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HYDROLYSIS OF 8-BROMOMETHYL[2.2]METACYCLOPHANES IN 50% AQUEOUS ACETONE SOLUTION[1)]

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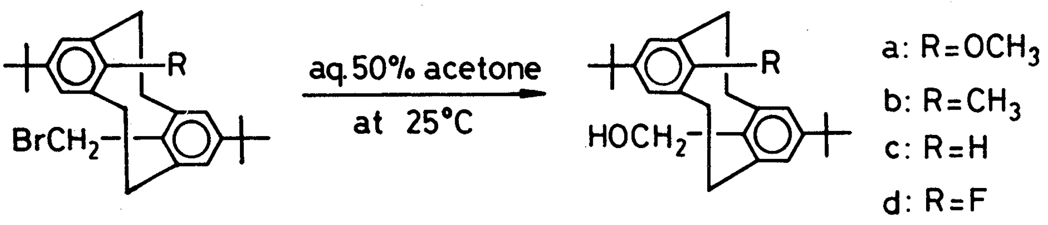
The hydrolysis rate of 8-bromomethyl[2.2]metacyclophanes (1a-1d) was measured in 50% aqueous acetone solution at 25°C.

KEYWORDS ——— [2.2]metacyclophane; internal bromomethyl group; hydrolysis; hydroxymethyl[2.2]metacyclophane; substituent effect through space on the hydrolysis

Although substituents at positions 8 and 16 in the [2.2]metacyclophane system seem to have interesting chemical natures since they are covered with the opposite aromatic rings, there are few investigations concerning these problems.

We wish to report the hydrolysis of four 8-bromomethyl[2.2]metacyclophanes (1a-1d)[2)] to the corresponding 8-hydroxymethyl derivatives (2a-2d)[3)] in 50% aqueous acetone solution at 25°C.



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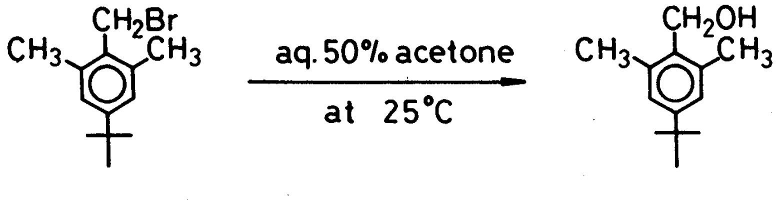

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The rate constants of the hydrolysis of 1 are summarized in the Table. The hydrolysis rate constant of 2,6-dimethyl-4-tert-butylbenzyl bromide 3 is 5.15×10^{-4} s^{-1}. This value shows that the steric hindrance of the bridged methylene groups of 1 may be larger than that of the two methyl groups of 3.

The data of the Table clearly show that the substituents affected the rate of the hydrolysis of bromomethyl group in the opposite aromatic ring and that electron donating groups such as methoxy and methyl functions increased the hydrolysis rate.

Table. The Rate Constants of Hydrolysis of 1[a)]

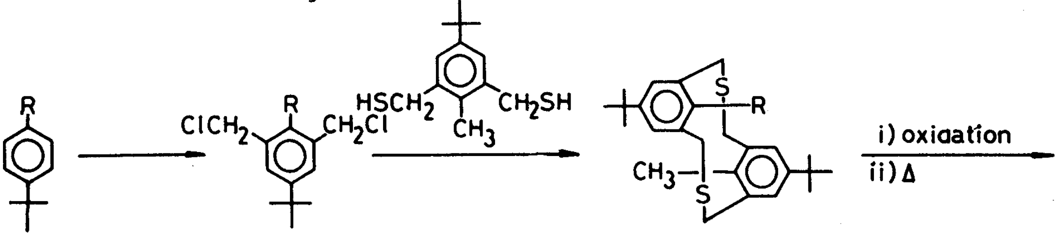
Substance	R	Rate constant ($k \times 10^3$ min^{-1})
1a	OCH_3	725
1b	CH_3	10.5
1c	H	6.3
1d	F	7.2

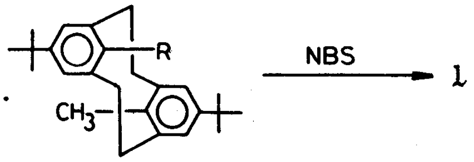
a) A solution of ca. 1 mmol of 1 in 100 ml of a mixture of water and acetone (1:1) was stirred at 25°C ± 0.5°C for the specified reaction time, and it was titrated with 0.005 N NaOH solution to measure the concentration of hydrogen bromide generated.

Such substituent effect through space on the rate of the hydrolysis of bromomethyl groups attached on the opposite aromatic ring was first found in this investigation.

REFERENCES AND NOTES

1) Metacyclophanes and Related Compounds. 9. Part 8. M. Tashiro and T. Yamato, submitted to J. Org. Chem..
2) Preparation of 1b has been previously described.[4)] The other compound 1a, 1c and 1d were prepared according to the reported method.[5)] These reaction routes are shown in the following chart.





1a: Colorless prisms (hexane); mp 239~240°C.
1b: Colorless prisms (hexane); mp 272~279°C (dec.).
1c: Colorless prisms (hexane); mp 132~133°C.
1d: Pale yellow prisms (hexane); mp 208~209°C.

3) Compounds 2 were obtained from the corresponding 1 by complete hydrolysis at 50°C for 12 h.
2a: Colorless prisms (hexane); mp 249~250°C. 2b: Colorless prisms (hexane); mp 250~252°C. 2c: Colorless prisms (hexane); mp 173~174°C. 2d: Colorless prisms (hexane); mp 184~185°C.
4) M. Tashiro and T. Yamato, Chem. Lett., 61 (1982).
5) M. Tashiro and T. Yamato, J. Org. Chem., 46, 1543 (1981).

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