TABLE I

DEHALOGENATION OF SOME HALONITROBENZENES

| Halonitro-benzene | Starting material recovered, % | Dehalogenation product yield, % |
|---|---|---|
| *o*-Fluoro- | 53 | 0 |
| *m*-Fluoro- | 65 | 0 |
| *p*-Fluoro- | 59 | 0 |
| *o*-Bromo- | 0 | 52[a] |
| *m*-Bromo- | 70 | 0 |
| *p*-Bromo- | 78 | 0 |
| *o*-Iodo- | 0 | 53[a] |
| *m*-Iodo- | 10 | 32[a] |
| *p*-Iodo- | 22 | 32[a] |
| 2,5-Dichloro- | 0 | 37[b] |
| 2,5-Dibromo- | 0 | 38[c] |

[a] Product is nitrobenzene. [b] Product is *m*-chloronitrobenzene. [c] Product is *m*-bromonitrobenzene.

***o*-Fluoronitrobenzene.**—To a molten mixture of 14 g. (0.11 mole) of benzoic acid and 5 g. (0.035 mole) of *o*-fluoronitrobenzene at 150–200° was added 10 g. of copper powder in several portions over a period of five minutes. Heating was stopped and the solidified mixture was taken up in 50 ml. of 20% sodium carbonate solution. The alkaline mixture was steam distilled until the distillate was clear. The distillate was extracted with ether and dried over barium oxide. The ether solution was filtered and evaporated. There was recovered 2.6 g. (53% recovery) of *o*-fluoronitrobenzene, m.p. −7 to −6°.

**2-Chloro-3,5-dinitrotoluene.**—In a 600-ml. beaker was placed 60 g. of fuming nitric acid (sp. gr. 1.59–1.60), 60 g. of concentrated nitric acid (sp. gr. 1.42) and 360 g. of concentrated sulfuric acid. To this solution was added 40 g. (0.318 mole) of *o*-chlorotoluene and the mixture was heated on the steam-bath for 3 hours. The solution was cooled, poured over ice, and extracted with a total of 500 ml. of ether. Evaporation of the ether gave a heavy yellow oil, which partly crystallized on standing in the ice-box for several days. The light yellow crystalline material was separated by drying on a clay plate. The product thus obtained weighed 24 g. and melted at 55–60°. It was recrystallized from carbon tetrachloride to give 16 g., m.p. 58–60°. Recrystallization from alcohol gave 12 g. (8.8%) of 2-chloro-3,5-dinitrotoluene, m.p. 62–63° (lit. m.p. 62–63°[2]).

**Synthesis of 3,5-Dinitrotoluene.**—To a hand-stirred mixture of 14 g. (0.11 mole) of benzoic acid and 5 g. (0.023 mole) of 2-chloro-3,5-dinitrotoluene was added 10 g. of copper powder, in several portions over a period of 5 minutes (temperature at 150–200°). Heating was stopped and the solidified mixture was then taken up with 50 ml. of 20% sodium carbonate solution. The insoluble residue was removed by filtration, dried, and extracted with ether. Evaporation of the ether gave 3.8 g., m.p. 90–91°. Recrystallization from 50 ml. of alcohol gave 3.5 g. (83%) of 3,5-dinitrotoluene, m.p. 93°.

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[2] G. R. Yohe, *Trans. Ill. State Acad. Sci.*, **33**, No. 2, 125 (1940).

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# Azeotropes of Bromine. III. Azeotropes of Bromine with 1,2,2-Trichloro-1,1-difluoroethane and 1,1-Dichloro-2,2-difluoroethane

BY WILLIAM M. SPICER AND HENRY D. R. PAGE

RECEIVED MARCH 23, 1953

As a continuation of an investigation to prepare binary azeotropes consisting of one colored and one colorless component,[1,2] it was decided to study further possibilities in systems of bromine with colorless bromine solvents. Azeotropes of this general type are valuable in the study of the methods employed to separate azeotropic mixtures, since separation can be observed visually.

It was decided to investigate $CHCl_2CHF_2$ and $CHCl_2CF_2Cl$ as bromine solvents since these liquids possess boiling points near that of bromine, a condition favorable for azeotrope formation. Besides it was anticipated that these liquids would be miscible with and inert toward bromine.

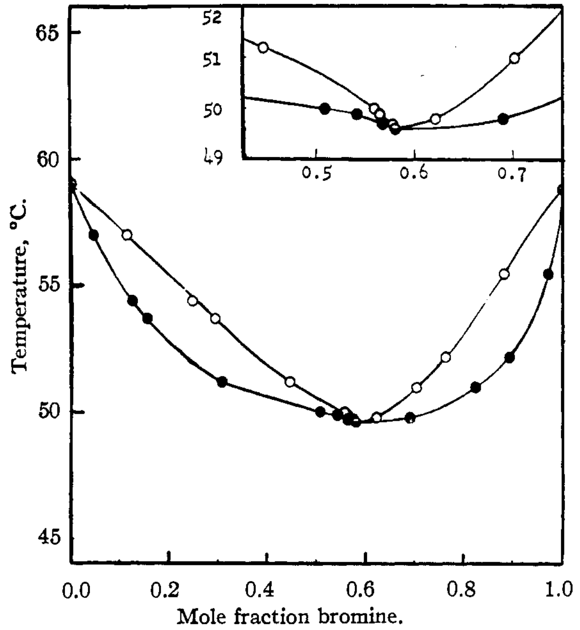

Fig. 1.—Temperature–composition diagram for the system $Br_2$–$CHCl_2CHF_2$ at 760 mm. pressure: ○, vapor; ●, liquid; ◒, vapor and liquid.

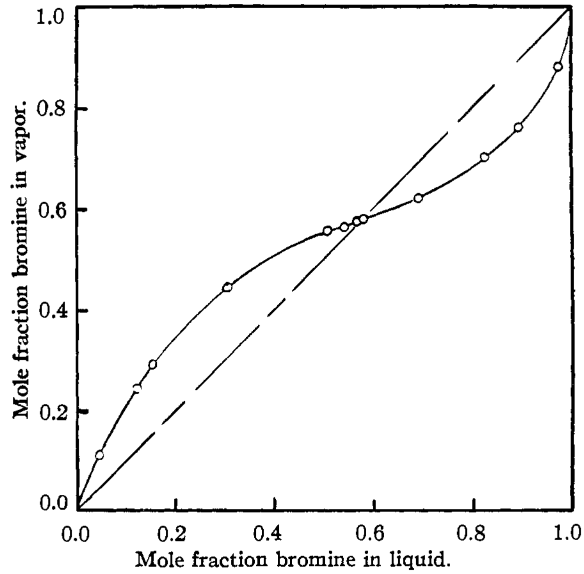

Fig. 2.—Vapor–liquid equilibrium diagram for the system $Br_2$–$CHCl_2CHF_2$ at 760 mm. pressure.

## Experimental

Merck and Co., Inc., analyzed C.P. bromine was used without further purification. The $CHCl_2CHF_2$ and $CHCl_2CF_2Cl$ were obtained from Halogen Chemicals, Inc., and were listed as being better than 95% pure. These were

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[1] W. M. Spicer and J. Kruger, THIS JOURNAL, **72**, 1855 (1950).

[2] W. M. Spicer and L. H. Myer, *ibid.*, **73**, 934 (1951).

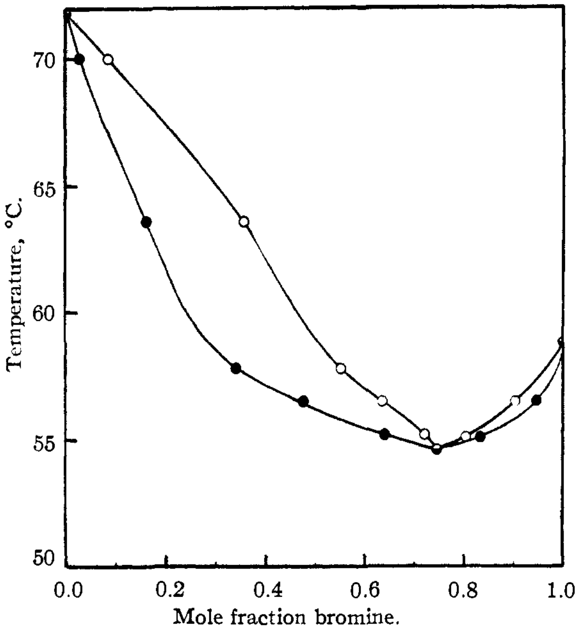

Fig. 3.—Temperature–composition diagram for the system $Br_2$-$CHCl_2CF_2Cl$ at 760 mm. pressure: ○, vapor; ●, liquid; ◒, vapor and liquid.

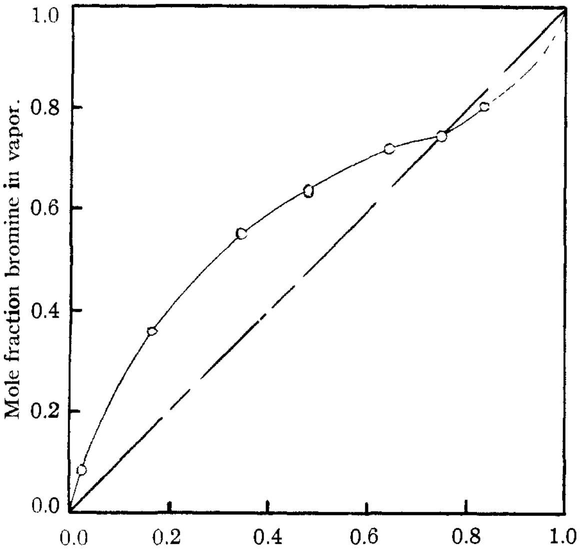

Fig. 4.—Vapor–liquid equilibrium diagram for the system $Br_2$-$CHCl_2CF_2Cl$ at 760 mm. pressure.

purified further by fractionation in a five-foot glass helix-packed column, taking a middle cut. The boiling point range of the $CHCl_2CHF_2$ was 58.4–59.5° at 735.2 mm. and that of the $CHCl_2CF_2Cl$ was 71.1–71.2° at 736.3 mm.

Vapor–liquid equilibrium data were obtained at 760 mm. as has been described previously.[1,2]

For each system exhibiting azeotrope formation, the azeotrope itself was prepared by fractionation at 760 mm. pressure of a liquid mixture of very nearly the azeotropic composition in a small glass helix-packed column (packed section 40 cm. in length and 2 cm. in diameter). After the column had reached equilibrium, the azeotropic temperature was read directly and the composition of the azeotrope determined by analyzing small samples of the condensed vapor.

To test the systems for evidence of reaction, although the likelihood of such was considered small, approximately 10% (by weight) bromine solutions were fractionated, the bromine being distilled off in the azeotrope. After removal of the bromine the refractive index of the residue in the still pot was determined and compared with that of the pure solvent at the same temperature. The index of the $CHCl_2CHF_2$ changed from 1.3769 to 1.3773 and that of the $CHCl_2CF_2Cl$ from 1.3900 to 1.3899. This slight change was felt to be due, not to reaction but to some slight fractionation of the solvents.

The azeotropic boiling points and compositions for these systems as obtained from the column mentioned above were found to be as follows: $Br_2$-$CHCl_2CHF_2$, 49.6°, 58.1 mole per cent. bromine and $Br_2$-$CHCl_2CF_2Cl$, 54.6°, 74.7 mole per cent. bromine.

The equilibrium data are plotted in the usual manners in the figures shown.

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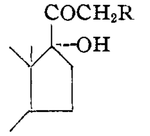
## Molecular Rotation Differences for 17-Hydroxy-20-ketosteroids

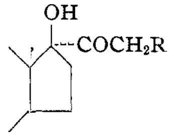
By Richard B. Turner

Received January 5, 1953

The method of molecular rotation differences[1] has been employed with outstanding success by Barton, Klyne and others in the elucidation of stereochemical and related structural problems encountered in investigations of a wide variety of steroids. An important application has been the correlation of configuration of hydroxyl substituents with the change in molecular rotation accompanying acetylation of these groups.[2] Recent development of procedures for acetylation of the hitherto refractory 17α-hydroxy-20-ketosteroids (I)[3] makes possible extension of the method to this important group of substances. Results of correlations in this series are summarized in Table I, which includes also available data for three epimeric 17β-hydroxy-20-keto derivatives (II).



I



II

It is at once apparent that conversion of compounds possessing an α-oriented hydroxyl group at C-17 into the corresponding tertiary acetates involves a large negative shift in molecular rotation. The effect is enhanced in those products (Nos. 7–11) that possess an additional acetoxyl group at C-21 and is particularly pronounced in S acetate (No. 10) and in cortisone acetate (No. 11), which contain an α,β-unsaturated ketonic grouping as well. A negative increment of intermediate magnitude is observed for the 17α-hydroxy ester (No. 6),

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(1) A discussion of the method as developed by Barton, together with literature citations, is given in "Natural Products Related to Phenanthrene," 3rd ed., L. F. Fieser and M. Fieser, Reinhold Publ. Corp., New York, N. Y., 1949, p. 206. See also D. H. R. Barton, *Angew. Chem.*, **61**, 57 (1949), and D. H. R. Barton and W. Klyne, *Chemistry and Industry*, 755 (1948).

(2) D. H. R. Barton, *J. Chem. Soc.*, 813 (1945); W. Klyne and D. H. R. Barton, This Journal, **71**, 1500 (1949).

(3) Huang-Minlon, E. Wilson, N. L. Wendler and M. Tishler, *ibid.*, **74**, 5394 (1952); R. B. Turner, *ibid.*, **74**, 4220 (1952); *ibid.*, **75**, 3484 (1953).