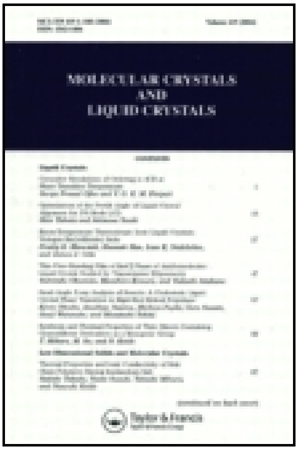

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Gas-Solid Reactions : Part VI. Interaction of Solid Chalcones With Bromine and Iodine Vapours

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GAS-SOLID REACTIONS : PART VI. INTERACTION OF SOLID CHALCONES WITH BROMINE AND IODINE VAPOURS

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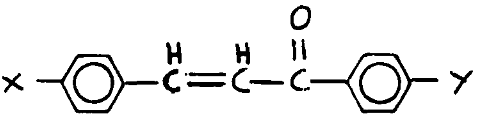
Abstract: Solid chalcones (azylidene acetophenones) give, on exposure to bromine vapour at room temperature, the "trans-adduct" in quantitative or near-quantitative yield. Polymorphic forms of several compounds do not differ in their bromination products. Iodine vapours do not cause cis-trans isomerisation in the solid cis-chalcones.

INTRODUCTION

Previous studies[1-5] on the bromination of solid olefins by bromine in the vapour phase showed that the addition of bromine generally proceeds by trans-addition to cis- and trans--substituted ethylenes, and suggested that the abnormal direction of addition to cis-substituted styrenes, stilbenes and dibenzoylethylenes is due to cis-trans isomerisation prior to or during addition which leads to erythro or meso dibromides, respectivelly.

The solid-state cis-trans isomerisation of a number of alkoxy-cis-cinnamic acids and dibenzoylethylenes has been demonstrated by treatment with iodine vapour[2,3]. However, the only examples of cis-trans isomerisation prior to or during bromine addition that we have found so far is the reaction of solid cis-stilbene and of cis-1,2-di-p-methyl--benzoylethylene to give the meso-dibromides[1,2]. Since we need more examples for a detailed analysis of the various processes involved in such two-phase (solid-gas), two-component reactions, we extended the study to solid chalcones which can be visualised, structurally, as compounds "in-between" stilbenes and dibenzoylethylenes.

The present work reports the results of gas-solid bromination and iodination of three groups of substituted cis- and trans-chalcones (I) for which some information about the solution bromination is available. Thus all of the trans-forms



(I)

of the chalcones of Table I, are known to give two dibromides in solution and therefore the behaviour of cis-and trans-solids towards bromine vapour was of great interest.

The three groups of chalcones result by placing the substituents on the styryl side or on the phenyl side of the molecule or on both.

EXPERIMENTAL

All the trans-chalcones were prepared following the procedure of Kohler[6] and were recrystallised from ethanol until a constant melting point was obtained. Cis-chalcone was prepared with a procedure similar to that used by Lutz and Jordan[7] and cis-4-methoxychalcone according to Black and Lutz[8].

The cis-p-methylchalcone and the cis-p,p' -dimethyl chalcone were prepared in a similar way as the cis-4-methoxy chalcone. Table I lists the melting points (uncorrected) obtained and those from literature.

TABLE I. Chalcones

Compound	Mp, °C	Lit. mp, °C	Ref.
trans-chalcone	57	55-56	a
cis-chalcone	45	45-46	b
trans-p-Cl-chalcone			
form-I	114-115	112-113	a
from-II	111-112		
trans-p-MeO-chalcone	76-78	76-78(74.5-75.3)	c,d
cis-p-MeO-chalcone	33-34	33-33.5	e
trans-p'-Me-chalcone	75-76	75-76	f
cis-p'-Me-chalcone	65	?	
trans-p,p'-dimethyl chalcone	132	132	g
cis-p,p'-dimethyl chalcone	46-50	?	

a. N.L. Silver and D.W. Boukin: J.Am.Chem.Soc.,35,759(1970), b. Ref.7; c.Ref.8; d. N. Kochetkov and V. Belyaev:Zh. Obshch.Kim., 30,1495(1960); e.Ref.7; f. C. Weygand and H. Banmgärtel: Ann.469,225(1929): g .Ref.13.

METHODS

I.R. and NMR spectra (δ/p.p.m) were taken on a Perkin-Elmer 521 spectrophotometer and on a Varian A60 instrument respectivelly. Powder photographs were taken on a Debye-

-Scherer camera with Cu-kα radiation.

BROMINATION

The bromine uptake was carried out on samples (average weight 30 mg) and placed on a microscope coverslip. The samples were introduced into a modified washbottle containing liquid bromine, and immersed in a thermostat at 25±0.2°C; completion of bromination was achieved in less than 45 min. The samples were removed and introduced into a Cahn R.G. Electrobalance and weighed. The balance was attached to a vacuum pump and the loss of weight during evacuation was displayed on a recorder. The evacuation was continued until constant weight. Solution brominations were carried out according to the literature.

ISOMERISATION

The solid-state cis-trans isomerisation of the cis-chalcones was attempted by treatment with iodine vapour, by introducing approximately 10mg of crystalline powder into a reaction vessel containing solid iodine. The whole was immersed in a thermostat at 25±0.2°C. The vessel was vigorously shielded from light. Samples of the material were withdrawn from the reaction vessel (usually after 24 hours) and checked for trans-isomers by I.R. measurements in potassium bromide pellets (200 mg) and with U.V., m.p. and X-ray powder photograph measurements.

RESULTS

BROMINATION

trans-Chalcone : The ketone gave a dibromide of m.p. 158°, δ 6.21 (2H, ABq, J 12 H_2), identical with that obtained from the similar reaction in solution[9]. However a second dibromide, m.p. 108-110[10], resulted from solution bromination.

cis-Chalcone : The cis-ketone gave a dibromide of m.p. 158°, identical with that obtained from the solid trans-ketone. The I.R. spectrum was the same as that of the dibromide prepared from the similar reaction in solution[7].

trans-p-Cl-Chalcone : This compound exists in two crystalline modifications, form-I m.p. 114-115° and form-II m.p. 111-112°. Both crystalline forms on exposure to bromine vapour give the same dibromide, m.p. 180-183°. Bromination in solution results in two dibromides of m.p. 125-126° and 180-183°(the N.M.R. spectrum shows a mixture of approximately 50% for each dibromide). We prepared these two dibromides according to Dodforss[11] and we verified that the dibromide from the gas-solid reaction is identical to that with the higher melting point (180-183°) was obtained from solution.

trans-p-MeO- Chalcone : The compound gave a dibromide of m.p. 172-175°, identical with that obtained from solution.

cis-p-MeO-Chalcone : The cis-compound gave a dibromide of m.p. 172-175°, identical with that obtained from the solid trans-ketone and therefore identical also with that obtained from solution.

trans-p-MeO-Chalcone : This compound on exposure to bromine vapour gave a dibromide of m.p. 174-175°, identical with the dibromide prepared from solution[12]. However the reaction from solution gives an additional dibromide with m.p. 140-145°.

cis-p-Me-Chalcone : The cis-isomer gave a dibromide of m.p. 174-175°, identical with that obtained from the solid trans-isomer and therefore identical also with the higher melting pointing one from solution[12].

trans-p,p'-dimethyl Chalcone :This compound on exposure to bromine vapour gives a dibromide with m.p. 175-179°. This dibromide is the erythro-form and is accompanied by optical activity induction to the extent of 6%[13]. Bromination in solution leads to 3-Bromo-p-p'-dimethyl chalcone-dibromide[13] m.p. 153-154°.

cis-p,p'-dimethyl Chalcone: The cis-isomer gave an identical isomer with that obtained from the trans-isomer. Whenever however bromine condensed on the solid material the result was 3-bromo-p,p'-dimethyl chalcone-dibromide m.p. 155°.

ISOMERISATION

All the cis-compounds have been tested for cis-trans isomerisation as it was described in the experimental section. The results showed that the cis-compounds remained unchanged and therefore cis — trans isomerisation does not take place in the solid state under the described conditions.

In one case (cis-p-MeO-Chalcone) there was an indication of iodine addition to the carbon-carbon double bond.

DISCUSSION

Addition of **gaseous** bromine to solid trans and cis chalcones is rapid and quantitative in all the compounds studied. The reaction is stereoselective and the products are the trans-adducts. The stereo-structure of the trans-adducts is independent of the crystal structure of the organic component, thus the two crystal modifications of the trans-p-Cl-chalcone result in the same dibromide as it was noted also in the solid cinnamic acid series[1].

An important feature of the gas-solid bromination is the fact that it gives always one product (the higher melling point **one) instead of two as in** solution bromination, providing a way of preparing by, simple means, pure dibromides. These dibromides should be in the most stable conformation since the reaction in the solid state occurs with a minimum amount of atomic or molecular movement[14].

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REFERENCES

1. E. Hadjoudis, E. Kariv and G.M.J. Schmidt: J.Chem.Soc., Perkin II, 1056 (1972).
2. E. Hadjoudis and G.M.J. Schmidt: J.Chem. Soc., Perkin II, 1060 (1972).
3. E. Hadjoudis : Isr.J.Chem., 11, 63 (1973).
4. E. Hadjoudis: Isr.J.Chem., 12, 981 (1974).
5. E. Hadjoudis: in Reactivity of Solid, J. Eds.Wood, O. Lindqvist, C. Helgesson and N-G. Vannerberg, p. 493 Plenum Press, New York 1976.
6. E.P. Kohler and H.M. Chadwell, "Organic Synthesis", Coll.Vol.I, p.78 John Wiley; Sons, Inc., New York, 1932.
7. R.E. Lutz and R.H. Jordan: J.Am.Chem.Soc., 72, 4090 (1950).
8. W.B. Black and R.E. Lutz: J.Am.Chem.Soc., 77, 5134 (1955).
9. R.E. Buckles, R.C. Johnson and W.J. Probst: J.Org. Chem., 22, 55 (1957).
10. F.J. Pond, H.J. York and B.I. Moore: J.Am.Chem.Soc., 23, 789 (1901).
11. S. Dodforss: Ber., 43, 214 (1917).
12. S. Dodforss: Ber., 59, 2247 (1926).
13. K. Penzien and G.M.J. Schmidt: Angew.Chem., 81, 628 (1969).
14. M.D. Cohen and G.M.J. Schmidt, in Solid State Photochemistry, Ed. D. Ginsburg, p.2 Verlag Chemie, New York, 1976.