370. *Triazepines. Part II.*[1] *Reaction of Various Substituted Benzophenones with Hydrazine.*

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2-Phthalimidobenzophenones condense with hydrazine only when substituents with a large $+T$ effect are present in the 4′-position. Others, including those with substituents in position 2′ or 4 having $+T$ effects, or in positions 4, 2′, or 4′ having $+I$ effects, undergo the normal Ing and Manske cleavage with hydrazine. This opens a new synthetic route to some 2-aminobenzophenones.

WE have shown in Part I[1] that, depending on the nature of substituents, 2-phthalimidobenzophenones either undergo the Ing and Manske reaction with hydrazine or condense with it to form 1,2,4-triazacyclohepta-2,5,7-trienes. For further study we have used 2-phthalimidobenzophenones[2] with electron-repelling groups *ortho* and/or *para* to the benzophenone-carbonyl group since triazepine formation was observed when the strongly electron-donating methoxyl group was in the 2′,4′- or in the 4′-position.

Of the compounds investigated only 4-methylthio-2′-phthalimido- and 2,4-dimethoxy-2′-(3-nitrophthalimido)-benzophenone gave triazepines: the Ing and Manske reaction to give the amine proceeded smoothly with 4′-methoxy-, 2-methoxy-, 2,4′-dimethoxy-, 4-hydroxy-, 2,4-dimethyl-, 4-methyl-, 2-methyl-, and 4-bromo-2′-phthalimidobenzophenone as well as with 2,4′-diphthalimidobenzophenone and 2-phthalimidoacetophenone.

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[1] Part I, Engels, Lamchen, and Wicken, *J.*, 1959, 2694.

[2] Lamchen and Wicken, *J.*, 1959, 2779.

Thus triazepines are formed only when substituents with a large $+T$ effect are present in the 4′-position of 2-phthalimidobenzophenones. Substituents with large $+T$ effects in the 2′- or 4-position, and $+I$ effects in position 4′-, 2′-, or 4-, do not influence the reaction with hydrazine sufficiently to cause triazepine formation instead of the normal Ing and Manske reaction.

The effect of electron-attracting groups in the *ortho*- and *para*-positions would be of interest. Only 2,4′-diphthalimidobenzophenone has so far been prepared, and in this case the normal Ing and Manske reaction took place. The value of this reaction is, however doubtful, since the product obtained was 2,4′-diaminobenzophenone, and the 4′-phthalimido-group may thus have decomposed first to give the electron-repelling amino-group in the 4′-position.

The Ing and Manske reaction has been utilised widely in the synthesis of aliphatic amino-compounds, but not in the synthesis of aromatic amines. Since some of these 2-phthalimidobenzophenones which decompose normally can be readily synthesised by Friedel–Crafts condensation of phthaloylanthraniloyl chloride with the correctly substituted benzene,[2] the Ing and Manske reaction is a valuable route to some 2-aminobenzophenones. Its limitations are unfortunately similar to those that restrict the use of the toluene-*p*-sulphonyl group as a protecting group. Thus, whereas strongly electron-repelling groups in 2-toluene-*p*-sulphonamidobenzophenones may cause sulphonation during the removal of the sulphonyl group by hydrolysis with sulphuric acid, the use of hydrazine on such 2-phthalimidobenzophenones may cause triazepine formation.

EXPERIMENTAL

5-(4-*Methylthiophenyl*)-12-*oxobenzo*[5,6]-1,2,4-*triazepino*[3,4-a]*isoindole*.—To powdered 4-methylthio-2′-phthalimidobenzophenone (20 g.) suspended in absolute ethanol (300 ml.) 96% hydrazine hydrate (1·72 ml.) was added and the mixture stirred and refluxed. After 30 min. all the benzophenone was in solution and soon afterwards white crystals started to separate. After 3 hr. the solution was chilled in ice and filtered. The crystals (18 g.) were washed with alcohol, dried, and recrystallised from glacial acetic acid, giving the *triazepine*, m. p. 242—244° (Found: C, 71·7; H, 4·1; N, 11·1; S, 8·6. $C_{22}H_{15}ON_3S$ requires C, 71·5; H, 4·1; N, 11·4; S, 8·7%).

5-(2,4-*Dimethoxyphenyl*)-9- *or*-11-*nitro*-12-*oxobenzo*[5,6]-1,2,4-*triazepino*[3,4-a]*isoindole*.—This was prepared as above from 2,4-dimethoxy-2′-(3-nitrophthalimido)benzophenone (1 g.), ethanol (30 ml.), and 96% hydrazine hydrate (0·08 ml.). Recrystallisation from glacial acetic acid gave the *triazepine* as yellow needles (0·95 g., 98%), m. p. 293—296° (Found: C, 64·8; H, 3·8; N, 13·2. $C_{23}H_{16}O_5N_4$ requires C, 64·5; H, 3·8; N, 13·1%).

Reaction of Hydrazine with Some 2-Phthalimidobenzophenones.—A suspension of 2-methoxy-2′-phthalimidobenzophenone (1 g.) in ethanol (40 ml.) was refluxed with an equimolar amount of 96% hydrazine hydrate. Within minutes the solution became yellow and soon (20 min.) phthalhydrazide began to crystallise. After 2 hours' refluxing the solution was cooled and filtered. The white precipitate of phthalhydrazide was washed and dried, m. p. and mixed m. p. 330—334°. The filtrate was evaporated to dryness and extracted with ether. The insoluble solid was phthalhydrazide (total, 90%). The ether solution on evaporation gave 2-amino-2′-methoxybenzophenone (0·6 g.; 94%), m. p. and mixed m. p. 109—111°.

The other benzophenones listed above also gave phthalhydrazide (90—98%) and the amines (mixed m. p.) (~90%).

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[*Received, June 8th*, 1959.]