SHORT COMMUNICATIONS

A NEW SEMI-STABILIZED FLUORINATED YLID: *p*-FLUOROBENZYLIDENE TRIPHENYLPHOSPHORANE

K. C. GUPTA, R. K. NIGAM and
NIRUPMA SRIVASTAVA
Department of Chemistry, D.V. (P.G.) College, Orai 285 001, India.

THE course of decomposition of cyclic betaine formed by the nucleophilic attack of ylidic carbanion on carbonyl group into *cis*-olefin or *trans*-olefin or both is controlled by structural features of the ylid, the aldehyde and the reaction conditions[1-6]. Thus, the behaviour of the stabilized, non-stabilized and semi-stabilized ylids are different with regard to their stereochemistry in the Witting reaction[7-9]. Recently, we have examined the effect of halogen atoms other than fluorine on the halogenated ylids and observed that *trans*-olefins were formed exclusively[10-13]. In the present investigation, the influence of the fluorine atom in *p*-fluorobenzylidenetriphenylphosphorane on the geometry of the resulting olefin is studied.

The quaternisation of TPP with *p*-fluorobenzyl bromide in benzene at reflux temperature gave *p*-fluorobenzyltriphenylphosphonium bromide (1). The structure of the latter was evidenced by spectral data. The NMR spectrum showed a characteristic peak (doublet) centered at δ 5.60 due to $\rightarrow \overset{+}{P}-CH_2-$group and aromatic protons at δ 6.95–8.15. The IR spectrum showed a diagnostic band in the region 1440 cm^{-1} due to $\rightarrow P-C<$ stretching vibrations. The action of sodamide on salt (1) in benzene solution gave an intense yellow colour due to formation of ylid *p*-fluorobenzylidenetriphenylphosphorane (2) which could not be isolated and hence the reaction was carried out *in situ*. The structure of ylid (2) was evident from the spectral data of its precursor, salt (1).

In order to test the reactivity of the ylid (2), it was reacted with equimolar amounts of substituted benzaldehydes in anhydrous benzene to give trans-4-fluorostilbenes (4a–f) in 50–80% yields (route A). The alternative route (B) to synthesise the same stilbenes (4a–f) involved the condensation of substituted benzylidenetriphenylphosphoranes (5a–f) with *p*-fluorobenzaldehyde in methanolic solution.

Factors such as variation of solvents have no influence in changing the stereochemistry of the products formed. However, the reaction was facile in polar solvents and gave better yields of the products.

Mechanistically it appears that the ylid (2) or ylid (5a–f) attacks the carbonyl group of aldehyde (3a–f) or 4-fluorobenzaldehyde to give a betaine having either a *threo* or an *erythro* configuration. The former on decomposition gives *trans*-olefins; whereas the latter affords *cis*-olefins[14]. It is not surprising that *trans* olefins are often the dominant products, since they are thermodynamically more stable[15]. The typical absence of the formation of *cis*-isomers in the reaction may be due to the bulky size of the substituted phenyl rings of benzaldehyde (3a–f) and the ylid carbanion which would not be eclipsed. The non-availability of *cis*-isomers in the reaction could also be due to non-stability of the *erythro* betaine since in this case there would be an interaction between the phenyl ring of ylid carbanion portion (2). These observations led us to conclude that in case of benzylidenetriphenylphosphorane-a semistable ylid (5a–f) will react with substituted benzaldehydes to give the *trans*-isomers exclusively.

All the *trans*-stilbenes (4a–f) gave satisfactory elemental analysis; the m.ps. of *trans*-fluorostilbenes (3a–f) agree with those reported in literature[16]. The IR spectra of products showed characteristic absorption bands at 1600 cm^{-1} (C=C) and at 980–970 cm^{-1}. The latter absorptions are associated with out-of-plane deformations of the hydrogen attached to the C=C double bond. The NMR spectra in general exhibited *trans*-olefinic protons in the range δ 6.95–7.2 and aromatic protons centred in the range δ 7.05–8.3.

Melting points were determined on a Gallenkamp apparatus and are uncorrected, IR spectra were recorded on a Perkin–Elmer infracord instrument. The NMR spectra were recorded ($CDCl_3$) on a Varian A-60 spectrometer using TMS as standard. All the compounds were separated and purified by column chromatography on alumina. Purity was checked by TLC.

All the phosphonium salts (5a–f) were prepared by heating TPP with substituted benzyl bromides in benzene at reflux temperature[17-19]

Preparation of p-fluorobenzyltriphenylphosphonium bromide (1)

A solution of TPP (4 mmol) and *p*-fluorobenzyl bromide in (4 mmol) anhydrous benzene (400 ml) was

Table 1 *Physical and spectral properties of fluorostilbenes (4a–f)*

Compounds*	X	Yield %	m.p.[16] (°C)	IR (KBr) data cm^{-1} ν C=C	IR (KBr) data cm^{-1} ϕ C–H	^{1}H-NMR ($CDCl_3$) δ ppm
4a	H	70	122–124	1605	975	6.65 (d, J = 16 6 Hz, 1H, Ha); 6.87 (d, J = 16 6 Hz, 1H, Hb); 6.90–7.30 (m, 9H, ArH)
b	4-CH_3	60	150–51	1615	972	3.50 (s, 3H, CCH_3); 6.60 (d, J = 16.2 Hz, 1H, Ha); 6.85 (d, J = 16.2 Hz, 1H, Hb); 6.95–7.40 (m, 8H, ArH)
c	3-Cl	60	43–44	1605	970	6.80 (d, J = 16.5 Hz, 1H, Ha); 7.10 (d, J = 16, 5Hz, 1H, Hb); 7.15–7.65 (m, 8H, ArH)
d	4-Cl	50	141–42	1610	977	6.85 (d, J = 16.4 Hz, 1H, Ha); 7.15 (d, J = 16.4 Hz, 1H, Hb); 7.25–7.70 (m, 8H, ArH)
e	3-NO_2	75	81–82	1618	970	7.05 (d, J = 16.5 Hz, 1H, Ha); 7.28 (d, J = 16.5 Hz, 1H, Hb); 7.30–8.35 (m, 8H, ArH)
f	4-NO_2	80	134–36	1620	975	7.10 (d, J = 16.5 Hz, 1H, Ha); 7.30 (d, J = 16.5 Hz, 1H, Hb); 7.45–8.50 (m, 8H, ArH)

* = All the compounds (4a–f) gave satisfactory elemental analysis for C & H and crystallized from ethanol benzene anf methanol. ν = Stretching vibrations of C=C; ϕ = Out of plane deformations of trans-hydrogen attached to C=C. s = Singlet, m = multiplet centred, d = doublet.

heated under reflux on a steambath for 3 hr. The reaction was allowed to cool to give a light yellow crystalline solid which was recrystallized from $CHCl_3$-pet. ether (1 : 1) to give colourless crystals of *new p*-fluorobenzyltriphenylphosphonium bromide (1), m.p. 270–72°C, yield 80%. Found: C 66.9; 4.61; $C_{25}H_{21}FBrP$ requires; C, 66.66, H, 4.66% IR spectrum (KBr) 1010, 1455 (ν P-Aryl), 720 (ν P-Ar) NMR ($CDCl_3$) δ 6.95–8.15 (m, 19H, ArH) δ 5.60 (d, J_{cPH} = 15 cps, 2H, $\rightarrow \overset{+}{P}-CH_2-$).

Preparation of trans-4-Fluorostilbenes (4a–f)

Route A – To a stirred suspension of the ylid (2) generated from 4 mmol of salt (1) and 5 mmol of sodamide in 100 ml of anhydrous benzene) was added under nitrogen, 4 mmol of aromatic aldehyde (3a–f). The mixture was stirred at room temperature for 2–3 hr and then stirred at reflux temperature, for additional 5–8 hr till the colour of solution faded. The mixture was cooled and filtrate concentrated under vacuum to give a solid which was chromatographed over neutral alumina using benzene-pet-ether (1 : 2) as eluent to give *trans*-fluorostilbenes (4a–f) (table 1).

Route B – To a solution of 4 mmol of salt (5a–f) and 4 mmol of sodium methoxide in 100 ml of methanol was added 4 mmol *p*-fluorobenzaldehyde. The mixture was stirred at room temperature for 6–8 hr. The precipitate formed was collected, washed with methanol and crystallised from an appropriate solvent or by chromatography using benzene-pet-ether (1 : 2) as eluent to give transfluorostilbenes (4a–f).

The authors thank the Principal and Dr S. P. Saxena, for facilities. They also thank UGC, and CSIR New Delhi for financial assistance.

7 October 1982; Revised 16 September 1983

1. Johnson, A. W., *Ylid chemistry*, Academic Press, New York, 1966.
2. Mercker, A., *Organic reactions*, (ed.) R. Adam, John Wiley, New York, 1965, **14**, 270.
3. Lowe, P. A., *Chem. India* (*London*), 1970, 1070.
4. Hudson, R. F., *Chem. Ber.*, 1970, **7**, 287.
5. Brium, G. H. and Mathews, C. N., *J. Chem. Soc. Chem. Commun.*, 1967, 137.
6. Wittig, G., Weigmann, H. D. and Schlosser, M., *Chem. Ber.*, 1961, **95**, 676.
7. Schlosser, M., *Topics in stereochemistry*, (eds) E. L. Eliel and N. L. Allinger, Wiley Interscience, 1970, **5**, 13.
8. Schlosser, M., Muller, G. and Christmann, K. F., *Angew. Chem. Int. Ed.*, 1966, **5**, 667.
9. Schlosser, M. and Christmann, K. F., *J. Liebigs Ann. Chem.*, 1967, **708**, 1.
10. Tewari, R. S. and Gupta, K. C., *Indian J. Chem.*, 1976, **B14**, 419; 1978, **B16**, 665.
11. Tewari, R. S., Kumari, N. and Gupta, K. C., *J. Indian Chem. Soc.*, 1978, IV, 810.
12. Gupta, K. C., Srivastava, N. and Nigam, R. K., *Indian J. Chem.*, 1981, **B20**, 902.

13. Tewari, R. S. and Gupta, K. C., *J. Organomet. Chem.*, 1976, **112**, 279.
14. Tripett, S., *Pure Appl. Chem.*, 1964, **9**, 255.
15. Kendurkar, P. S. and Tewari, R. S., *Z. Naturforsch*, 1973, **B28**, 475.
16. Pews, R. G. and Ojha, N. D., *J. Am. Chem. Soc.*, 1961, **91**, 5769.
17. Kendurkar, P. S. and Tewari, R. S., *Indian J. Chem.*, 1977, **B15**, 290.
18. Friedrich, K. and Henning, H., *Chem. Ber.*, 1959, **92**, 2756.
19. Compbell, T. W. and McDonald, R. N., *J. Org. Chem.*, 1959, **24**, 1969.

THE ROLE OF SURFACE EXCESS OXYGEN IN THE CATALYTIC DEHYDROGENATION OF 2-PROPANOL ON $ZnCrFeO_4$ SPINEL

K. BALASUBRAMANIAN and
J. C. KURIACOSE,
Department of Chemistry, Indian Institute of Technology, Madras 600036, *India.*

AMONG the many physical and chemical properties of the oxides considered to explain their observed catalytic activities, the amount of surface excess oxygen has been a useful variable to correlate with catalytic activity. Such a correlation has been demonstrated for the oxidation of ammonia on nickel oxide and manganese oxide catalysts[1] and the decomposition of hydrogen peroxide on nickel oxide[2] and chromia catalysts[3]. A similar correlation is attempted in $ZnCrFeO_4$. This catalyst system has been chosen because of its good selectivity for the dehydrogenation of 2-propanol.

Zinc chromium ferrite was prepared by the slurry method described by Batist[4]. 2-Propanol and acetone were purified by standard procedures[5] and their purity confirmed by vapour phase chromatography. Nitrogen and hydrogen were purified by passing through a vanadium(II) solution and the moisture removed by passing through towers packed with anhydrous calcium chloride.

Catalytic reactions were carried out in a differential tubular flow reactor operating at atmospheric pressure, mercury being used to displace the reactant from a feeder into the reactor[6]. The liquid products were condensed in a cold trap and analysed by vapour phase chromatography using a carbowax column maintained at 65°C and hydrogen as the carrier gas. The surface excess oxygen was estimated by the method reported by Uchijima *et al.*[7].

$ZnCrFeO_4$ is selective and promotes the dehydrogenation of 2-propanol. The incorporation of Cr in the $ZnFe_2O_4$ spinel lattice increases both the activity and the selectivity. The Cr^{+3} incorporated into the octahedral sites of the spinel lattice inhibits the bulk reduction of the Fe^{+3} to an oxidation state lower than Fe^{+2} as can be concluded from the absence of reduction of the Fe^{3+} to the metallic state when Cr^{3+} is present. Neither $ZnFe_2O_4$ nor $ZnCr_2O_4$ exhibit the selectivity shown by $ZnCrFeO_4$.

The surface excess oxygen on $ZnCrFeO_4$ samples subjected to various pretreatments and their catalytic activities are given in table 1.

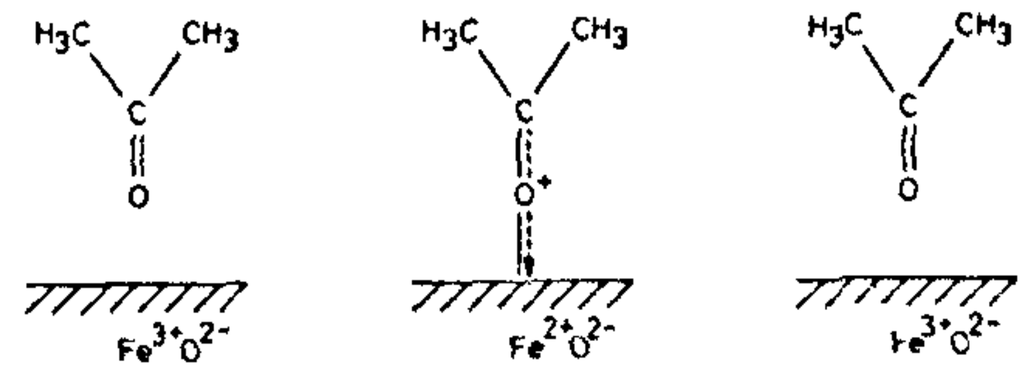
Table 1 *Influence of various pretreatments on the surface excess oxygen of $ZnCrFeO_4$ and the catalytic activity*

Type of pretreatment	Condition of pretreatment	Percentage conversion of 2-propanol	Surface excess oxygen mM/g
Hydrogen	500°C, 3 hr	57.5	0
2-propanol	"	52.5	0.030
Fresh catalyst	"	47.2	0.073
Air	500°C, 3 hr	45.2	0.087
Oxygen	"	40.0	0.109

It is clear from these results that increase in the surface excess oxygen which can be related to oxidation of the catalyst brings down the dehydrogenation activity while reduction increases it.

Adsorption of acetone on Fe_2O_3 is a donor process[8]. Ferric oxide is a semiconductor in which the density and the nature of current carriers are known to change when it is subjected to slight oxidation or reduction[9]. As in Fe_2O_3 the active site in $ZnCrFeO_4$ is also likely to be iron since the chromium present in the catalyst does not undergo any change in the oxidation state so readily. The decrease in the formation of acetone with an increase in the surface excess oxygen can be rationalized on the basis of the following mechanism.

The adsorption and desorption of acetone may be visualised as follows.



a) before adsorption b) adsorbed state c) after desorption