3,4,5,6,7,8-hexahydro-7,7-dimethyl-5-oxo-2*H*-chromene, 87698-48-4; 2-carbethoxycyclopentanone, 611-10-9; 2-(hydroxymethylene)cyclohexanone, 823-45-0; (*E*)-2-(3-ethoxy-2-propenyl)cyclohexanone, 87698-49-5; acrolein ethylene ketal, 3984-22-3; 2-nitro-1,3-indandione, 3674-33-7; dimedone, 126-81-8; 2-methyl-1,3-cyclohexanedione, 1193-55-1; 2-(3-ethoxy-2-methyl-2-propenyl)-2-methyl-1,3-cyclohexanedione, 87698-50-8; 2-[3,3-(ethylenedioxy)-1-propyl]-2-methyl-1,3-cyclohexanedione, 87698-51-9; 2-acetylcyclopentanone, 1670-46-8; 1-[3,3-(ethylenedioxy)-1-propyl]-2-oxocyclopentanecarbonitrile, 87698-52-0; 2-oxocyclohexanecarbonitrile, 4513-77-3; pyridinium *p*-toluenesulfonate, 24057-28-1; 2-amino-1-cyclopentene-1-carbonitrile, 2941-23-3; ethyl 1-(3-ethoxy-2-phenyl-2-propenyl)-2-oxocyclopentanecarboxylate, 87698-58-6.

Reductive Dehalogenation of *vic*-Dihaloalkanes to Alkenes with Sodium Sulfide under Phase-Transfer Conditions

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Reductive dehalogenation of *vic*-dihaloalkanes to alkenes with aqueous Na_2S under phase-transfer catalysis conditions is reported. Debromination reaction occurs at room temperature, giving alkenes in ≥90% yields. Meso and erythro *vic*-dihaloalkanes afford only trans olefins and react faster than the corresponding diastereomeric *d,l* and threo derivatives, which are converted into a mixture of cis and trans olefins. *vic*-Dichloroalkanes react much more slowly than the bromo compounds, affording the dehydrochlorination products instead of the reductive dehalogenation ones.

The olefin-forming dehalogenation of vicinal dibromo alkanes (widely used intermediates for the purification of olefins and for the protection of C=C double bonds[1-5]) can be accomplished with a variety of reagents.[6] One of the most recent dehalogenating systems involves the reaction of *vic*-dibromo derivatives with $Na_2S{\cdot}9H_2O$ in DMF solution.[6,7]

Here we report that the latter reaction can be more advantageously performed under liquid–liquid phase-transfer catalysis (PTC) conditions (eq 1).

$$RCXH{-}CXHR' \xrightarrow[\text{catalyst, toluene, 25 °C}]{Na_2S\ \text{aqueous}} RCH{=}CHR' + 2NaX + S \quad (1)$$

$$X = Br,\ \text{catalyst} = n\text{-}C_{16}H_{33}P^+Bu_3Br^-$$

The debrominations were carried out by stirring at room temperature a heterogeneous mixture of a toluene solution of substrate (1 mol) and an aqueous solution of $Na_2S{\cdot}9H_2O$ (2.5 mol) in the presence of catalytic amounts (0.01 mol) of hexadecyltributylphosphonium bromide as phase-transfer agent.

Under these conditions the dehalogenation reaction is complete in 5 min–12 h, and the yields in the olefins are ≥90%. As expected, reaction times increase on decreasing the amount of the catalyst; in the absence of the latter the reaction does not occur. The debromination can be performed even at 0 °C (Table I). As shown in the case of *meso*-1,2-dihalo-1,2-diphenylethanes, the chloro derivative reacts much more slowly than the bromo compound and affords the α-chloro-*cis*-stilbene instead of the *trans*-stilbene. In the case of the *vic*-dibromides the order of reactivity is qualitatively the same as previously found in the reductive dehalogenation with sodium sulfide in DMF[6] or with iodide ion both in a homogeneous organic solution[9] and in an aqueous–organic two-phase system:[10] meso or erythro derivatives react faster than the corresponding diastereoisomeric *d,l* or threo compounds. Moreover the presence of electron-withdrawing groups bound to the halogenated carbon accelerates the reactions (Table I). Also the stereochemical behavior observed under the present conditions is practically the same found by working in DMF solution with Na_2S[6] or by using iodide ion both under PTC conditions[10] and in a homogeneous organic solution.[11-15] In particular, meso and erythro *vic*-dihaloalkanes yield only trans alkenes, whereas the corresponding diastereoisomeric *d,l* and threo derivatives afford a mixture of cis and trans alkenes. The cis/trans ratio strongly depends on the nature of the groups bound to the halogenated carbons (Table I). On the reasonable assumption that a common mechanism is at work[16] in the reductive de-

† Deceased January 1983.

(1) Hickinbottom, W. J. "Reactions of Organic Compounds", 3th ed.; Longmans, Green and Co. LTD: London, 1962; p 534.
(2) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 1089.
(3) Harrison, I. T.; Harrison, S. "Compendium of Organic Synthetic Methods"; Wiley: New York, 1971; p 510.
(4) Buelher, C. A.; Pearson, E. "Survey of Organic Synthesis"; Wiley: New York, 1970; p 80.
(5) Solo, A. J.; Sinigh, B. *J. Org. Chem.* **1965**, *30*, 1658.
(6) Fukunaga, K.; Yamaguchi, H. *Synthesis* **1981**, 879 and references therein.
(7) Iron graphite[8a] and zinc in the presence of a catalytic amount of $TiCl_4$[8b] were very recently reported as new reagents for the dibromination of *vic*-dibromoalkanes.
(8) (a) Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1982**, *47*, 876. (b) Sato, F.; Akiyma, T.; Iida, K.; Sato, M. *Synthesis* **1982**, 1025.
(9) Buckles, R. E.; Bader, J. M.; Thurmaier, R. J. *J. Org. Chem.* **1962**, *27*, 4523.
(10) Landini, D.; Quici, S., Rolla, F. *Synthesis* **1975**, 397.
(11) Trumball, E. R.; Ibue-Rasa, K. M. *J. Org. Chem.* **1963**, *28*, 1907.
(12) Tasi, Lee, C. S.; Mathai, I. M.; Miller, S. I. *J. Am. Chem. Soc.* **1970**, *92*, 4602.
(13) Winstein, S.; Presman, D.; Young, W. G. *J. Am. Chem. Soc.* **1939**, *61*, 1645.
(14) Hine, J.; Bader, W. H. *J. Am. Chem. Soc.* **1955**, *77*, 361.
(15) Baciocchi, E.; Lillocci, C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 38.
(16) In the case of Na_2S a one electron transfer mechanism similar to that proposed by Kornblum[17] for the reductive elimination of *vic*-dinitro compounds seems to be excluded. Indeed the dehalogenation reaction, performed under PTC conditions, is not inhibited by the presence of radical scavengers such as 2,2,6,6-tetramethyl-4-hydroxypiperidinyl *N*-oxide or N,N-diphenylpicrylhydrazyl.

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Table I. Dehalogenation of *vic*-Dihaloalkanes to Alkenes (1 mol) with Sodium Sulfide (2.5 mol) under Phase-Transfer Conditions[a]

substrate	cat., mol	T, °C	time, min (h)	conv,[b] %	yield,[c] %	products	% cis	% trans
meso-1,2-dibromo-1,2-diphenylethane	0.01	25	30[d]	100	97	*trans*-stilbene		100
	0.02	25	15	100		*trans*-stilbene		
	0.05	25	<10	100		*trans*-stilbene		
	0.00	25	(24)	0.00				
	0.01	0	(4)	100		*trans*-stilbene		
d,l-1,2-dibromo-1,2-diphenylethane	0.01	25	95	100	94	stilbene	90.5	9.5
meso-1,2-dichloro-1,2-diphenylethane	0.05	80	(42)	90		α-chloro-*cis*-stilbene		100
methyl *erythro*-2,3-dibromo-3-phenylpropanoate	0.01	25	≤5	100	97	methyl *trans*-cinnamate		100
methyl *threo*-2,3-dibromo-3-phenylpropanoate	0.01	25	10	100	97	methyl cinnamate	50	50
trans-1,2-dibromocyclohexane	0.01	25	(12)	100	90	cyclohexene		
5α,6β-dibromocholestan-3β-ol	0.01	25	40	100	95	5-cholesten-3β-ol		

[a] A toluene solution of substrate and catalyst (20 mL) and an aqueous solution of $Na_2S \cdot 9H_2O$ (24 mL). [b] By GC, NMR, and/or TLC analyses. [c] Isolated pure products. [d] The same reaction time was found by working in the presence of 2,2,6,6-tetramethyl-4-hydroxypiperidinyl *N*-oxide or of *N,N*-diphenylpicrylhydrazyl (0.05 mol), as radical scavengers.

halogenation promoted by iodide ions and Na_2S, the rationale for this behavior should be the same, already discussed[10] in the former case.

Experimental Section

General Methods. GC data were obtained on a Varian 3700 gas chromatograph equipped with a 3% Carbowax 20M on chromosorb W column and were evaluated with a Varian Model 401 data system by the internal standard method. NMR analyses were performed on a Varian EM-390 90-MHz spectrometer in $CDCl_3$ solution with Me_4Si as an internal standard.

Materials and Substrates. Sodium sulfide and toluene were commercial Analar grade products used without further purification. Hexadecyltributylphosphonium bromide was prepared by a standard procedure.[18] All substrates were known products and were prepared according to the literature: *meso*- and *d,l*-1,2-dibromo-1,2-diphenylethane[19] *meso*-1,2-dichloro-1,2-diphenylethane,[20] methyl *erythro*- and *threo*-2,3-dibromo-3-phenylpropanoates,[21] *trans*-1,2-dibromocyclohexane,[22] and 5α,6β-dibromocholestan-3β-ol.[23] The physical properties of the above compounds were in agreement with those reported.

Typical Procedure. Debromination of *meso*-1,2-Dibromo-1,2-diphenylethane. A toluene solution (20 mL) of *meso*-1,2-dibromo-1,2-diphenylethane (6.8 g, 20 mmol) and hexadecyltributylphosphonium bromide (0.1 g, 0.2 mmol), and an aqueous solution (24 mL) of $Na_2S \cdot 9H_2O$ (12 g, 50 mmol) were mixed in a flask and magnetically stirred at 25 °C. The reaction was monitored by TLC (silica gel, light petroleum). After 30 min, conversion was complete. The organic layer was separated and the organic phase extracted with toluene (3 times). The combined organic extracts were filtered from an amount of sulfur, washed with water and dried with Na_2SO_4. Evaporation of the solvent and column chromatography over silica gel (eluent: light petroleum) gave *trans*-stilbene: 3.5 g (97% yield); mp 123-125 °C (lit.[12] mp 124-125 °C); NMR ($CDCl_3$) δ 7.1 (s, 2 H) and 7.2-7.6 (m, 12 H).

Note Added in Proof: After submission of this paper Nakayama et al. reported an analogous system for the reductive debromination of *vic*-dibromides under phase-transfer conditions (Nakayama, J.; Machida, H.; Hoshino, M. *Tetrahedron Lett.* **1983**, *24*, 3001).

Registry No. *meso*-1,2-Dibromo-1,2-diphenylethane, 13440-24-9; *d,l*-1,2-dibromo-1,2-diphenylethane, 13027-48-0; *meso*-1,2-dichoro-1,2-diphenylethane, 15951-99-2; methyl *erythro*-2,3-dibromo-3-phenylpropanoate, 52777-73-8; methyl *threo*-2,3-dibromo-3-phenylpropanoate, 52742-03-7; *trans*-1,2-dibromocyclohexane, 7429-37-0; 5α,6β-dibromocholestan-3β-ol, 1857-80-3; hexadecyltributylphosphonium bromide, 14937-45-2; sodium sulfide, 1313-82-2.

(17) Kornblum, N.; Boyd, D. S.; Pinnick, H. W.; Smith, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4316.
(18) Starks, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 195.
(19) Fieser, L. F. *J. Chem. Educ.* **1954**, 291.
(20) Bergman, E.; Bondi, A. *Chem. Ber.* **1931**, *64*, 1455.
(21) Krimmel, C. P.; Thielu, L. E. "Organic Syntheses"; Wiley: New York, 1963; Vol. IV, p 960.
(22) Snyder, H. R.; Brooks, L. A. "Organic Syntheses"; Wiley: New York, 1943; Vol. II, p 171.
(23) Fieser, L. F. "Organic Syntheses"; Wiley: New York, 1963; Vol. IV, p 195.

A New Method for Cyclopentanone Annelation

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$MeAlCl_2$-initiated cyclization of enone **6d** provides an 85% yield of a 9:1 mixture of trans- and cis-fused hydroazulenones **9** and **10**. Similarly, cyclization of **7d** gives a 31% yield of **11** with an equatorial methyl group, and cyclization of **8d** affords a 46% yield of **12** and a 7% yield of **13**.

Introduction

We have recently published a novel approach to the synthesis of *trans*-hydrindanones.[1] Treatment of γ,δ-unsaturated ketone **1** with 2 equiv of $MeAlCl_2$ in CH_2Cl_2 at 25 °C for 24 h leads to **3** in 30-50% yield. We have subsequently shown that the reaction may be extended to provide an intermediate **4** for steroid syntheses in which the trans-fused CD ring junction has been stereospecifically constructed.[2] Treatment of the readily available dienone

(1) Karras, M.; Snider B. B. *J. Am. Chem. Soc.* **1980**, *102*, 7951.
(2) Snider, B. B.; Kirk, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2364.

0022-3263/84/1949-0153$01.50/0