained following the synthesis of de Clercq and Martin[6] which had m.p. 165–166° (lit. m.p. 165–166°).

3,5,8-*TricarboxymethylpyrenJ* (IX). The filtrate of the preparation of dicarboxymethylpyrene was acidified with conc HCl (pH 1) and the ppt (7·2 g) filtered off. Two crystallizations from AcOH gave pale yellow crystals, m.p. 313–315° dec. (Found: C, 70·1; H, 4·3. $C_{22}H_{16}O_6$ requires: C, 70·2; H, 4·3).

3,5,8-*Trimethylpyrene*. 3,5,8-Tricarboxymethylpyrene (0·25 g) and soda–lime (0·25 g) were distilled using a free flame. The distillate was dissolved in light petroleum (100–120°) and chromatographed on alumina. The crystals obtained from the eluate were twice recrystallized from light petroleum. Trimethylpyrene forms colourless plates, m.p. 179–180° (lit.[6] 178–179°). (Found: C, 93·1; H, 6·8. $C_{19}H_{16}$ requires: C, 93·4; H, 6·6%).

3,5,8,10-*Tetracarboxymethylpyrene* (X). The residue from the condensation of pyrene with chloroacetic acid (80 g) was dissolved in dil NaOH and filtered from the insoluble material (2 g). The soln was acidified with AcOH and the ppt filtered off hot. A further ppt was obtained on cooling (5·9 g). This was extracted with AcOH (1 l) filtered and washed with hot AcOH. The residue (2·1 g) was recrystallized twice from a mixture of pyridine and AcOH. Yellow crystals were obtained which decomposed over 350°. (Found: C, 66·3; H, 4·0. $C_{24}H_{18}O_8$ requires: C, 66·4; H, 4·2%).

3,5,8,10-*Tetramethylpyrene*. The crude condensation product (100 g) from the reaction of pyrene with chloroacetic acid was extracted with hot xylene (500 ml), filtered hot and washed with benzene. The residue (84 g) was refluxed with AcOH (1 l) filtered and washed with ether. The insoluble part (16·5 g) was decarboxylated with soda–lime as described above. The distillate (4 g) was dissolved in light petroleum (100–120°) and chromatographed on alumina. The different fractions were tested spectroscopically. They contained first dimethylpyrene then trimethylpyrene and finally tetramethylpyrene. The latter fraction was concentrated and gave colourless plates (0·36 g) m.p. 269° (lit.[6] 269°). (Found: C, 93·1; H, 7·1. $C_{20}H_{18}$ requires: C, 93·0; H, 7·0%).

REFERENCES

[1] E. Clar, Ü. Sanigök and M. Zander, *Tetrahedron* **24**, 2817 (1968)

[2] M. L. Heffermann, A. J. Jones and P. J. Black, *Austral. J. Chem.* **20**, 589 (1967); E. Clar, A. Mullen and Ü. Sanigök, *Tetrahedron* **25**, 5639 (1969)

[3] N. Jonathan, S. Gorden and B. P. Dailey, *J. Chem. Phys.* **36**, 2443 (1962); R. H. Martin, N. Defay, F. Geerts-Evrard and S. Delavarenne, *Tetrahedron* **20**, 1073 (1964)

[4] E. Clar and A. Mullen, *Ibid.* **24**, 6719 (1968)

[5] E. Clar, B. A. McAndrew and M. Zander, *Ibid.* **23**, 985 (1967)

[6] M. de Clerq and R. Martin, *Bull. Soc. Chim. Belg.* **64**, 367 (1955)

[7] H. Vollmann, H. Becker, M. Corell and H. Streeck, *Liebigs Ann.* **531**, 33, 59, 62, 72 (1937)