623. *Carbanion–Halogen Fission by Nucleophilic Attack of Mercaptoacetic Acid on α-Benzoyldiphenylmethyl Halides, Dibenzoylmethyl Bromide, and Di-*p*-nitrophenylmethyl Chloride.*

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Whereas the action of a weak base or alkali on α-benzoyldiphenylmethyl chloride or bromide and on dibenzoylmethyl bromide leads to normal carbonium-halide fission, the action of mercaptoacetic acid on them and on di-*p*-nitrophenylmethyl chloride leads to carbanion–halogen fission (easier with the bromide than with the chloride) as well as the formation of the alkylthio-acids from the chlorides. The latter, abnormal, fission seems therefore to depend on the tendency of the sulphur atom to expand its shell and on the nature of the halogen.

The ease with which 2-ketoalkyl thio-compounds (scheme 1a) and 4-nitrobenzyl thio-compounds (scheme 1b) undergo carbanion–sulphenium fission by alkalis[1, 2] led us to investigate the carbanion–halogen fission of similar compounds (into carbanions and a halogen cation): however, we modified the structures so as to increase the anion stabilities, in order to overcome the higher electronegativity of halogen than of sulphur, thus creating a possibility of heterolysis of the carbon–halogen bond in spite of the electronegative nature of the halogen.

$$\mathrm{Ph{\cdot}CO{\cdot}CXY{\cdot}SZ} + \mathrm{OH^-} \longrightarrow [\mathrm{Ph{\cdot}CO{\cdot}CXY}]^- + \mathrm{ZSOH}$$

$$[\mathrm{Ph{\cdot}CO{\cdot}CXY}]^- + \mathrm{H_2O} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}CHXY} + \mathrm{OH^-} \quad . \; . \; . \; . \; . \; . \; . \quad (1a)$$

$$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}SZ} + \mathrm{OH^-} \longrightarrow [\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2}]^- + \mathrm{ZSOH}$$

$$2[\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2}]^- + 2\mathrm{H_2O} \xrightarrow{\text{Alkali}} (\mathrm{OHC{\cdot}C_6H_4})_2\mathrm{N_2O} + 2\mathrm{OH^-} \quad . \; . \; . \; . \quad (1b)$$

Published results indicated that independently of the electron-attracting influence and the expected anionic stabilities of such radicals the corresponding halides never underwent carbanion–halogen fission but always the normal carbonium–halide fission. Thus, α-benzoylbenzyl chloride gives benzoin under the influence of alkali;[3] the corresponding thiol and sulphides give deoxybenzoin with alkali.[1, 4] α-Benzoyldiphenylmethyl chloride or bromide[5] gives the corresponding alcohol when merely heated with aqueous acetone, and on treatment with alkali in dioxan; α-(benzoyldiphenylmethylthio)acetic acid gives α-benzoyldiphenylmethane.[1] Even when the carbanion stability of the radical was increased, as in dibenzoylmethyl bromide, the compound still underwent normal heterolysis of the C–Br bond,[6a] *e.g.*, on treatment with the weakly nucleophilic acetate ion, alkali changing the alcohol formed into other products.[6b, c]

The first indication of the possibility of the alternative fission of such compounds under other conditions was met during the preparation of α-(benzoyldiphenylmethylthio)acetic acid[1] by the action of mercaptoacetic acid on α-benzoyldiphenylmethyl chloride, whereby a small yield of α-benzoyldiphenylmethane was obtained along with the main product, the alkylthio-acid. α-Benzoylbenzyl chloride, on the other hand, on similar treatment, gives only the alkylthio-acid.[4]

In studying this reaction of mercaptoacetic acid we have taken into account the effects

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[1] Schönberg and Iskander, *J.*, 1942, 90.

[2] (*a*) Iskander and Tewfik, *J.*, 1951, 2050; (*b*) Iskander and Riad, *J.*, 1951, 2054; (*c*) Iskander and Salama, *J.*, 1951, 2058; (*d*) Iskander and Tewfik, *J.*, 1961, 2393; (*e*) Iskander and Riad, *J.*, 1961, 2397.

[3] Ward, *J.*, 1929, 1549.

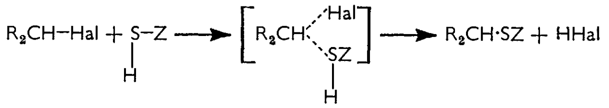
[4] Behaghel and Schneider, *Ber.*, 1935, **68**, 1588.

[5] Werner, *Ber.*, 1906, **39**, 1286; Gardeur, *Zentr.*, 1897, II, 661; Delacre, *Bull. Soc. chim. France*, 1895, **13**, 860.

[6] (*a*) De Neufville and von Pechmann, *Ber.*, 1890, **23**, 3375; (*b*) Bigelow, Rule, and Black, *J.*, 1935, 83; (*c*) Blatt and Hawkins, *J. Amer. Chem. Soc.*, 1936, **58**, 81.

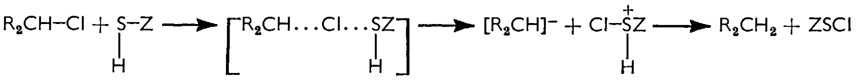
of the concentration of mercapto-acid, the nature of the halogen, and the structure of the radicals. The following preliminary results were obtained: (1) α-Benzoyldiphenylmethyl chloride with four equivalents of mercaptoacetic acid gave α-benzoyldiphenylmethane as the main product, with only 3% of the alkylthio-acid. The former product was proved not to result from interaction of the thio-acid and the excess of mercaptoacetic acid. (2) The corresponding bromide gave no alkylthio-acid when heated with one equivalent of mercaptoacetic acid: the sole product was α-benzoyldiphenylmethane. (3) Dibenzoylmethyl bromide gave only dibenzoylmethane and the disulphide from the mercapto-acid, no alkylthio-acid being formed. (4) The neutral main product from di-*p*-nitrophenylmethyl chloride and mercaptoacetic acid or β-mercaptopropionic acid[2e] was di-*p*-nitrophenylmethane, but low yields of the alkylthio-acids were also obtained. An excess of the mercapto-acid halved the yields of the alkylthio-acids, with a corresponding increase in the yield of di-*p*-nitrophenylmethane.

A feature of these reactions is reduction of the halide by the mercapto-acid which is oxidised to the disulphide. Di-*p*-nitrophenylmethyl chloride was recovered unchanged from the reaction mixture in absence of mercaptoacetic acid. This shows that the formation of the alkylthio-acid does not proceed by the S_N1 mechanism: if it did so, the chloride would have been converted into the corresponding alcohol, through a carbonium ion intermediate, in the same time required for formation of the alkylthio-acid. The formation of the alkylthio-acid presumably therefore occurs by bimolecular nucleophilic attack of the sulphur atom of the mercapto-acid on the α-carbon atom of the benzyl halide, the reaction being facilitated by electron-withdrawing factors in the aryl radical R (scheme 2a):



$$R_2CH{-}Hal + \underset{H}{\underset{|}{S}}{-}Z \longrightarrow \left[R_2CH\genfrac{}{}{0pt}{}{\cdot\cdot Hal}{\cdot\cdot \underset{H}{\underset{|}{S}}Z}\right] \longrightarrow R_2CH{\cdot}SZ + HHal \quad . \; . \; . \; . \; . \quad (2a)$$

On the other hand, carbanion–halogen fission requires approach of the sulphur to the halogen itself: a strong electron-attracting influence in the aryl group R facilitates the separation of halogen as cation, and the anion is stabilised by resonance. The formation of di-*p*-nitrophenylmethane is an example:



$$R_2CH{-}Cl + \underset{H}{\underset{|}{S}}{-}Z \longrightarrow \left[R_2CH\ldots Cl\ldots \underset{H}{\underset{|}{S}}Z\right] \longrightarrow [R_2CH]^- + Cl{-}\overset{+}{\underset{H}{\underset{|}{S}}}Z \longrightarrow R_2CH_2 + ZSCl \quad . \quad (2b)$$

$$ZSCl + ZSH \longrightarrow ZSSZ + HCl$$

($R = p\text{-}NO_2{\cdot}C_6H_4$; $Z = CH_2{\cdot}CO_2H$ or $CH_2{\cdot}CH_2{\cdot}CO_2H$.)

The same steps apply in the case of dibenzoylmethyl bromide.

The dominance of a particular mode of fission seems therefore to depend on its relative rate. With α-benzoylbenzyl chloride only reaction (2a) occurs. But with α-benzoyldiphenylmethyl chloride, the second phenyl group attached to the central carbon atom retards reaction (2a) and allows for partial occurrence of (2b); with α-benzoyldiphenylmethyl bromide, reaction (2a) is further retarded owing to the weaker —*I* effect of bromine, and accordingly reaction (2b) becomes predominant.

Since both fission into the organic anion and halogen cation and formation of the alkylthio-acid occur by S_N2 mechanisms, their rates were expected to be affected to the same degree by an increase in the concentration of the common reagent mercaptoacetic acid. The increase in the products of the fission over formation of the alkylthio-acid on increase in the concentration of the mercaptoacetic acid seems therefore to be due to steric retardation of the latter.

Since the use of other nucleophilic reagents, *e.g.*, hydroxide or acetate ion, did not lead to carbanion–halogen fission, it is not only resonance stabilisation of the anionic radicals that facilitates the process; it is necessary to seek an additional factor in the mercapto-acid and this we believe to be the tendency of sulphur to expand its valency shell temporarily. Similar observations have been recorded previously: tribenzoylmethyl chloride reacted with sodium *p*-tolyl sulphide to give the enolate of tribenzoylmethane;[7] carbon tetrachloride with sodium derivatives of thiols in alcohol gives tri(alkylthio)-methanes,[8] the first stage in this reaction being apparently fission of carbon tetrachloride to give a halogen cation.[9]

EXPERIMENTAL

The preparation of (benzoyldiphenylmethylthio)acetic acid from α-benzoyldiphenylmethyl chloride (15·3 g.) was repeated,[1] to determine the yield of the by-product, " α-benzoyldiphenylmethane." The following yields were obtained: dithiodiacetic acid 1·1 g.; α-benzoyldiphenylmethane 0·7 g.; alkylthio-acid 6·5 g. Use of four equivalents of mercaptoacetic acid gave 13·4 g. of α-benzoyldiphenylmethane and 0·5 g. of the alkylthio-acid.

When (benzoyldiphenylmethylthio)acetic acid was heated with mercaptoacetic acid (4 equivalents) for 2 hr. on the water bath the alkylthio-acid was unchanged.

The above reactions gave the same results when effected in boiling toluene.

Boiling α-benzoyldiphenylmethyl bromide (1 g.) and mercaptoacetic acid (0·26 g.) in dry toluene (10 ml.) for 1 hr. gave much hydrogen bromide. Cooling, and addition of light petroleum (b. p. 70—80°), precipitated dithiodiacetic acid. When the filtrate therefrom was left overnight α-benzoyldiphenylmethane (0·55 g.) was precipitated. Extraction of the toluene filtrate with sodium hydrogen carbonate did not yield any alkylthio-acid.

α-Benzoyldiphenylmethyl chloride (0·38 g.) in dioxan (15 ml. was treated with 0·2N-sodium hydroxide (6·25 ml.) and the mixture boiled for 5 min. Dilution with water precipitated α-benzoyldiphenylmethanol which, crystallised from light petroleum (b. p. 50—70°), had m. p. and mixed m. p. 87—88°.

α-Benzoyldiphenylmethyl chloride (1·53 g.), when heated with sodium hydrogen sulphide in absolute alcohol (a solution from 0·115 g. of sodium in ethanol, then saturated with hydrogen sulphide) gave unchanged chloride and α-benzoyldiphenylmethane which were separated by crystallisation from alcohol. Using two equiv. of the sulphide (prepared from 0·23 g. of sodium) gave only α-benzoyldiphenylmethane.

Heating dibenzoylmethyl bromide [6a] with mercaptoacetic, β-mercaptopropionic, or α-mercapto-α-methylpropionic acid at 110° alone, or in pyridine, alcohol, or acetone in presence of sodium hydrogen carbonate, did not give the expected dibenzoylmethylthio-acids. The product was always dibenzoylmethane, m. p. and mixed m. p. 77—78°, and the disulphide from the mercapto-acid.

Di-*p*-nitrophenylmethyl chloride (5 g.) and mercaptoacetic acid (2 g.) were boiled for 1 hr. in aqueous-alcoholic sodium hydrogen carbonate;[2e] the neutral product (3·5 g.) formed along with [di-(*p*-nitrophenylmethyl)thio]acetic acid (1·5 g.) was di-*p*-nitrophenylmethane, m. p. and mixed m. p. 187°. Using β-mercaptopropionic acid (2·2 g.) also gave di-*p*-nitrophenylmethane (3·6 g.) and the alkylthio-acid (1 g.).[2e] Using 4 equiv. of the mercapto-acid halved the yields of the last two alkylthio-acids, while the yields of di-*p*-nitrophenylmethane were slightly increased. If the mercapto-acid was omitted in these experiments the chloride was recovered unchanged.

When the chloride was heated with a mercapto-acid (one equiv. or excess) without a solvent at 140—150° for 2 hr., hydrogen chloride was evolved. Extraction with sodium hydrogen carbonate did not give the alkylthio-acid; material insoluble in the carbonate solution was a mixture of unchanged chloride and di-*p*-nitrophenylmethane which were separated by crystallisation from alcohol.

Heating di-*p*-nitrophenylmethyl chloride with sodium hydroxide in dioxan or alcohol or acetone led to a different reaction, namely, α-proton extraction and formation of tetra-*p*-nitrophenylethylene[10] (Found: C, 61·7; H, 3·5; N, 10·7. Calc. for $C_{26}H_{16}N_4O_8$: C, 60·9; H, 3·1;

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[7] Kohler and Potter, *J. Amer. Chem. Soc.*, 1936, **58**, 2166.

[8] Backer and Stedehouder, *Rec. Trav. chim.*, 1935, **52**, 437.

[9] Hughes, *Quart. Rev.*, 1951, **5**, 267.

[10] Gorvin, *J.*, 1959, 678.

N, 10·9%), m. p. 294°, which on ozonolysis gave 4,4′-dinitrobenzophenone, the reaction being similar to the formation of 4,4′-dinitrostilbene from 4-nitrobenzyl chloride.[11]

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[11] Hanna, Iskander, and Riad, *J.*, 1961, 217.