Reaction of Benzophenone Hydrazone with 1-Chlorobenzotriazole

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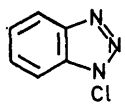
The reaction of benzophenone hydrazone with 1-chlorobenzotriazole is complex and consumes three equivalents of the oxidant. One equivalent causes oxidation to diphenyldiazomethane which reacts rapidly with a second equivalent to give benzotriazolyldiphenylmethyl chloride. This reacts slowly with further 1-chlorobenzotriazole to give chlorine and dibenzotriazol-1-yldiphenylmethane (2) and the isomeric 3-benzotriazol-1-yl-6-(benzotriazol-1-ylphenylmethylene)cyclohexa-1,4-diene (3).

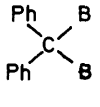
1-CHLOROBENZOTRIAZOLE (1) has been used extensively as an oxidant for the conversion of alcohols into carbonyl compounds,[1,2] sulphides into sulphoxides,[3] sulphoxides into sulphones,[3,4] hydrazo into azo-compounds,[1] hydroxylamines into nitroso-compounds, and *N*-amino-heterocycles into *N*-nitrenes.[1] During the course of our investigation of the scope of 1-chlorobenzotriazole as an oxidant we considered the possibility that it could be used for the conversion of benzophenone hydrazone into diphenyldiazomethane. This led to an unexpectedly complex reaction.

[1] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 1474.
[2] W. C. Ferrell and K-C. Yao, *J. Lipid Res.*, 1972, **13**, 23.
[3] W. D. Kingsbury and C. R. Johnson, *Chem. Comm.*, 1969, 365.
[4] M. Cinquini and S. Colonna, *Synthesis*, 1972, 259.

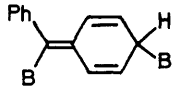
Treatment of benzophenone hydrazone with one equivalent of 1-chlorobenzotriazole in dichloromethane gave a reaction mixture which included much unchanged hydrazone together with benzotriazole hydrochloride, benzotriazole, and benzophenone. The reaction was equally complex using two equivalents of 1-chlorobenzotriazole and, again, appreciable amounts of the starting hydrazone remained. With three equivalents of 1-chlorobenzotriazole oxidation was complete after *ca.* 12 h



(1)



(2)

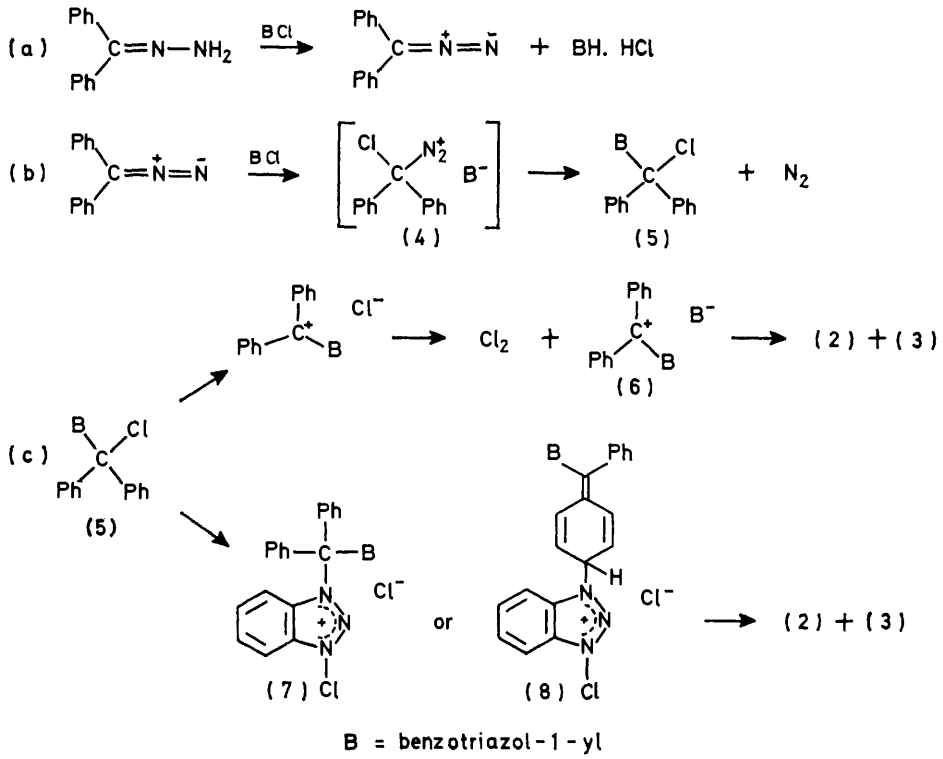


(3)

B = benzotriazol-1-yl

at room temperature or 2 h when heated under reflux. During the initial mixing of reactants rapid evolution of nitrogen occurred; this was followed by gradual separation of benzotriazole hydrochloride and slow evolution of chlorine. After removal of benzotriazole hydrochloride (1 equivalent) the remaining products were separated by chromatography on neutral alumina and comprised benzophenone (41%), benzotriazole and, unexpectedly, the dibenzotriazolyldiphenylmethane (2) (32%) together with an unstable isomeric compound (24%), believed to have structure (3). If the reaction mixture was heated for a longer time the cyclohexadiene (3) was not observed and the tetrasubstituted methane was isolated in increased yield.

Structure (2) was fully supported by analytical and spectral data. The n.m.r. spectrum lacked the characteristic AA'XX' pattern of a 2-substituted benzotriazole [5] and confirmed that both benzotriazole moieties were bonded through N-1. This was further supported by the u.v. spectrum, by the i.r. spectrum which showed two absorptions at 1 602 and 1 586 cm^{-1} diagnostic of a 1-substituted benzotriazole, and by the ready loss of two units of mass 28 in the mass spectrum. Full characterisation of the cyclohexadiene (3) was not possible because of its instability with respect to isomerisation to the more stable compound (2), which was rapid even in the n.m.r. probe, and towards hydrolysis to benzophenone and benzotriazole. The n.m.r. spectrum of a freshly obtained sample showed the presence of 5 protons between δ 4.3 and 6.4 p.p.m. which could be assigned as the olefinic and methine protons on the cyclohexadiene ring. A weak absorption at 1 659 cm^{-1} in the i.r. spectrum also indicated the presence of a carbon–carbon double bond and the highly unsaturated character was demonstrated by the instantaneous decolourisation of potassium permanganate which did not occur with the isomer (2).



B = benzotriazol-1-yl

SCHEME 1

An explanation for these observations is given in Scheme 1. Oxidation of the hydrazone to diphenyldiazomethane [step (a)] is rapid and results in the formation of benzotriazole and hydrogen chloride which ultimately separate out as the insoluble benzotriazole

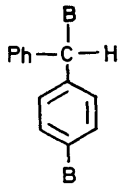
[5] R. E. Rondeau. H. M. Rosenberg, and D. J. Dunbar, *J. Mol. Spectroscopy*, 1969, **29**, 305.

hydrochloride. The diphenyldiazomethane, however, cannot be detected (even by the transient appearance of its characteristic colour) because of its even faster reaction with 1-chlorobenzotriazole to give benzotriazolylchlorodiphenylmethane (5) [step (b)]. Such a reaction is reasonable in view of the nucleophilic character of the diazomethane carbon and the highly electrophilic nature of the 1-chlorobenzotriazole chlorine. Rapid collapse of an intermediate diazonium cation–benzotriazole anion pair (4) would give the chloro-compound (5).

The final step (c) involves interaction of the reactive 'triaryl' chloromethane (5) with 1-chlorobenzotriazole to give chlorine and the dibenzotriazolyldiphenylmethane (2) and its less stable cyclohexadiene isomer (3). This unexpected but not unreasonable reaction depends on the high reactivity of (5) as an alkyl halide and could proceed by ionisation of the halide to give chloride ion which then liberates chlorine from 1-chlorobenzotriazole, products (2) and (3) being formed by combination of the benzotriazolyl anion with the benzotriazolyl diphenylmethyl cation (6) either at the central carbon or at the more exposed phenyl carbons. Alternatively, prior alkylation of 1-chlorobenzotriazole by the halide would give (7) or (8) which are even stronger positive halogen compounds and would undergo rapid collapse to chlorine and the observed products.

Isomerisation of the cyclohexadiene (3) to a mixture of cyclohexadiene (3) and tetrasubstituted methane (2) occurs slowly with time in dichloromethane and more rapidly when the mixture is warmed. The isomerisation is catalysed by benzotriazole hydrochloride and is to some extent reversible since the methane (2) when warmed with benzotriazole hydrochloride in dichloromethane gives some of the cyclohexadiene (3). If care is not taken to exclude moisture under these conditions benzophenone and benzotriazole are produced.

The isomerisation therefore appears to involve dissociation to give a benzotriazolyldiphenylmethyl cation–benzotriazolyl anion (or neutral benzotriazole under acid catalysis) pair which can recombine or be intercepted by water. The benzotriazolyl anion is a relatively good leaving group and its ability to ionise and return possibly explains why only the 1-substituted benzotriazolyl isomer (2) is observed in spite of the considerable steric crowding in this molecule. No benzotriazol-2-yl isomer was observed although the steric demand of a 2-substituted benzotriazole should be less and the benzotriazolyl anion is ambident. In general, however, 1-substituted benzotriazoles are more stable electronically and in other situations where the substituent is readily and reversibly removable only the 1-substituted isomer is obtained, *e.g.* H, Cl, COR, and CPh_3 (*vide infra*). The considerable twisting of the benzotriazolyl and phenyl rings in (2) reveals itself in the n.m.r. spectrum where the high field absorption (δ 6.46) can be attributed to the benzotriazole 7-protons which lie above the plane of the adjacent phenyl rings. It is presumably this severe crowding which is responsible for the formation of the less hindered cyclohexadiene (3) along with the tetrasubstituted methane in this system. Perhaps surprisingly the cyclohexadiene shows no tendency to

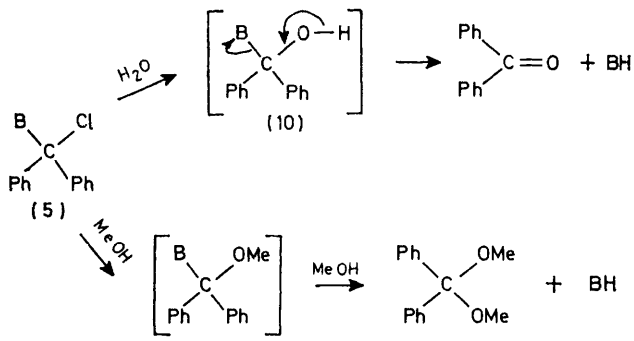


(9)

B = benzotriazol-1-yl

undergo aromatisation to (9) by a proton shift even under basic conditions.

Evidence in support of the mechanism outlined in Scheme 1 is as follows. When diphenyldiazomethane in dichloromethane is treated with two equivalents of 1-chlorobenzotriazole the colour is rapidly discharged and the expected products including dibenzotriazolyldiphenylmethane (2) are isolated after 3 days. With one equivalent of 1-chlorobenzotriazole the colour is again rapidly discharged but attempts to isolate and characterise the chloro-compound (5) were frustrated by its extreme reactivity towards hydrolysis to give benzotriazole and benzophenone presumably *via* the alcohol (10) (Scheme 2). Addition of methanol to the



SCHEME 2

crude chloro-compound gave benzophenone dimethyl acetal in high yield; this again illustrates the ease with which benzotriazole can function as a leaving group as is also apparent from the ready hydrolysis of (2) and (3). The intermediacy of the chloro-compound (5) is further supported by the reaction of diazomethane with 1-chlorobenzotriazole. This gave 1- and 2-chloromethylbenzotriazoles which were sufficiently stable not to undergo further reaction with 1-chlorobenzotriazole. Analogous reactions of *N*-halogeno-compounds with diazomethane have been reported.[6] The final step (c) is dependent on the high reactivity of chloro-compound (5). In line with this triphenylmethyl chloride also undergoes reaction with 1-chlorobenzotriazole slowly at room temperature to give 1-tritylbenzotriazole and chlorine.

[6] O. O. Orazi, R. A. Corral, and H. Schuttenberg, *J.C.S. Perkin I*, 1974, 2087.

Benzyl chloride reacts only very sluggishly at high temperature.[7]

In previous work we observed the formation of 1-benzylbenzotriazole and the benzotriazolated ethers

(11) (12)

B = benzotriazol-1-yl

(11) and (12) in the reactions of 1-chlorobenzotriazole with, respectively, toluene at elevated temperature and with diethyl ether and tetrahydrofuran at room temperature. These products were accounted for in terms of free-radical chain reactions in which the key step leading to benzotriazolated product was abstraction of a benzotriazolyl group from 1-chlorobenzotriazole by a benzyl or ether radical, for example (13). An alternative

(13) (14)

explanation must now involve polar reaction of chlorobenzotriazole with the reactive α-chlorinated toluene or ether, for example (14), so that it is no longer necessary to postulate radical abstraction of a benzotriazolyl group from chlorobenzotriazole to explain the formation of benzotriazolated products. Indeed in the photo-induced free radical additions of 1-chlorobenzotriazole to alkenes such radical abstractions are notably absent.[8]

EXPERIMENTAL

Reaction of 1-Chlorobenzotriazole with Benzophenone Hydrazone.—Benzophenone hydrazone (1.96 g, 10 mmol) in dry dichloromethane (25 ml) was added during 5 min to a solution of 1-chlorobenzotriazole (4.60 g, 30 mmol) in dry dichloromethane (25 ml). Rapid evolution of nitrogen occurred during the addition. The solution was then heated under reflux for 2 h, during which time the evolution of chlorine was detected by starch–iodide paper placed at the mouth of the condenser. Benzotriazole hydrochloride (1.74 g, 37%) was filtered off from the cooled solution; the solvent was evaporated under reduced pressure, and the residue was chromatographed on deactivated neutral alumina (5% water).

Elution with 10% ether–petroleum gave benzophenone (747 mg, 41%) identical with authentic material. Continued elution with 10% ether–petroleum gave *3-benzotriazol-1-yl-6-(benzotriazol-1-ylphenylmethylene)cyclohexa-1,4-diene* (3) (965 mg, 24% based on hydrazone) as a colourless crystalline solid, m.p. 70—75 °C, $\nu_{max.}$ 1 659w (C=C), 1 610, 1 594, 1 274, 1 165, 1 083, 951, 898, 885, 789, 752, and 705 cm^{-1}; δ(CCl_4) 8.01 (1 H, d, J = 7 Hz), 7.80—7.00 (12 H, complex), 6.34 (1 H, d, J = 7 Hz), 5.2—5.0 (2 H, m), and centred on 4.73 and 4.39 (m, 2 H); *m/e* 402 (M^+), 374 ($M - N_2$, base peak), 346 ($M - 2N_2$), 318, 284, 257, 256, 255, 254, 200, 182, 178, 160, 153, 132, 119, 117, 105, 91, 84, and 77. Attempted recrystallisation from a variety of solvents resulted in partial isomerisation to (2) or in hydrolysis.

Elution with 20% ether–petroleum gave dibenzotriazol-1-yldiphenylmethane (1.289 g, 32% based on hydrazone) as colourless prisms, m.p. 209 °C from benzene–petroleum (Found: C, 74.4; H, 4.7; N, 20.9. $C_{25}H_{18}N_6$ requires C, 74.6; H, 4.5; N, 20.9%), $\nu_{max.}$ 1 602, 1 586, 1 349, 1 284, 1 205, 1 156, 1 075, 940, 933, 884, 865, 788, 755, 705, and 700 cm^{-1}; δ($CDCl_3$) 7.99 (2 H, d, J = 7 Hz), 7.30—7.00 (14 H, complex), and 6.46 (2 H, d, J = 7 Hz); *m/e* 402 (M^+), 374 ($M - N_2$, base peak), 346 ($M - 2N_2$), 318, 297, 284, 257, 256, 255, 254, 178, 165, 153, 152, 151, 140, 139, 127, 119, 91, 78, and 77.

Benzotriazole was detected by t.l.c. but was not eluted from alumina.

Chromatography on silica gel resulted in continuous elution of benzophenone and benzotriazole together with the products (2) and (3).

When the reaction mixture was subjected to heating under reflux for 3 days followed by chromatographic work-up on silica gel the following products were isolated: benzophenone (44%), dibenzotriazol-1-yldiphenylmethane (52% based on hydrazone), and benzotriazole (56%).

The following tests were carried out on the cyclohexadiene (3). (i) One drop of a dilute solution of potassium permanganate in acetone was added to a solution of the cyclohexadiene in dichloromethane. The colour of the permanganate was immediately discharged. A similar test with the tetrasubstituted methane (2) led to only very slow decolouration. (ii) The cyclohexadiene was warmed in moist dichloromethane with benzotriazole hydrochloride. After 10 min t.l.c. indicated that complete hydrolysis to benzophenone and benzotriazole had occurred. In dry dichloromethane, the cyclohexadiene (3), the methane (2), benzotriazole, and benzophenone were detected by t.l.c. after 10 min. Under these conditions the methane (2) also gave a mixture of the same products. (iii) The cyclohexadiene (3) was heated under reflux in cyclohexane. After 5 min t.l.c. indicated that partial isomerisation to (2) had occurred. Warming in deuteriochloroform resulted in almost complete isomerisation of (3) to (2) within 10 min.

Reaction of 1-Chlorobenzotriazole (2 Equivalents) with Diphenyldiazomethane.—A solution of diphenyldiazomethane (1.17 g, 6 mmol) in dry dichloromethane (20 ml) was added dropwise to a solution of 1-chlorobenzotriazole (1.83 g, 12 mmol) in dry dichloromethane (20 ml). The red colour of the diazo-compound was immediately discharged and nitrogen was evolved. The solution was heated under reflux for 3 days after which time t.l.c. indicated the presence of benzophenone, dibenzotriazol-1-yldiphenylmethane, and benzotriazole. Several recrystallisations (dichloromethane–petroleum) of the crude solid obtained by evaporation of the reaction mixture gave dibenzotriazol-1-yldiphenylmethane (1.9 g, 78%), m.p. 209 °C.

Reaction of 1-Chlorobenzotriazole (1 Equivalent) with Diphenyldiazomethane.—1-Chlorobenzotriazole (2.2 g, 14.4 mmol) in dry dichloromethane (70 ml) was added dropwise to a solution of diphenyldiazomethane (2.8 g, 14.4 mmol) in dry dichloromethane (70 ml). Nitrogen was evolved, and the red colour of the diazo-compound was discharged. The resulting pale yellow solution was evaporated under reduced pressure to give a sticky solid. Addition of dry methanol gave a precipitate of benzophenone dimethyl acetal (2.6 g, 79%) as colourless crystals, m.p. 104.5 °C

[7] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 1478.
[8] M. J. Sasse and R. C. Storr, unpublished observations.

(lit.,[9] 106.5—107.5 °C); δ(CCl_4) 7.6—7.1 (10 H, complex m, ArH) and 3.12 (6 H, s, OMe).

Reaction of 1-Chlorobenzotriazole with Diazomethane.—1-Chlorobenzotriazole (3.2 g, 20.8 mmol) in dichloromethane (100 ml) was added dropwise with stirring to a solution of diazomethane (20 mmol) in ether (45 ml) maintained at −40 °C. The reaction mixture was allowed to warm up to room temperature overnight. A small amount of colourless precipitate was filtered off and the filtrate was evaporated under reduced pressure and the residue chromatographed on silica gel. Elution with 20% ether–petroleum gave *2-chloromethylbenzotriazole* (480 mg, 14%) as colourless needles, m.p. 59.5—60.5 °C from petroleum (Found: C, 50.3; H, 3.6; N, 24.8. $C_7H_6ClN_3$ requires C, 50.2; H, 3.6; N, 25.1%), $\nu_{max.}$ 1 560, 1 332, 1 309, 1 264, 1 147, 977, 854, 742, 721, and 706 cm^{-1}; δ(CCl_4) 7.87 and 7.27 (4 H, 2 observed q, AA′BB′ system) and 6.26 (2 H, s, CH_2).

Elution with 60% ether–petroleum gave 1-chloromethylbenzotriazole (607 mg, 18%) as colourless needles, m.p. 135—136 °C (lit.,[10] 136—138 °C) from methanol.

1-Tritylbenzotriazole.—(*a*) A mixture of trityl chloride (2.78 g, 10 mmol) and 1-chlorobenzotriazole (1.53 g, 10 mmol) in dichloromethane (50 ml) was set aside until evolution of chlorine had ceased. The solvent was then evaporated off and the resulting solid was crystallised from benzene to give 1-tritylbenzotriazole (2.13 g, 59%) as colourless crystals, m.p. 224 °C (Found: C, 82.8; H, 5.2; N, 11.8. $C_{25}H_{19}N_3$ requires C, 83.1; H, 5.3; N, 11.6%), $\nu_{max.}$ 1 600, 1 575, 1 480, 1 430, 774, 763, and 741 cm^{-1}; δ($CDCl_3$) 8.0 (d, 1 H), 7.3—6.9 (m, 17 H), and 6.4 (d, 1 H).

(*b*) A mixture of trityl chloride (0.43 g, 1.5 mmol) and benzotriazole (1.79 g, 1.5 mmol) was stirred overnight in ether solution (30 ml) over an excess of anhydrous potassium carbonate. The resulting mixture was filtered off and the filtrate was concentrated and light petroleum was added to give 1-tritylbenzotriazole (0.50 g, 79%), m.p and mixed m.p. 224 °C.

[7/1896 *Received*, 31*st October*, 1977]

[9] J. E. Mackenzie, *J. Chem. Soc.*, 1896, 988.
[10] J. H. Burckhalter, V. C. Stephens, and L. A. R. Hall, *J. Amer. Chem. Soc.*, 1952, **74**, 3868.