

derivation^{2,6,7,9}. Hence, the latter possesses the (*S*)-configuration (I).

The present correlation supports the configurational assignment arrived at by application of Prelog's rule¹¹ to the reported preferential synthesis of *dextro* rotatory barium 2-hydroxy-2-methyl-butyrate from (–)-menthyl pyruvate and ethylmagnesium bromide¹².

1. Nash, H. A. and Brooker, R. M. *J. Am. Chem. Soc.* **75** (1953) 1942.
2. Stoll, A. and Seebeck, E. *Helv. Chim. Acta* **36** (1953) 718.
3. Glen, W. L., Myers, G. S., Barber, R., Morozovitch, P. and Grant, G. A. *Nature* **170** (1952) 932.
4. Klohs, M. W., Arons, R., Draper, M. D., Keller, F., Koster, S., Malesh, W. and Petracek, F. J. *J. Am. Chem. Soc.* **74** (1952) 5107.
5. Kupchan, S. M., Ayres, C. I. and Hensler, R. H. *J. Am. Chem. Soc.* **82** (1960) 2616.
6. Myers, G. S., Glen, W. L., Morozovitch, P., Barber, R., Papineau-Couture, G. and Grant, G. A. *J. Am. Chem. Soc.* **78** (1956) 1621.
7. Poethke, W. *Arch. Pharm.* **275** (1937) 571.
8. Fried, J., White, H. L. and Wintersteiner, O. *J. Am. Chem. Soc.* **72** (1950) 4621.
9. Ham, E. H., Schafer, H. M., Denkwalter, R. G. and Brink, N. G. *J. Am. Chem. Soc.* **76** (1954) 6066.
10. Christensen, B. W. and Kjær, A. *Proc. Chem. Soc.* **1962** 307.
11. Prelog, V. *Helv. Chim. Acta* **36** (1953) 308.
12. McKenzie, A. *J. Chem. Soc.* **89** (1906) 365.

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The Structures of some Polybromo Substituted Simple Ketones

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In a recent paper it was shown by Rappe and Schotte¹ using NMR-techniques that the two bromo atoms in dibromodiethyl ketone are symmetrically substituted on both sides of the keto group and not unsymmetrically as earlier proposed by Schotte². Among the di-, tri- and tetrabromo compounds of the lower aliphatic ketones several are described in the literature as having unsymmetric structures. As the methods used previously for structure determinations are rather ambiguous owing to possible rearrangements during the procedure³ it is of interest to make a new determination of the structures of these bromo ketones by means of NMR-spectroscopy.

The direct treatment of aliphatic ketones with bromine is reported to give impure products since the liberated hydrogen bromide tends to promote the formation of condensation products⁴. Although several other methods are available, the author made the bromo ketones by an acid catalyzed bromination of ketones dissolved in hydrobromic acid. The ketones used are acetone, methyl ethyl ketone, methyl propyl ketone and diethyl ketone. By using two, three or four equivalents of bromine, the di-, tri- or tetrabromo compound of the corresponding ketone could be obtained. In Table 1 the results of these syntheses are collected, and new structures (based on NMR-spectra) for most of the bromoketones are proposed. In some cases the yield of pure bromo ketone was better than the yield previously reported employing bromination with other methods.

It appears to be a common feature that the two and four bromo atoms in di- and tetrabromo ketones are symmetrically placed one or two on each side of the keto group. The tribromo compounds of symmetrical ketones have two of the bromo atoms on one side and the third on the other. The unsymmetrical ketones give mixtures of the two possible σ -substituted tribromo isomers.

A more detailed account of these works is to be published in *Arkiv för Kemi*.

Table 1.

| Starting material | Formula | Analyses | | | Calculated | | |
|----------------------|-----------------|----------|------|-------|------------|------|-------|
| | | C | H | Br | C | H | Br |
| Acetone | $C_3H_4Br_2O$ | 16.70 | 1.87 | 74.14 | 16.69 | 1.87 | 74.03 |
| » | $C_3H_3Br_3O$ | 12.34 | 1.07 | 81.01 | 12.22 | 1.03 | 81.32 |
| » | $C_3H_2Br_4O^a$ | 9.60 | 0.56 | 85.48 | 9.64 | 0.54 | 85.54 |
| Methyl ethyl ketone | $C_4H_6Br_2O^a$ | 20.70 | 2.65 | 69.50 | 20.90 | 2.63 | 69.52 |
| » » » | $C_4H_5Br_3O^a$ | 15.43 | 1.62 | 77.63 | 15.56 | 1.63 | 77.63 |
| » » » | $C_4H_4Br_4O^a$ | 12.42 | 1.10 | 82.42 | 12.39 | 1.04 | 82.44 |
| Diethyl ketone | $C_5H_8Br_2O^a$ | 24.68 | 3.35 | 65.34 | 24.62 | 3.31 | 65.52 |
| » » » | $C_5H_7Br_3O^a$ | 18.59 | 2.22 | 74.22 | 18.60 | 2.19 | 74.26 |
| Methyl propyl ketone | $C_5H_8Br_2O$ | 24.36 | 3.28 | 65.55 | 24.62 | 3.31 | 65.52 |
| » » » | $C_5H_7Br_3O^a$ | 18.64 | 2.21 | 74.08 | 18.60 | 2.19 | 74.26 |
| » » » | $C_5H_6Br_4O^a$ | 14.74 | 1.55 | 79.41 | 14.95 | 1.51 | 79.56 |

^a new structure.

^b product from the oxidation of the carbinol.

Experimental. General procedure. The ketone was mixed with 48 % hydrobromic acid (100 ml/mole ketone) and chilled with ice-water. The bromine was added dropwise. After addition of water (200 ml/mole bromine), the heavier organic layer separated and was washed with sodium bicarbonate and sodium bisulphite solutions and dried with calcium chloride. The crude product was fractionated under reduced pressure.

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1. Rappe, C. and Schotte, L. *Acta Chem. Scand.* **16** (1962) 2060.
2. Schotte, L. *Acta Chem. Scand.* **5** (1951) 969.
3. Reid, E., Gompf, T. and Atwater, N. *J. Org. Chem.* **16** (1951) 1566.
4. Catch, J. R., Elliott, D. F., Hey, D. H. and Jones, E. R. H. *J. Chem. Soc.* **1948** 272.
5. Weygand, F. and Schmied-Kowarzik, V. *Chem. Ber.* **82** (1949) 33.
6. Faworsky, A. and Issatschenko, B. *J. prakt. Chem.* [2] **88** (1913) 655.
7. Petrov, A. A. *J. Gen. Chem. USSR* **11** (1941) 713. *Chem. Abstr.* **36** (1942) 404⁵.
8. Pastureau, M. *Compt. Rend.* **143** (1906) 967.
9. Shah, S. V. and Pishawikar, G. *Current Sci. (India)* **7** (1938) 182, *Chem. Abstr.* **33** (1939) 1660⁸.
10. Pastureau, M. *Bull. Soc. Chim. France* [4] **5** (1909) 226.

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| B.p. °C/mm Hg | M.p. °C | Structure | Previously given structure |
|---------------|-----------|-------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| 79.5—80.5/9 | 25.5—27.0 | CH ₂ BrCOCH ₂ Br | CH ₂ BrCOCH ₂ Br ⁵ |
| 107—107.5/9 | 30.0—30.5 | CHBr ₂ COCH ₂ Br | CHBr ₂ COCH ₂ Br ⁵ |
| 129—130/7 | 37—38 | CHBr ₂ COCHBr ₂ | CBBr ₂ COCH ₂ Br ⁵ |
| 79—80/8 | — | CH ₃ CHBrCOCH ₂ Br | CH ₃ CBBr ₂ COCH ₃ ⁶ |
| 100—102.5/9 | — | CH ₃ CBBr ₂ COCH ₂ Br + CH ₃ CHBrCOCHBr ₂ | CH ₃ CHBrCOCH ₂ Br ^{7b} |
| — | 52.5—53.5 | CH ₃ CBBr ₂ COCHBr ₂ | xxx-Tribromo ⁶ |
| 67—68/8 | — | CH ₃ CHBrCOCHBrCH ₃ | CBBr ₃ CH ₂ COCH ₂ Br ⁸ |
| 95—95.5/7 | — | CH ₃ CHBrCOCBBr ₂ CH ₃ | xxxx-Tetrabromo ⁹ |
| 88—89/10 | — | CH ₃ CH ₂ CHBrCOCH ₂ Br | CH ₃ CBBr ₂ COCH ₂ CH ² |
| 119—119.5/10 | — | CH ₃ CH ₂ CBBr ₂ COCH ₂ Br + CH ₃ CH ₂ CHBrCOCHBr ₂ | CH ₃ CHBrCOCHBrCH ₃ ¹ |
| — | 58—59.5 | CH ₃ CH ₂ CBBr ₂ COCHBr ₂ | CH ₃ CHBrCOCHBrCH ₂ Br ¹⁰ |
| — | — | — | CH ₃ CH ₂ CHBrCOCH ₂ Br ³ |
| — | — | — | CH ₃ CHBrCH ₂ COCBBr ₃ ¹⁰ |

Mutual Arrangement of the Iodo-Cyano-Acetylene Molecules in the Solid

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In solid cyanogen iodide¹ and bromide² bonds are present between nitrogen and halogen atoms of neighbouring molecules and infinite linear chains of atoms result. All the chains are parallel and the packing of the chains is at least approximately that to be expected if the chains may be regarded as cylinders of infinite length. The structure of iodo-cyano-acetylene might be expected to be of a similar kind. As this substance had so far not been described in

the literature we suggested to Dr. Else Kloster-Jensen to try to synthesize it. When the synthesis had been successfully carried out³ we prepared rotation X-ray diagrams of crystals obtained by sublimation of the substance at temperatures well below 0°C. The crystals, fibre-like and poorly developed, turned out to have an identity period along their fibre axis of 8.60 Å, a value which corresponds to that estimated for chains of the kind we had expected. The mutual arrangement of the

Table 1.

| Atomic coordinates | | | |
|--------------------|----------|----------|----------|
| | <i>x</i> | <i>y</i> | <i>z</i> |
| I | 0.0569 | 0.25 | 0.3255 |
| C | 0.864 | 0.25 | 0.112 |
| C | 0.702 | 0.25 | 0.969 |
| C | 0.546 | 0.25 | 0.805 |
| N | 0.400 | 0.25 | 0.667 |

| Interatomic distances in the chain | | | |
|------------------------------------|--------|-----|--------|
| N---I | 2.93 Å | C—C | 1.39 Å |
| I—C | 1.79 Å | C≡N | 1.20 Å |
| C≡C | 1.27 Å | | |

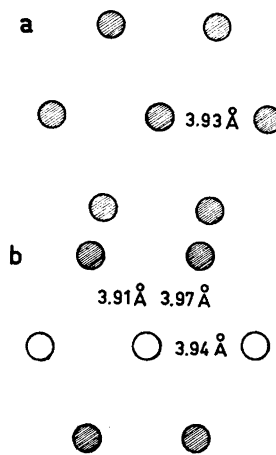


Fig. 1. Arrangement of chains in a) the low temperature form, b) the monoclinic form.