

Reductive Debromination of *vicinal*-Dibromides with Thiophenoxide Ion

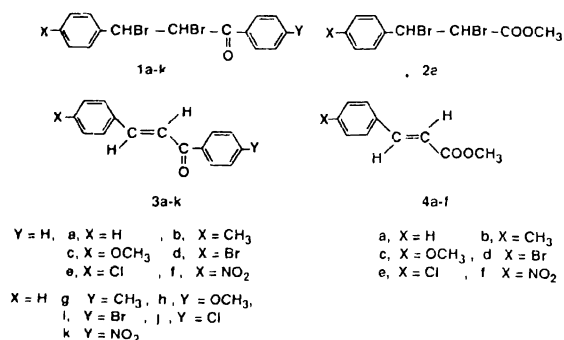
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The olefin-forming dehalogenation of *vicinal*-dibromoalkanes can be accomplished with a variety of reagents such as sodium iodide¹, triphenylphosphine², thiolacetic acid², sodium sulphide³, thiourea⁴, sodium hydrogen sulphide⁵, phenylhydrazine hydrochloride⁶ and metals^{1,7}.

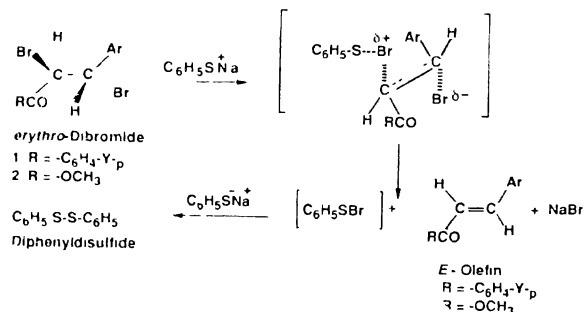
In this communication, the treatment of *erythro*-2,3-dibromo-1,3-diarylpropan-1-ones (**1a-k**) and *erythro*-methyl-2,3-dibromo-3-arylpropanoates (**2a-f**) with sodium thiophenoxide in ethanol or dimethylformamide (DMF) gave *E*-1,3-diaryl-2-propen-1-one (**3a-k**, > 95%) and *E*-methyl-*p*-substituted cinnamates (**4a-f**, > 80%), respectively.



This debromination reaction was carried out by stirring ethanolic solutions of the substrate (0.01 mol), thiophenol (0.02 mol) and sodium metal (0.02 mol) for 5–20 min at room temperature. Excess thiophenol was removed by treating the reaction mixture with 5% sodium hydroxide solution. When the reaction mixture was left overnight, the olefinic product was found to be contaminated with diphenyl disulphide which was separated by fractional crystallisation. ¹H nmr spectra revealed that the olefins obtained, in all cases, have the *E*-configuration, suggesting that these debromination reactions are stereoselective.

This debromination reaction probably occurs *via* a typical *I*2 mechanism in which the thiophenoxide ion removes a positive bromine atom (the one occupying the α -position is the most reasonable^{2,4}) and simultaneously with departure of bromide ion and the formation of the π -bond (Scheme 1). A high yield of diphenyl disulphide was obtained when the reaction was left for long time, without the isolation of the intermediate PhSBr.

The above mentioned mechanism is analogous to that proposed for the thiolacetic acid in pyridine², iodide ion¹,



Scheme 1

and thiourea^{4a} employed debromination reactions of substituted *vicinal*-dibromides and also similar to the mechanism suggested by Kornblum *et al.*⁸, for the reductive elimination of *vicinal*-dinitro compounds (one-electron transfer mechanism).

The method presented herein is likely to be a useful addition to the reported ones owing to its simplicity and the high yield obtained under mild conditions.

Experimental

The ¹H nmr spectra (CDCl₃) were measured on a Varian EM-390 spectrometer (90 MHz).

The synthesis of *erythro*-2,3-dibromo-1,3-diarylpropan-1-ones⁹ (**1a-k**) and *erythro*-methyl-2,3-dibromo-3-arylpropanoates¹⁰ (**2a-f**) were reported previously.

Reaction products : To the appropriate dibromoketone (**1a-k**) or dibromo ester (**2a-f**) (0.01 mol) dissolved in absolute ethanol, a solution of two equivalent amounts of sodium and thiophenol (0.02 mol) in absolute ethanol was added. The reaction mixture was stirred at room temperature under nitrogen atmosphere. At the end of reaction time (as indicated by tlc) the reaction mixture was poured into a large volume of ice-cold water containing 5% NaOH. The resulting solid was filtered and dried. The same procedure was repeated in dimethylformamide as solvent.

The dibromoketones (**1a-k**) under the previous conditions gave the corresponding 1,3-diaryl-2-propen-1-ones¹¹ (**3a-k**) which were crystallised from ethanol : 3-aryl, *p*-H, m.p. 57°; *p*-CH₃, 95°; *p*-Cl 112°; *p*-Br, 121°; *p*-NO₂, 164°; 1-aryl, *p*-CH₃, 75°; *p*-OCH₃, 106°; *p*-Cl, 98°; *p*-Br, 101°; *p*-NO₂, 145°. Evaporation of the mother liquor of crystallisation gave a small quantity of diphenyl disulphide, m.p.

60°. The *E*-configuration of the products¹² (**3a-k**) are indicated from their ¹H nmr which showed two doublets at δ 7.1–7.55 for H-2 and 6.61–6.75 for H-3 with coupling constants $J_{2,3}$ 15 Hz.

The dibromo esters (**2a-f**) under the above conditions gave the corresponding methyl *p*-substituted cinnamates (**4a-f**) which were crystallised from methanol : 3-aryl, *p*-H, 36°; *p*-OCH₃, 85°; *p*-CH₃, 56°; *p*-Cl, 77°; *p*-NO₂, 155°. Evaporation of the mother liquor of crystallisation gave a small quantity of diphenyl disulphide. The *E*-configuration of the products¹³ (**4a-f**) are indicated from their ¹H nmr spectra which showed two doublets at δ 6.33–6.51 for H-2 and 7.62–7.74 for H-3 with coupling constants $J_{2,3}$ 15 Hz.

References

1. W. H. SAUNDERS, JR. and A. F. COCKERILL, "Mechanism of Elimination Reactions", Wiley, New York, 1973; D. LANDINI, S. QUICI and F. ROLLA, *Synthesis*, 1975, 397.
2. A. J. SPEZIALE and C. C. TUNG, *J. Org. Chem.*, 1963, **26**, 1353, 1521.
3. K. FUKUNAGA, *Synthesis*, 1981, 879; D. LANDINI, L. MILESI, M. L. QUADRI and F. ROLLA, *J. Org. Chem.*, 1984, **49**, 152.
4. K. M. IBNE-RASA, A. R. TAHIR and A. RAHMAN, *Chem. Ind.*, 1973, 232; T. C. SHARMA and M. M. BOKADA, *Indian J. Chem., Sect. B*, 1976, **14**, 65; N. J. REDDY and T. C. SHARMA, *Indian J. Chem., Sect. B*, 1979, **17**, 645.
5. A. G. DOSHI and B. J. GILY, *J. Indian Chem. Soc.*, 1986, **63**, 404.
6. M. G. JOSHI and K. N. WADODKAR, *Indian J. Chem., Sect. B*, 1981, **20**, 1090.
7. T. SUGITA, T. NAKAGAWA, K. NISHIMOTO, Y. KASAI and K. ICHIKAWA, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 871; G. A. OLAH and G. K. S. PRAKASH, *Synthesis*, 1976, 607.
8. N. KORNBLUM, S. D. BOYED, H. W. PINNICK and R. G. SMITH, *J. Am. Chem. Soc.*, 1971, **93**, 4316; K. FUKUNAGA and M. KIMURA, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1107; Y. MIZUSHIMA, H. MIYAKE, K. FUJIWARA, N. ONO and K. TAKIKAWA, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 3295.
9. S. K. EL-SADANY, S. M. SHARAF, M. E. ELBA and A. A. YOUSSEF, *Egypt. J. Chem.*, 1992, **35**, 149.
10. E. A. HAMED, S. M. SHARAF, S. K. EL-SADANY, A. K. IBRAHIM and A. A. YOUSSEF, *Egypt. J. Chem.*, 1992, **35**, 149.
11. S. K. EL-SADANY, S. M. SHARAF, E. A. HAMED, J. FLEISHAUR, A. I. DARWISH and A. A. YOUSSEF, *Egypt. J. Chem.*, 1991, **34**, 401.
12. K. L. WILLIAMSON, N. C. JACOBUS and K. T. SOUCY, *J. Am. Chem. Soc.*, 1964, **86**, 4021; A. R. KATRETZKY and F. J. SWINBOURNE, *J. Chem. Soc.*, 1965, 6707; G. BUTT and R. D. TOPSOM, *Spectrochim. Acta*, 1980, **36**, 811.
13. P. B. D. DE LA MARE, M. A. WILSON and M. J. ROSSER, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1480.