



Debromination of Aurone Dibromide with Sodium Hydrogen Sulphide

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INTRODUCTION

Debromination of Vicinal-dihaloalkanes and dibromoketones have been studied by earlier workers using the debrominating agents like potassium iodide in acetone¹, stannous chloride in different solvent², sodium hydrogen selenide³, thiourea in ethanol^{4,5} and also by some workers using hydrated sodium sulphide under phase transfer condition^{6,7}. Photochemical and chemical reduction of vicinal dihalides via phase transfer of 4,4' bipyridinium radical⁸ for solar energy conversion, use of cobalt octacarbonyl on alumina have been reported for selective dehalogenation of α -bromo sulphoxides⁹. Chromium (II) acetate also brings reductive debromination in vicinal dihaloalkanes¹⁰ and chalcone dibromide¹¹. Sodium sulphide with vicinal dibromo derivative of certain oximes is reported to give sulphoxide derivatives.¹² Chalcone with anhydrous sodium sulphide in acetyl acetone at room temperature is reported to give (Ph-CO -CH₂-CO -Ph) Thiourea with 2-hydroxy

Chalcones gives 1,3 thiamine derivatives in alkaline ethanol on refluxing for 3 hours while in 10 min in DMSO.¹⁴ Sodium polysulphide with chalcone is reported to form 2,4-dibenzoyl -3,5-diphenyl thiolanes¹⁵.

Recently sodium hydrogen sulphide reacts with chalcone dibromide and stilbene dibromide in methanol to give chalcone and stilbene respectively¹⁶.

It was thought interesting to use sodium hydrogen sulphide for debromination of aurone dibromide in methanol.

Aurone dibromide (0.01 mole) was treated with freshly prepared sodium hydrogen sulphide (0.02 mole) in dry methanol (30 ml.). The reaction mixture was heated for 20 mins, diluted with water and the product was crystallized from ethanol. The product was found to be identical with aurone on the basis of m.p., m.m.p. (mixed melting point) and

cO-TLC and spectral data of uv-vis, IR and NMR 2,α (4' methoxy benzyl)coumaran -3- one mp 158 °C. It is white powdery solid compound having m.p.-158°C. It does not give any colouration with neutral ferric chloride solution. From the analytical data, the molecular formula was found to be C₁₇H₁₄Br₂

The molecular wt is 426

TLC

Rf value was found to be 0.36 for benzene as a solvent on silica gel G plate with a layer thickness of 0.3 mm. elemental analysis.

C : found 47.627 C : Calculated (47.88%)
H : found 3.10% H : Calculated (3.28%)
Br found 38.15% Br : Calculated (37.55%)

UV Spectra

UV spectrum was recorded in methanol and is reproduced on plate no. 4 (0). λ max value are recorded 203.8 nm, 252.2 nm, 363.2 nm and 395.4 nm corresponding II – II* and n - II* in aurone dibromide

IR spectrum

IR spectrum was recorded in Nujol and reproduced on plate No 4b

| Region | Frequency | Co-rotation |
|-----------|-----------|--|
| 1750-1725 | 1730 (s) | C = O stretching in 5-membered ring |
| 1300-1200 | 1280 (s) | Ar-O stretching in aromatic ether |
| 1350-1100 | 1180 (s) | C-O stretching |
| 1050-1010 | 1010(s) | -OCH ₃ stretching in aromatic ether |
| 750-500 | 750 (s) | C-Br stretching |

NMR spectrum

P.M.R. spectrum who recorded in CDCl₃ with TMS as an internal standard and in reproduced on plate No 4c

The observed chemical shift can be correlated as follows.

| | | | |
|---------------------|---|----|--------------------|
| 1.6 δ | s | 1H | C-H |
| 2.44 δ | s | 3H | Ar-CH ₃ |
| 3.94 δ | s | 3H | - OCH ₃ |
| 6.92 – 8.1 δ | m | 7H | Ar-H |

The white powder having m.p.=112. It gave blood red colouration with conH₂So₄ from analytical data, the molecular formula was found to be C₁₇H₁₄O₃ and molecular mass being 266(by mass spectra.)

Elemental Analysis

C: found 75.82% Calculated 76.13%
H: found 5.324% Calculated 5.66%

TLC studies

The RF values was found to be 0.64 – 0.67 for CCL₄ as a solvent on silica gel .G plate with layer thickness of 0.3mm. The UV spectrum it is reproduced on plate No.3a. It shows λ max value 403.2, 342.8, 254.0 nm corresponding π-π* and n-π* in the compound.

IR Spectrum

IR Spectrum recorded in nujol and is reproduced on plate No.3b. The imp correlation are as follows.

| Region | Frequency | Co-rotation |
|-----------|-----------|--|
| 1750-1550 | 1700 (s) | C = O stretching in cyclic ketone |
| 1700-1550 | 1210 (s) | C=C Stretching |
| 1310-1210 | 1210 (s) | Ar-O stratching in aromatic rung |
| 1280-1200 | 1200(s) | C-O-Cstretching in 5-membered cyclic ring |
| 1050-1010 | 1020 (s) | -OCH ₃ stretching in aromatic ether |

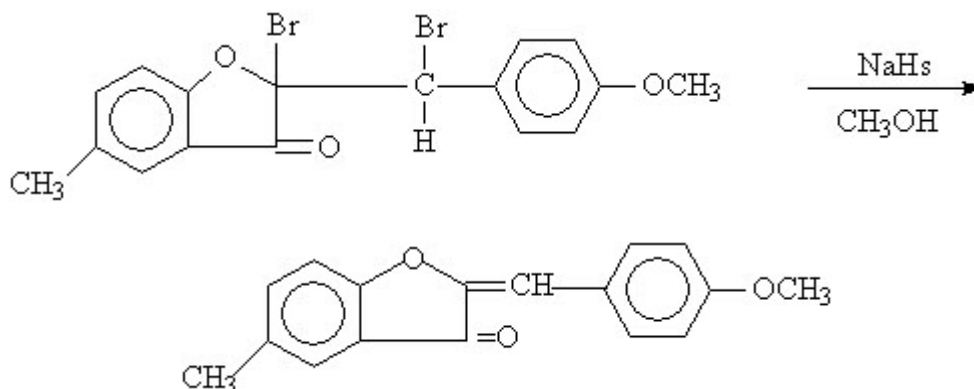
In addition to after mentioned peaks spectrum also consist peaks coversponding to other common bending, stretching vibration .

PMR spectrum

The PMR spectrum was recorded in CDCL₃ in TMS a internal standard and is reproduced on plate No 36.

The observed chemical shift can be correlated as follows.

| | | | |
|--------------------|---|----|-----------------------|
| 1.6 δ | S | 1H | = CH |
| 2.35 δ | S | 3H | Ar – CH ₃ |
| 3.8 δ | S | 3H | Ar – OCH ₃ |
| 6.87 TO 8 δ | m | 7H | Ar – H |
| 6.67 δ | S | 1H | = CH |



Scheme

Table 1.

| S. No | Aurone dibromide | Aurone | m.p.°C |
|-------|---|--|--------|
| 1 | 2 ,<Xj-dibromo-2-(4' methoxy benzylA—5-methyl-coumaran-3-one | 2-(4'-methoxy benzylidene)-5-methyl coumaran-3-one | 154 |
| 2 | 2, <-dibromoe-2- benzyl 5-methyl-coumaran-3-one | 2-benzylidene-5-methyl coumaran-3-one | 112 |
| 3 | 2,<-dibromo-2 (4' methoxy-benzyl) coumaran-3-one | 2-(4'methoxy benzylidene)-4-methoxy-coumaran-3-one | 140 |
| 4 | 2 ,o-dibromo-2-(4' methoxy benzyl) 4-tmethoxy coumaran-3-one | 2-(4'-methoxy benzylidene)-3-nitro-5-methyl coumaran-3-one | 180 |
| 5 | 2 ,o<-dibromo-2(4' methoxy benzyl)-3-nitro-5-methyl coumaran-3-one | 2-(4'-methoxy benzylidene)-3-nitro-5-methyl coumaran-3-one | 230 |
| 6 | 2,°(-dibromo-2- benzyl -3-nitro-5-methyl coumaran-3-one | 2-(4 ¹ -methoxy benzylidene)-3-bromo-5-methylcoumaran-3-one | 226 |
| 7 | 2X-di.bromo-2(4' methoxy-benzyl)-3-bromo-5-methyl coumaran-3-one | 2-(4'-methoxy benzylidene) coumaran-3-one | 176 |
| 8 | 2,o(-dibromo-2— benzyl —3-bromo-5-methyl coumaran-3-one | 2- benzylidene -3-bromo-5-methyl coumaran-3-one | 160 |

REFERENCES

1. T.S. Wheeley and M.P. Dodwadna-lh, *Proc. Ind. Acad. Sci. India, Sect. A* **2**: 438 (1955).
2. P.A. Soni and B.J. Ghiya, *Cury. Sci* **41**: 137 (1972).
3. T.K. Raja, *Indian J. Chem, Sect* **137B**: 812 (1976).
4. T.C. Sharma and M.M. Bokadia, *Indiain J.Chem. Sect. B*, **14**: 65 (1976).
5. R .5. Raghavan, M. Govindrajan and K.G. Sanjeev Babu, *Curr. Sci*, **48**: 1072 (1979).
6. D. Landini, L., Mi lest, M.L., Quadri and F. Rolla, *J. Org. Chem.***49**: 152 (1984).
7. J. Nakayama, H. Machida and' M. Hoshino, *Tetrahedron Let.* **24**: 3001 (1983).

8. Z. Goren and I. W. Miner, *J. Am. Chem. Soc.*, **165**: 7764 (1983).
9. H. Alper and M. Copal, *J. Org. Chem.* **48**: 4390 (1983).
10. K. Fukunaga and M. Yamaguchi, *Synthesis*, 879 (1981).
11. S. W. Sathe and B. J., Ghiya, unpublished work.
12. V. P. Tashchi, A. F. Rukasov, T. I. Orlova, Yu. G. Putsykin and Yu. A. Baskakov, *Khim. Geterotsikl. Soedini*, **6**: 75 (1982). (*Chemabst S7*: 109794 (1982)).
13. R. T. Lalonde, *J. Chem. Soc. Chem. Commun* **7**: 401 (1982).
14. V. S. Jamode, *Indian J. Chem. Sect. B* **17**: 629 (1979).
15. R. T. Lalonde, B. A. Horenstein, K. Schwandler, R. C. Fritz and R. A. Florence, *J. Org. Chem* **48**: 4049 (1983).
16. A. G. Doshi and B. J. Ghiya *J. Indian Chem. Soc.* **LX III**: 404-405 (1986).
17. A. G. Doshi, Ph.D. thesis, Amravati University, Amravati.