LXIX.—*The Nitration of* m-*Acetamido*-tert.-*butylbenzene.*

By JOHN BALDWIN SHOESMITH and ALEXANDER MACKIE.

GELZER (*Ber.*, 1888, **21**, 2949) was the first to nitrate *m*-acetamido-*tert.*-butylbenzene and claimed to have isolated 2-nitro-3-acetamido-*tert.*-butylbenzene as the sole reaction product. The constitution of this compound was determined as follows. On hydrolysis it yielded the corresponding nitroamine, which when reduced gave a diamino-*tert.*-butylbenzene of m. p. 109°, and this readily condensed with phenanthraquinone to give a phenanthra-*tert.*-butylphenazine (compound A), m. p. 144°. In a parallel series of experiments with *p*-acetamido-*tert.*-butylbenzene, the phenazine obtained, m. p. 146·5°, was considered by Gelzer to be different from compound A, and since the nitration of *p*-acetamido-*tert.*-butylbenzene was known to give 3-nitro-4-acetamido-*tert.*-butylbenzene the composition of the nitration product from *m*-acetamido-*tert.*-butylbenzene was as stated above.

In view of the difficulty with which the position ortho to the *tert.*-butyl group in *tert.*-butylbenzene is attacked (J., 1928, 2334) Gelzer's observation appeared remarkable, since it requires direct attack of a position which is ortho to both substituent groups in *m*-acetamido-*tert.*-butylbenzene. The nitration of *m*-acetamido-*tert.*-butylbenzene has now been repeated, the nitroamine obtained by hydrolysis of the reaction product reduced, and the diamine condensed with phenanthraquinone. The resulting phenazine has been found to have m. p. 148·5—149° and to be identical in all respects with that obtained from 3 : 4-diamino-*tert.*-butylbenzene prepared from 3-nitro-4-amino-*tert.*-butylbenzene. This result proves that the nitration of *m*-acetamido-*tert.*-butylbenzene takes place as expected in position 4, and it is interesting to note the difference between this nitration and that of aceto-*m*-toluidide, which is nitrated predominantly in the 6-position. The reluctance of the group to enter the ortho-position to a *tert.*-butyl group in *tert.*-butylbenzene is again apparent.

EXPERIMENTAL.

The compounds described in Gelzer's paper as derivatives of *iso*-butylbenzene are in reality derived from *tert.*-butylbenzene.

4-*Nitro*-3-*amino*-tert.-*butylbenzene*.—*m*-Acetamido-*tert.*-butylbenzene (Shoesmith and Mackie, *loc. cit.*, p. 2338) was added to vigorously agitated nitric acid (*d* 1·46) at 25—30° during 15 minutes; the mixture was then poured into a large excess of ice-water. The nitro-compound crystallised from alcohol in pale yellow needles, m. p. 116° (Gelzer, *loc. cit.*, gives m. p. 105·5°) (Found: N, 12·1. Calc.: N, 11·9%); yield, 41%. When hydrolysed with alcoholic potassium hydroxide, it gave 4-nitro-3-amino-*tert.*-butylbenzene, which crystallised from alcohol in yellow leaflets, m. p. 91—92° (Gelzer gives 124°) (Found: N, 14·1. Calc.: N, 14·4%); yield, 81%.

Phenanthra-tert.-*butylphenazine*.—The above nitroamine (3 g.) was dissolved in warm concentrated hydrochloric acid, the calculated quantity of stannous chloride added, and the whole *vigorously* agitated. The resulting solution was cooled, freed from tin by the addition of zinc, and decanted from the metal, and a large excess of concentrated aqueous sodium hydroxide added. The liberated diamine, isolated by means of ether, was obtained as a light brown solid which crystallised from water in micaceous colourless leaflets, rapidly darkening in the air and of m. p. 97—98°. The diamine in alcoholic solution, when added to the calculated quantity of phenanthraquinone in glacial acetic acid, gave the phenazine as a mass of pale yellow, interlaced needles; these recrystallised from aqueous alcohol in very small, yellow needles, m. p. 148·5—149° (Gelzer gives 144°). It was more satisfactory to proceed to the phenazine in this way than to attempt to purify the diamine completely, as there was present a very small quantity of impurity which was removable with great difficulty from the diamine, whereas there was no difficulty in purifying the phenazine.

In order to characterise this compound, 3-nitro-4-amino-*tert.*-butylbenzene, prepared by the nitration of *p*-acetamido-*tert.*-butylbenzene and subsequent hydrolysis, was reduced to the diamine, which was condensed with phenanthraquinone as before. The phenazine obtained had m. p. 148·5—149·5° (Gelzer gives 146·5°) and was identical in all respects with that obtained from the nitrated *m*-acetamido-*tert.*-butylbenzene; a mixture of the two compounds melted at 148—149°.

The authors wish to state that the investigation was completed during the tenure of a teaching fellowship awarded to one of them (J. B. S.) by the Carnegie Trustees.

EDINBURGH UNIVERSITY. [*Received, January 23rd*, 1929.]