# An Attempt to effect Allenic Elimination by a Thiolate Ion in *NN*-Dimethylformamide

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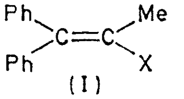
2-Halogeno-1,1-diphenylpropenes (halogen = Cl or Br), when treated with sodium toluene-*p*-thiolate in dimethylformamide, gave exclusively 1,1-diphenyl-2-(*p*-tolylthio)propene. The reaction was investigated to determine whether it proceeded *via* a direct nucleophilic substitution or an elimination to 1,1-diphenylallene followed by nucleophilic addition of thiol to the allenic intermediate. By examining the kinetics and products of the reaction, by searching for deuterium incorporation when the reaction is carried in the presence of $p$-MeC$_6$H$_4$·SD, and by independently studying the addition of thiol to diphenylallene, the allenic elimination–addition mechanism was ruled out. The behaviour of this system in ethanol is briefly compared with that in dimethylformamide.

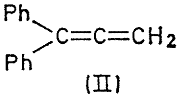
OLEFINS containing the group C=C(CHR$^1$R$^2$)X, where X = halogen, can be attacked by basic nucleophiles, Nu$^-$, to give allenic products and/or their derivatives. When a compound with the group C=C(CHR$^1$R$^2$)Nu is produced, nucleophilic substitution *via* allenic elimination–addition may have taken place. 2-Halogeno-1,1-diphenylpropenes,[1] β-halogenobut-2-enoates,[2a] β-halogenovinyl-acetates and -acetonitriles,[2b] and other substrates [3] show such behaviour.

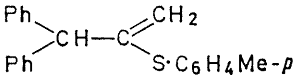
Allenic elimination is typically caused by alkoxide ions; [1,2,4] however in some molecules (R$^1$ = H; R$^2$ = CN or CO$_2$Et) it was also induced by less basic nucleophiles such as EtS$^-$ or PhS$^-$ in ethanol.[2b] Thiolates are less efficient than alkoxide ions in β-eliminations,[5] except in particular cases.[6]

This paper describes an attempt to obtain allenic elimination from the substrates (Ia) and (Ib), for which acetylenic elimination is impossible, using toluene-*p*-thiolate as base/nucleophile in *NN*-dimethylformamide (DMF). Possible products are 1,1-diphenylallene (II) and its derivatives (Ic) and (III), if only nucleophilic attack at the central atom is considered.


(I)

a; X = Cl
b; X = Br
c; X = $p$-MeC$_6$H$_4$·S


(II)


(III)

RESULTS AND DISCUSSION

The product of the reactions of (Ia) and (Ib) with sodium toluene-*p*-thiolate in DMF at 100 °C, was identified as (Ic) by elemental analysis and spectra. In particular, the n.m.r. spectrum indicates the presence of two methyl groups. Assignment of the signals, by comparison with similar compounds, is given in Table 1.

TABLE 1

N.m.r. signals of methyl protons [τ (CDCl$_3$)]

| Compound | $p$-C*H*$_3$C$_6$H$_4$·S | C*H*$_3$C= |
|---|---|---|
| $p$-Z$^1$C$_6$H$_4$($p$-Z$^2$C$_6$H$_4$)C=C(H)S·-C$_6$H$_4$CH$_3$-$p$ [a] (Z$^1$, Z$^2$ = H, Me, MeO, Cl, or NO$_2$) | 7·63—7·68(s) | |
| Ph$_2$C=C(X)Me [b] | | |
| X = Br (Ia) | | 7·57(s) |
| X = H | | 8·26(d) |
| X = $p$-CH$_3$C$_6$H$_4$·S (Ic) | 7·70(s) | 8·06(s) |

[a] Refs. 7 and 11 and P. Beltrame and P. L. Beltrame, *Gazzetta*, 1968, **98**, 367. [b] This work.

The u.v. spectrum of the product in methanol shows three absorption bands at 221, 260, and 287 nm (ε 29,500, 16,400, and 13,800), comparable with those of 1,1-diphenyl-2-(phenylthio)ethylene and 1,1-diphenyl-2-(*p*-tolylthio)ethylene in the same solvent.[7] The wavelength and intensity of the third band are lower than those observed in the ethylenic derivatives [$\lambda_{max.}$ = 309—310 nm (ε *ca.* 19,000)]. A reasonable explanation is that the conjugated system deviates more from coplanarity when an additional methyl group is present on the ethylenic double bond.

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[1] (*a*) P. Beltrame, S. Carrà, P. Macchi, and M. Simonetta, *J. Chem. Soc.*, 1964, 4386; (*b*) P. Beltrame, D. Pitea, A. Marzo, and M. Simonetta, *J. Chem. Soc.* (*B*), 1967, 71.

[2] (*a*) F. Théron, *Bull. Soc. chim. France*, 1969, 278; (*b*) p. 285.

[3] Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, **7**, 1.

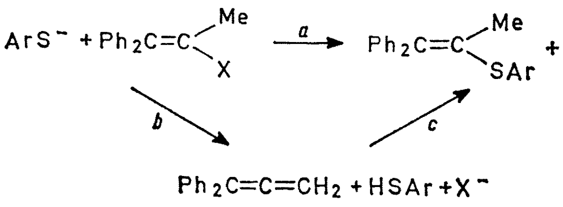
[4] S. W. Staley and R. F. Doherty, *Chem. Comm.*, 1969, 288.

[5] Y. C. Mac and A. J. Parker, *Austral. J. Chem.*, 1966, **19**, 517.

[6] J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, 1967, **32**, 11.

[7] P. Beltrame, D. Pitea, and M. Simonetta, *J. Chem. Soc.* (*B*), 1967, 1108.

The reaction that gives (Ic) as the unique product could be either a direct nucleophilic substitution by $ArS^-$ at the ethylenic carbon (path *a* in Scheme 1), or an allenic elimination followed by a specific addition of ArSH (paths *b* and *c*):



SCHEME 1

The rate of the reactions was measured in the range 70—100 (Ib) and 100—130 °C (Ia). Reactions were assumed to be first order with respect to each reactant. This has been checked for compound (Ib). Second-order rate coefficients and activation parameters are collected in Table 2. A marked dependence of the rate on the leaving group is noticeable [$k(Br) : k(Cl) = 17.7$ at 100 °C]. Although moderately large values of this ratio are common for nucleophilic substitution,[8] and a value as large as 16·7 has been found in one case,[9] this result is also consistent with an elimination mechanism.

TABLE 2

Rate coefficients for substitution of 2-halogeno-1,1-diphenylpropenes (0·09—0·10M) by sodium toluene-*p*-thiolate (0·12—0·15M) in DMF

Halogen = Cl (Ia)

| $t$/°C | 100·0 | 110·0 | 120·0 | 130·0 |
|---|---|---|---|---|
| $10^4k$/l mol$^{-1}$ s$^{-1}$ | 0·390[a] | 0·839[a] | 2·08 | 3·96 |

$\Delta E^‡ = 23,482 \pm 417$ cal mol$^{-1}$; $\log Z = 9.338 \pm 0.237$; $\Delta S^‡ = -18.25 \pm 1.09$ cal mol$^{-1}$ K$^{-1}$

Halogen = Br (Ib)

| $t$/°C | 70·0 | 80·0 | 90·0 | 100·0 |
|---|---|---|---|---|
| $10^4k$/l mol$^{-1}$ s$^{-1}$ | 0·520 | 1·381 | 3·18 | 6·91[b] |

$\Delta E^‡ = 21,897 \pm 305$ cal mol$^{-1}$; $\log Z = 9.675 \pm 0.186$; $\Delta S^‡ = -16.71 \pm 0.85$ cal mol$^{-1}$ K$^{-1}$

[a] Average of two runs. [b] Other values from runs at different initial concentrations: [(Ib)] = 0·013M, [$ArS^-$] = 0·10M, $10^4k$ = 6·34 l mol$^{-1}$ s$^{-1}$; [(Ib)] = 0·09M, [$ArS^-$] = 0·03M, $10^4k$ = 6·68 l mol$^{-1}$ s$^{-1}$.

On the other hand, the values of the activation entropy (Table 2) are of the same order of those (*ca.* —20 cal mol$^{-1}$ K$^{-1}$) found for several direct substitutions in the series of 1,1-diaryl-2-halogenoethylenes, for halogen = Cl [7,10] or F,[11] and with both DMF [7,11] and ethanol [10] as solvents. The entropy of activation is a distinctive criterion, since its values for competing eliminations are usually positive, both in case of α-elimination [10] and of allenic elimination.[1a]

The rate coefficient for the reaction of the chloro-compound (Ia) with $p$-$MeC_6H_4{\cdot}S^-$ in DMF can be compared with that of 2-chloro-1,1-diphenylethylene in the same reaction.[7] As shown in Table 3, the effect of the α-methyl group on the rate is comparable with that of cases of direct substitution.[3,12]

TABLE 3

Effect of α-methyl group on rate of halogen substitution by thiolate ions

| Reaction | $10^4k$/l mol$^{-1}$ s$^{-1}$<br>R = H | <br>R = Me | $\frac{k(H)}{k(Me)}$ |
|---|---|---|---|
| $Ph_2C{=}C(R)Cl$ + $p$-$MeC_6H_4{\cdot}S^-$-(DMF; 100 °C) | 158[a,b] | 0·390[c] | 405 |
| $p$-$NO_2{\cdot}C_6H_4{\cdot}SO_2(H)C{=}C(R)Cl$ + $PhS^-$(MeOH; 0 °C) | 48,000[d] | 141[e] | 340 |
| $p$-$MeC_6H_4{\cdot}SO_2(H)C{=}C(R)Br$ + $PhS^-$(MeOH; 0 °C) | 2480[f] | 7·7[e] | 320 |

[a] Extrapolated by means of Arrhenius equation. [b] Ref. 7. [c] This work. [d] G. Modena and P. E. Todesco, *Gazzetta*, 1959, **89**, 866. [e] L. Maioli, G. Modena, and P. E. Todesco, *Boll. sci. Fac. Chim. Ind. Bologna*, 1960, **18**, 66. [f] A. Campagni, G. Modena, and P. E. Todesco, *Gazzetta*, 1960, **90**, 694.

Kinetic evidence seemed to favour path *a* (Scheme 1). Further support was looked for, through the following experiments: (i) g.l.c. analysis of the reaction mixture along the course of the reaction, (ii) search for deuterium incorporation in the product during reactions carried in the presence of ArSD, and (iii) independent study of path *c* (Scheme 1).

In the analyses (i) neither 1,1-diphenylallene nor its previously isolated dimer 2-methylene-3,3-diphenyl-1-diphenylmethylenecyclobutane) [1] were detected [1% of the former and 0·1% of the latter are easily detectable in control mixtures with (Ib)]. Only (Ic) was found at every point along the reaction course. Experiments (ii) revealed no deuterium incorporation by n.m.r. analysis of the product (Table 4). Taking into account the intrinsically lower response of the allylic protons, as shown by the control experiments, and the isotopic purity of ArSD, one could expect an intensity ratio 3·0 : 2·2 between *para* and allyl methyl groups for an allenic elimination followed by random addition of thiol to 1,1-diphenylallene.

TABLE 4

Product from $Ph_2C{=}C(Me)Br$ (Ib) and $ArS^-$ in DMF at 98—100 °C in the presence of ArSH and ArSD (Ar = $p$-$MeC_6H_4$)

| Reactants<br>[(Ib)]/M | <br>[$ArS^-$]/M | <br>Thiol (concn.) | N.m.r. signal intensities for<br>($p$-C$H_3$) : (allyl C$H_3$) |
|---|---|---|---|
| 0·07 | 0·30 | | 3·00 : 2·84[a] |
| 0·1 | 0·13 | ArSH (1·0M) | 3·00 : 2·92 |
| 0·1 | 0·13 | ArSD[b] (1·0M) | 3·00 : 2·86 |
| 0·1 | 0·12 | ArSD[b] (1·0M) | 3·00 : 2·90 |

[a] Integration on a different spectrometer (Varian A–100) gave the ratio 3·00 : 2·95. [b] Isotopic purity = 72% (from n.m.r. spectrum).

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[8] P. Beltrame, P. L. Beltrame, G. Carboni, and M. L. Cereda, *J. Chem. Soc.* (*B*), 1970, 730.

[9] E. S. Lewis and H. Suhr, *J. Amer. Chem. Soc.*, 1960, **82**, 862.

[10] P. Beltrame and G. Cortili, *Rend. Accad. naz. Lincei*, 1965, **39**, 475.

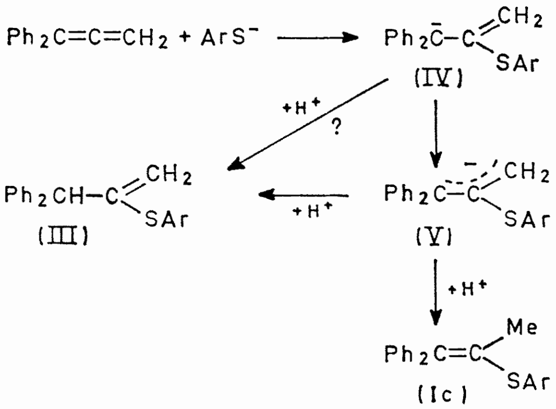
[11] P. Beltrame, P. L. Beltrame, M. L. Cereda, and G. Lazzerini, *J. Chem. Soc.* (*B*), 1969, 1100.

[12] G. Modena, *Accounts Chem. Res.*, 1971, **4**, 73.

Study (iii) was done by varying the temperature and the concentration of the thiolate ion. At —25 °C the addition was possible only when catalysed by $ArS^-$. At +45 °C the reaction was carried without thiolate ion. In both cases two addition products were found, one of which was isolated and identified as (Ic), while the other was examined only in the mixture by its spectral properties. The unknown product has an n.m.r. spectrum that substantially overlaps that of (Ic) in the region for aromatic and *para*-methyl protons, and differs in that for the other protons, being characterized by singlets at $\tau$ 4·82 and 5·10 (in deuteriochloroform) (intensities 1 : 2). In $[^2H_6]$acetone the latter is split into a quartet (AB system, $J$ 2 Hz). The peak at $\tau$ 4·82 corresponds to that of the methine proton in the diphenylmethyl group, and the AB system can be attributed to a methylene group. Formula (III) seems reasonable for this product. By n.m.r. and g.l.c., the products are in the approximate ratio 1 : 1. Comparison of the u.v. spectrum of the mixture with that of pure (Ic), shows that the non-isolated product has little absorption, particularly at $\lambda > 270$ nm, in agreement with the reduced conjugation of (III). Phenyl vinyl sulphide, which has a similar conjugated system, has absorption maxima at 266 and 247 nm ($\varepsilon$ 10,000 and 10,500).[13]

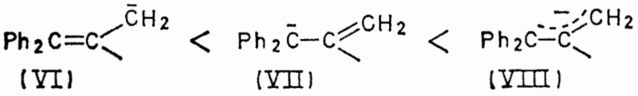
The mixture of products was tested for stability. It remained unaltered when heated at 70 °C under the conditions of the kinetic runs of (Ib); however isomerization of (III) to (Ic) was observed by treatment with hydrochloric acid or column chromatography on alumina.

The results of experiments (i) and (ii) are compatible with the allenic mechanism, if diphenylallene was present in undetectably small concentration and if addition *c* (Scheme 1) took place immediately after elimination *b* and in the same solvent cage. However experiments (iii) rule out the allenic elimination–addition mechanism in DMF since, if operating, it would give rise to two detectable products.



SCHEME 2

A possible route for the addition of thiol to 1,1-diphenylallene which provides product (III) is suggested in Scheme 2. A carbanion intermediate seems a reasonable primary product since catalysis by $ArS^-$ has been observed. Molecular orbital calculations using the Hückel approximation indicate the order of increasing stability of the isomeric carbanions shown in Scheme 3. For (VI) and (VII) two $\pi$-electron systems are present, orthogonal to each other, while coplanarity has been reached in ion (VIII) by internal rotation around a single bond.



SCHEME 3

Therefore the intermediate (IV) is suggested (Scheme 2). If (IV) isomerizes with sufficient velocity to the delocalised allyl anion (V), products (Ic) and (III) derive essentially from (V) only. The reaction (IV) ⟶ (III) cannot however be excluded. Similar processes in alcoholic solvents are reported [14,15] to give primarily a non-conjugated olefin, that later isomerizes to the conjugated one. The lack of isomerization in our case can be attributed to the choice of the solvent.

*Reactions in Ethanol.*—The reactions of (Ib) and (II) with sodium toluene-*p*-thiolate were investigated using ethanol as solvent [the chloro-derivative (Ia) could not be tested because of its very low reactivity]. The reaction of (Ib) is much slower than in DMF ($k$ *ca.* $10^{-5}$ l mol$^{-1}$ s$^{-1}$ at 120 °C). Both (Ic) and (III) are present in the product mixture, together with minor amounts of other unidentified compounds. During the course of the reaction, the ratio (Ic) : (III) steadily increased roughly from 3 (time zero) to 6·5 (50% reaction) to higher values, indicating a thermal isomerization.

The reaction of 1,1-diphenylallene (II) was investigated at temperatures between 0 and 50 °C. The reaction was incomplete and gave both (Ic) and (III) in a ratio *ca.* 3. These results indicate that in ethanol the allenic elimination–addition mechanism is operating, alone or in competition with direct substitution. This point has not been further investigated.

## EXPERIMENTAL

U.v., i.r., and n.m.r. spectra were usually taken on a Beckmann DK-2A, a Perkin-Elmer 21, and a Varian A-60 apparatus, respectively. DMF was purified as usual.[11] Toluene-*p*-thiol was a commercial product; its deuteriated counterpart $p$-$MeC_6H_4{\cdot}SD$, was obtained (72% isotopic purity) by acidifying the sodium salt with DCl in $D_2O$. Other details were given previously.[7] 2-Chloro- and 2-bromo-1,1-diphenylpropene and 1,1-diphenylallene were prepared as described.[1]

*1,1-Diphenyl-2-(*p*-tolylthio)propene* (Ic).—2-Bromo-1,1-diphenylpropene (3·6 mmol) and sodium toluene-*p*-thiolate (15 mmol) in DMF (50 cm³) were left during 90 h at 100 °C under nitrogen. The usual separation procedure [7] gave *crystals* (2·5 mmol), m.p. 88—89 °C (from methanol) (Found: C, 83·0; H, 6·3. $C_{22}H_{20}S$ requires C, 83·5; H, 6·35%),

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[13] C. C. Price and H. Morita, *J. Amer. Chem. Soc.*, 1953, **75**, 4747.

[14] C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5856.

[15] M. Verny and R. Vessière, *Tetrahedron*, 1969, **25**, 263.

$\tau$ 2·6—3·0 (14H, m) (other n.m.r. data in Tables 1 and 4), $\lambda_{max.}$ (methanol) see Results section, $\lambda_{max.}$ (n-hexane) 292, 263, and 223sh ($\varepsilon$ 12,600, 14,300, and 24,400), and $\lambda_{max.}$ (dimethylformamide) 290 nm ($\varepsilon$ 11,600).

2-Chloro-1,1-diphenylpropene gave the same product, identified by mixed m.p. and comparison of i.r. spectra.

*Reactions of* 1,1-*Diphenylallene* (II).—This compound (0·1M), toluene-*p*-thiol (0·3M), and toluene-*p*-thiolate (0·02—0·04M) reacted in DMF at −25 °C with *k ca.* $10^{-3} \times [\mathrm{ArS}^-]$ l mol$^{-1}$ s$^{-1}$. Samples were withdrawn and quickly extracted by addition of cold carbon tetrachloride and aqueous sodium hydroxide; the organic layer was analysed by g.l.c.

The reaction at 45 °C was between (II) and toluene-*p*-thiol (both *ca.* 0·1M) only, without thiolate being added; samples were analysed directly by g.l.c. Substantially complete conversion was attained in 2 h. 1,1-Diphenylallene reacts with the thiolate at −25 °C even without addition of thiol, giving the same products as previously, but in low yields. Traces of water in the solvent may explain this.

*U.v. Spectrum of the Isomeric Products.*—The mixture of the isomers was obtained from diphenylallene and toluene-*p*-thiol in DMF. Solvent was completely evaporated at reduced pressure from a sample and the residue was dissolved in n-hexane and examined. This procedure was repeated several times, in order to improve the comparison of the spectrum of the mixture with that of (Ic). The presence of diphenyl disulphide as an impurity is a source of complication.

*Stability of the Isomeric Products at* 70 °C.—A solution of (Ic) and (III) in DMF (overall concentration *ca.* 0·1M) was left for 24 h. Another sample was left for 116 h in the presence of an equal amount of thiolate, and a third sample for 8 h in the presence of thiolate and (Ib) (both 0·05M). In all cases samples were withdrawn at intervals and analysed by g.l.c.; in one case also the n.m.r. spectrum was scanned. The initial ratio (Ic) : (III) (*ca.* 1) remained constant within experimental error.

*G.l.c.*—A flame-ionisation apparatus was employed. The column (2·5 m) contained 5% methylvinyl silicone polymer SE-31 on Chromosorb W (60—80 mesh). Nitrogen (20 cm$^3$ min$^{-1}$) was used as carrier. Column temperature was programmed from 170 to 240 °C (heating rate 5 °C min$^{-1}$) and injector and detector were at 250 °C. The order of increasing retention time was (II) < (Ia) = (Ib) < diphenyl disulphide $\ll$ (III) < (Ic).

*Kinetic Runs* (*Table* 2).—Reactants were weighed, dissolved in DMF, and transferred to a series of Pyrex tubes (5 cm$^3$) pre-flushed with nitrogen and then flushed again before stoppering them with screw caps. The temperature in the thermostat was constant to within 0·2 °C. Tubes were withdrawn at intervals and the contents quenched by cooling. After dilution with ' spectrograde ' DMF, absorbance was measured at 300 nm, and rate coefficients calculated by the second-order rate equation. Reactions were followed to 30—40% completion. When measured, the absorbance at ' infinite time ' was, on the average, 104 ± 4% of the theoretical. Theoretical values were used for calculations. Every spectroscopic analysis was checked by g.l.c.; results by the two methods were in good agreement.

We thank Dr. A. Lai for recording some n.m.r. spectra on a Varian A-100. Financial support of the C.N.R. (Rome) is acknowledged.

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