

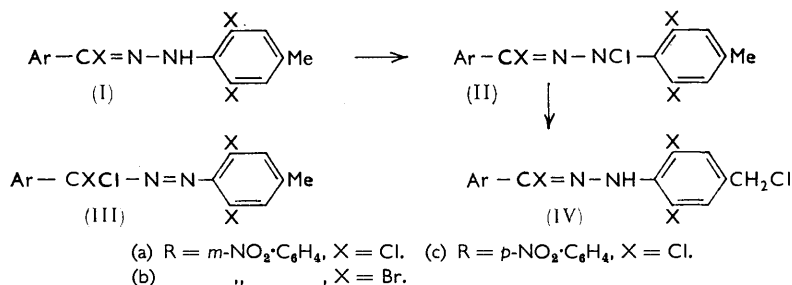
436. The Chattaway-Adamson Rearrangement.

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Re-examination of the Chattaway-Adamson rearrangement requires re-formulation of the reaction as (II) \rightarrow (IV).

CHLORINATION of *N*- α -chloro-3-nitrobenzylidene-*N'*-(2,6-dichloro-4-methylphenyl)-hydrazine (Ia) in warm glacial acetic acid gives the orange *N'*-chloro-compound (IIa); this rearranges in boiling, slightly aqueous acetic acid to give a sparingly soluble, pale yellow isomer, hitherto formulated as (IIIa).¹ The latter formula, proposed with some reservations, was based on two pieces of evidence which showed that the migrating chlorine atom had not entered either aromatic ring. Thus, (i) reduction with tin and hydrochloric acid gave, as basic product, 2,6-dichloro-4-methylaniline, and (ii) reaction with anhydrous sodium acetate and boiling acetic acid gave a viscid solid which yielded *m*-nitrobenzoic acid on decomposition with hot hydrochloric acid. The analogues (IIb) and (IIc) gave similar isomers, and the latter isomer was degraded as in (i) and (ii) to give the same base and *p*-nitrobenzoic acid.

The rearrangement products, isomer-a and isomer-b, from (IIa) and (IIb) have now been re-examined. Spectroscopic evidence requires that the structures (IIIa, b, and, by inference, c) should be amended to (IVa, b, and c).



The ultraviolet absorption spectra of isomer-a and -b are virtually identical with those of (Ia and b, respectively), *i.e.*, the rearrangement of (II) regenerates the chromophore of (I). The visible region spectra of the pairs (Ia) and isomer-a, and (Ib) and isomer-b are likewise identical, showing only low-intensity end-absorption. The pale yellow colour of the rearrangement products was the basis of one of Chattaway and Adamson's reservations about structures (III): the azo-group should, they felt, have conferred a red colour. These spectroscopic similarities are paralleled by the coincidence of m. p. in the compounds (Ib) and isomer-b, which, however, is fortuitous, as a mixed m. p. shows a large depression.

The infrared spectra (as mulls in Nujol) of isomer-a and isomer-b are generally similar to those of (Ia and b, respectively), all showing a band near 3270 cm^{-1} (N-H); the compound (IIb) shows no such band. The principal difference lies in the appearance of a new band at 710 cm^{-1} (C-Cl) in the spectra of isomer-a and -b.

¹ Chattaway and Adamson, *J.*, 1930, 843.

The earlier chemical evidence¹ [cf. points (i) and (ii) above] implies that the rearrangement involves no change in the aromatic substitution pattern. In agreement, the weak aromatic summation bands (for 1,3-di- and 1,2,3,5-tetra-substitution) in the 2000—1650 cm^{-1} region (in CHCl_3) correspond in the compounds (Ia and b) and isomer-a and -b, though the last two compounds show a band at 1690 cm^{-1} superimposed on the original pattern.²

Finally, compounds (Ia and b) and isomer-a and -b, as mulls in hexachlorobutadiene (calcium fluoride prism), showed bands near 3280 (N-H) and 3070 cm^{-1} (aromatic C-H). Compounds (Ia and b) showed further bands at 2915 and 2860 cm^{-1} (methyl asymmetrical and symmetrical C-H stretching). For isomer-a and -b, the aromatic C-H band showed an inflexion at 3050 cm^{-1} , attributable to a symmetrical C-H in chloromethyl, and a weak separate band at 2950 cm^{-1} (symmetrical C-H in chloromethyl) (cf. benzyl chloride).

The spectroscopic evidence thus supports the scheme (II) \rightarrow (IV), the methyl group being necessary for the rearrangement.^{1,3} The reaction probably proceeds by an ionic mechanism, involving electrophilic attack by chlorine at the carbon atom carrying the methyl group, the resulting quinonoid intermediate undergoing aromatisation to the compound (IV). It is relevant that bromination, in acetic acid, of *e.g.*, 2,6-dibromo-4-methylphenol yields 2,4,6-tribromo-4-methylcyclohexadienone, and that this compound rearranges to 2,6-dibromo-4-bromomethylphenol when warmed alone or in solution.⁴ Similar considerations almost certainly apply to the anomalies observed in the Orton rearrangements of the *N*-halogenated aceto-*p*-toluidides⁵ and to similar reactions involving partial displacement of nuclear bromine by chlorine.⁶

EXPERIMENTAL

Spectra for the ultraviolet and visible region were measured for ethanol solution; infrared spectra were measured (by a Perkin-Elmer 21 double-beam instrument) as mulls in Nujol, for (A) the 2000—1650 cm^{-1} region as CHCl_3 solutions, and (B) the 4000—2500 cm^{-1} region as mulls in hexachlorobutadiene with a calcium fluoride prism.

Materials were prepared by the described methods,¹ except for *N*- α -chloro-3-nitrobenzylidene-*N'*-(2,6-dichloro-4-chloromethylphenyl)hydrazine (IVa), which was prepared from compound (Ia) [without isolation of the *N*-chloro-compound (IIa)] by chlorination in acetic acid, addition of a small amount of water, and boiling under reflux to effect rearrangement. M. p.s agree with the reported figures except for the compound (IIb), which has m. p. 83—84.5° (Kofler block) (Chattaway and Adamson¹ report m. p. 77°). Compounds (Ib) and (IVb) have m. p. 155—156° and 156—157°, respectively (mixed m. p. 131—135°).

In the rearrangement (IIb) \rightarrow (IVb), the refluxing acetic acid immediately acquired a red colour, probably owing to liberation of traces of bromine (cf. ref. 6). The compound (IIb) did not rearrange at or above its m. p. to (IVb), the melt remaining clear up to the onset of decomposition at 132—140°.

Spectroscopic results were (log ϵ in parentheses):

m-Nitrobenzaldehyde *p*-tolylhydrazone: λ_{max} . 235 (4.19), 298 (3.88), 310 (3.88), and 357 (4.31); λ_{min} . 275 (3.81), 304 (ϵ 3.86), and 316 (ϵ 3.85); λ_{infl} . 250 (4.17), 290 (3.86), and 342 $\text{m}\mu$ (4.21); ν_{max} . 675, 700, 736, 820, 915, 997w, 1078, 1092, 1108, 1120w, 1155, 1178w, 1254, 1285, 1315, 1350 (*ar*-NO₂), 1520 (*ar*-NO₂), 1585, 1600, 1615, and 3280 (N-H) cm^{-1} .

N- α -Chloro-3-nitrobenzylidene-*N'*-(2,6-dichloro-4-methylphenyl)hydrazine (Ia): λ_{max} . 317 (4.27), λ_{min} . 265 (ϵ 4.06), λ_{infl} . 280 $\text{m}\mu$ (4.15); ν_{max} . 670, 700, 730sh, 736, 772, 800, 816, 830, 860, 890, 925w, 980, 1000w, 1050, 1080, 1100, 1132sh, 1142, 1158, 1170sh, 1205, 1236, 1266, 1285, 1315, 1350, 1520, 1530sh, 1575, 1585, 1612, and 3280 cm^{-1} ; summation bands, 1736, 1790, 1835, 1855w, 1895, 1910, and 1965 cm^{-1} ; 3300, 3075, 2915, and 2860 cm^{-1} .

N- α -Chloro-3-nitrobenzylidene-*N'*-(2,6-dichloro-4-chloromethylphenyl)hydrazine (IVa): λ_{max} . 315 (4.37), λ_{min} . 265 (4.11), λ_{infl} . 280 $\text{m}\mu$ (4.15); ν_{max} . 670, 695, 710, 730sh, 736, 776, 800,

² Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 67.

³ Chattaway and Walker, *J.*, 1925, 1687.

⁴ Fries and Oehmke, *Annalen*, 1928, 462, 1.

⁵ Chattaway and Orton, *J.*, 1900, 77, 789.

⁶ Chattaway and Orton, *J.*, 1901, 79, 816, 822.

840, 870, 900, 916w, 940, 980, 1085w, 1102w, 1145, 1158sh, 1170sh,w, 1215sh, 1236, 1265, 1290, 1335, 1350, 1400, 1520, 1530sh, 1570, 1585, 1600, 1612sh, and 3270 cm^{-1} ; summation bands, 1690, 1736, 1793, 1835, 1855w, 1895sh, 1910, and 1965 cm^{-1} ; 3280, 3070, 3050_{infl.}, and 2950 cm^{-1} .

N- α -Bromo-3-nitrobenzylidene-*N'*-(2,6-dibromo-4-methylphenyl)hydrazine (Ib): λ_{max} 316 (4.19), λ_{min} 265 (4.03), $\lambda_{\text{infl.}}$ 250 (4.07) and 280 $\text{m}\mu$ (4.05); ν_{max} 665, 690w, 705w, 715w, 735, 800, 815sh, 860, 890, 895sh, 925w, 965, 995w, 1065w, 1100sh, 1140, 1180w, 1210sh, 1225, 1255w, 1285, 1300, 1325, 1350, 1515, 1530, 1565, 1585, 1612, and 3240 cm^{-1} ; summation bands, 1736, 1790, 1832, 1855w, 1895, 1910, and 1965 cm^{-1} ; 3270, 3070, 2915, and 2860 cm^{-1} .

N- α -Bromo-3-nitrobenzylidene-*N'*-chloro-*N'*-(2,6-dibromo-4-methylphenyl)hydrazine (IIb): λ_{max} 293 (3.82) and 413 (2.62), λ_{min} 285 (3.81) and 380 (2.51), $\lambda_{\text{infl.}}$ 250 $\text{m}\mu$ (4.13); ν_{max} 670, 700, 726, 736, 778, 813, 860, 900w, 905w, 940w, 960, 985, 1100, 1170w, 1200, 1225, 1290, 1310, 1350, 1515sh, 1530, 1590 and 1610 cm^{-1} .

N- α -Bromo-3-nitrobenzylidene-*N'*-(2,6-dibromo-4-chloromethylphenyl)hydrazine (IVb): λ_{max} 315 (4.44), λ_{min} 265 (4.11), $\lambda_{\text{infl.}}$ 250 (4.27) and 280 $\text{m}\mu$ (4.23); ν_{max} 670, 690, 710, 735, 755w, 775w, 800, 835, 865, 900, 930, 975, 1100w, 1140, 1230, 1260, 1290, 1335, 1350, 1515sh, 1528, 1568, 1580sh, 1595, 1610 and 3240 cm^{-1} ; summation bands 1690, 1736, 1790, 1832, 1855w, 1895sh, 1910, and 1965 cm^{-1} ; 3280, 3070, 3050_{infl.}, and 2950 cm^{-1} .

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