Oxidation of Ketone and Aldehyde Hydrazones, Oximes, and Semicarbazones and of Hydroxylamines and Hydrazo-compounds, using Benzeneseleninic Anhydride

By **Derek H. R. Barton,* David J. Lester,** and **Steven V. Ley,** Department of Chemistry, Imperial College, London SW7 2AY

Benzeneseleninic anhydride (1; BSA) is an effective reagent for the mild regeneration of the carbonyl group from ketone phenylhydrazones, *p*-nitrophenylhydrazones, tosylhydrazones, oximes, and semicarbazones at 40—50 °C. Tosylhydrazones and oximes of aldehydes are also readily converted into the parent aldehyde. The phenylhydrazone and *p*-nitrophenylhydrazone derivatives of aldehydes afford ketoazo-compounds. The ketoazo-species could also be prepared by oxidation of the corresponding hydrazide with compound (1). Both aromatic and aliphatic hydrazo-compounds and hydroxylamines can be oxidised to azo- and nitroso-derivatives respectively.

THE regeneration of carbonyl derivatives from hydrazones,[1] oximes,[2] and semicarbazones[3] has been well studied. Many of these literature methods are however not universally applicable. For example, as is discussed below, it proved impossible by known methods to regenerate cholesta-1,4-dien-3-one from its *p*-nitrophenylhydrazone. Benzeneseleninic anhydride[4] (1; BSA) should, on mechanistic arguments (see later), be a suitable reagent to effect this and related transformations. We have, therefore, prepared a series of ketone derivatives and studied their conversion with the anhydride into the parent carbonyl compound under a standard set of reaction conditions (Table 1). From these results it is obvious that phenylhydrazones, *p*-nitrophenylhydrazones, oximes, tosylhydrazones, and semicarbazones can be readily transformed under mild reaction conditions while 2,4-dinitrophenylhydrazones, *NN*-dimethylhydrazones, and *O*-methyl oximes are particularly unreactive even under more vigorous circumstances.

Of special interest was the observation that both the *p*-nitrophenylhydrazones of cholesta-1,4-dien-3-one (3) and cholesta-1,4,6-trien-3-one (4) smoothly gave the parent ketones (5) and (6) respectively. Since these hydrazones had been prepared previously by a novel dehydrogenation procedure[5] of cholestanone *p*-nitrophenylhydrazone their deprotection was important, particularly as many of the literature methods had failed. For convenience we found it useful not to isolate the 1,4,6-trienone (6) but to convert it directly into its 1,2-α-epoxide (7) by treatment with basic hydrogen peroxide as this was required for other synthetic transformations.[6]

In blank reactions neither selenium dioxide nor benzeneseleninic acid proved to be an effective alternative reagent to the anhydride (1). The major by-product of the reaction was diphenyl diselenide which was easily separated and could be reoxidised to the anhydride.[7]

The mechanism for the regeneration of the ketone function from the various derivatives with the anhydride follows from the Scheme 1.

In support of these proposals we find that in one experiment nitrobenzene (95%) could also be isolated from the deprotection of cholesta-1,4-dien-3-one *p*-nitrophenylhydrazone. Also the fact that the *NN*-dimethylhydrazones and oxime *O*-methyl ethers are not oxidised under standard conditions supports Scheme 1. Additionally if the reactions were followed by i.r. spectroscopy under strictly anhydrous and oxygen-free conditions the formation of the ketone could be monitored. Clearly the oxygen atom of the final product is derived from the anhydride.

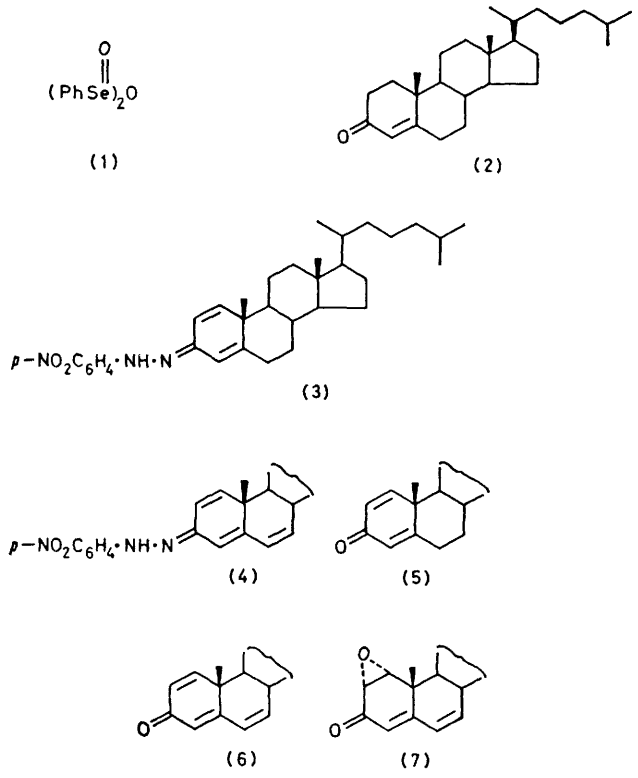
Finally, that initial reaction of the anhydride takes place on nitrogen to form a species which subsequently

TABLE 1

Conversion of ketone derivatives into the parent ketone with $(PhSeO)_2O$ [a]

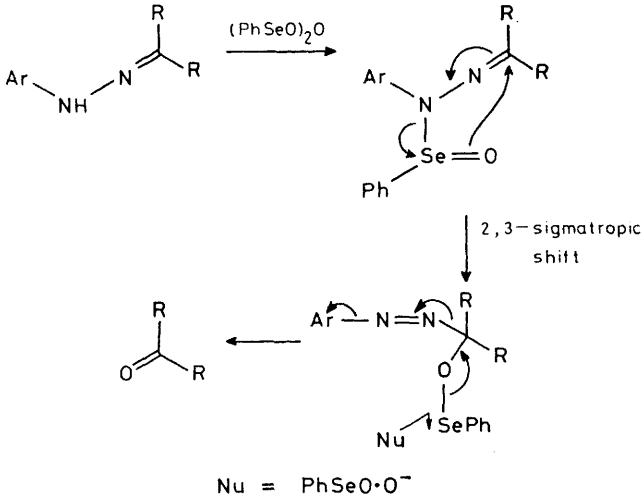
	Benzophenone		(2)		(3)		(4)		(5)	
Derivative	% Yield [b]	Time	% Yield	Time	% Yield	Time	% Yield	Time	% Yield	Time
Phenylhydrazone	90 (81)	3 h	64 (52)	10 h	57 (40)	10 h				
p-Nitrophenylhydrazone	56	3 d	95 (83)	10 h	57 (41)	40 h	81 (73)	18 h	96 (43) [c]	18 h
2,4-Dinitrophenylhydrazone	N.R.	3 d	25 (8)	24 h	3—5	40 h				
Tosylhydrazone	95 (89)	20 min	97 (87)	20 min	86 (24)	20 min				
Oxime	89 (76)	3 h	83 (60)	50 min	96 (80)	50 min				
Semicarbazone	89 (71)	2 h	83 (67)	4 h	85 (21)	4 h				
NN-Dimethylhydrazone	N.R.	23 h								
O-Methyl oxime	N.R.	24 h								

[a] 1 Molar equivalent. [b] Recrystallised yields in parentheses. [c] Isolated as the 1,2-α-epoxide.



undergoes 2,3-sigmatropic rearrangement is indicated by the fact that 2,6-dimethylphenyl analogue of benzophenone phenylhydrazone reacts some 10 times slower than the parent phenyl derivative. An alternative reaction scheme involving radicals can also be proposed but we have been unable to detect any radical species when the reaction was studied in an e.s.r. cavity.

In a similar manner we have also prepared a series of aldehydo-derivatives and studied their reactions with benzeneseleninic anhydride. However it was found that in addition to regeneration of the carbonyl group an alternative reaction could take place to give the novel formation of ketoazo-derivatives. The formation of



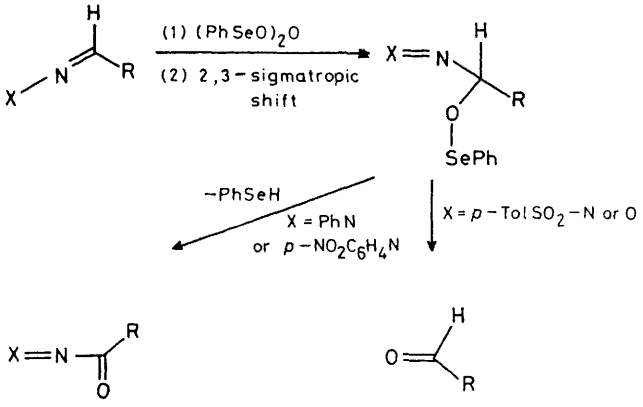
SCHEME 1

these latter compounds depended on the leaving-group ability of the initial derivative (Scheme 2). Good leaving groups gave back aldehyde, poor leaving groups fragmented to azocarbonyl compounds.

Thus in order to produce the parent aldehyde the oxime or the tosylhydrazone derivative should be chosen.

In order to extend the range of examples to non-aromatic substrates we have also studied the regeneration of the aldehyde group from isobutyraldehyde, cinnamaldehyde, crotonaldehyde, heptaldehyde, and valeraldehyde tosylhydrazones. In all cases a good yield of aldehyde was obtained using 1 equivalent of the anhydride at room temperature in tetrahydrofuran (THF).

Although ketoazo-compounds had been prepared previously by oxidation of the corresponding hydrazide with *N*-bromosuccinimide the yields were not always very



SCHEME 2

high.[8] It seemed attractive therefore to study the use of the anhydride (1) as an alternative oxidant. Indeed in a number of examples investigated the anhydride proved to be the superior reagent (Table 2).

This ready oxidation of hydrazides with BSA prompted a study of other nitrogenous substrates the obvious candidates being hydrazo-compounds, hydroxylamines, and hydrazines.

We find that both aromatic and aliphatic hydrazo-compounds can be converted into the corresponding azo-derivative rapidly and in high yield (Table 3). Similarly hydroxylamines can be oxidised with BSA to give nitroso-derivatives which are not oxidised further even in the presence of an excess of reagent.

Since *N*-phenyltriazolinedione is a commonly used dienophile and is usually prepared by oxidation of the corresponding hydrazide we have explored the possibility of its generation *in situ*. It was found that ergosterol acetate acted as an efficient trap [9] for the *in situ* generated *N*-phenyltriazolinedione which was derived from equimolar quantities of the hydrazide precursor and the anhydride.

Finally oxidation of *p*-nitrophenylhydrazine with BSA (1 equiv.) afforded a mixture of nitrobenzene (26%) and phenyl *p*-nitrophenyl selenide (63%). If an excess of

reagent was used the yields of the two changed to 72% and 16% respectively.

Some work on the oxidation of lactams [10] and of amines [11] by BSA has also been reported.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. ^{1}H N.m.r. spectra were obtained for solutions in $CDCl_3$ ($SiMe_4$ as internal standard) at 60 MHz. Thin-layer and preparative-layer chromatography were carried out on silica gel (Merck GF_{254} Typ 60). Light petroleum refers to the fraction b.p. 60—80 °C. Solutions were dried over magnesium or sodium sulphate and solvents by standard techniques. Benzeneseleninic anhydride (BSA) was prepared by a literature method.[7]

General Procedure for Reactions of Carbonyl Derivatives with Benzeneseleninic Anhydride.—To a solution of the carbonyl derivative in dry THF was added finely powdered BSA (1 mol equiv.). The mixture was stirred and warmed to 50 °C if necessary and followed to completion by t.l.c. Solvent was removed under reduced pressure and the residue separated by preparative-layer chromatography to afford the product.

Reactions giving Benzophenone as Product.—(*a*) Benzophenone phenylhydrazone (50 mg, 0.18 mmol) in THF (5 ml) with BSA (66 mg, 0.18 mmol) gave benzophenone (29.8 mg, 89.5%), m.p. 47—48 °C (from ethanol; 27.0 mg, 81%) (lit.,[12] 48 °C), identical with an authentic sample.

(*b*) Benzophenone *p*-nitrophenylhydrazone (50 mg, 0.16 mmol) in THF (5 ml) with BSA (58.9 mg, 0.16 mmol) gave benzophenone (16.1 mg, 56%), m.p. 45—47 °C.

(*c*) Benzophenone tosylhydrazone (50 mg, 0.14 mmol) in THF (5 ml) with BSA (51.5 mg, 0.14 mmol) gave benzophenone (24.7 mg, 95%), m.p. 47—48 °C (from ethanol; 23.1 mg, 89%).

(*d*) Benzophenone oxime (50 mg, 0.25 mmol) in THF (5 ml) with BSA (92 mg, 0.25 mmol) afforded benzophenone (41.0 mg, 89%), m.p. 47—48 °C (from ethanol; 35.0 mg, 76%).

(*e*) Benzophenone semicarbazone (50 mg, 0.21 mmol) in THF (5 ml) with BSA (75 mg, 0.21 mmol) afforded benzophenone (34 mg, 89%), m.p. 47—48 °C (from ethanol; 27.1 mg, 71%).

Preparation of Benzophenone 2,6-Dimethylphenylhydrazone.—To a solution of 2,6-dimethylphenylhydrazine hydrochloride (0.5 g, 3.2 mmol) and potassium acetate (0.3 g) in methanol (5 ml) containing water (1.8 ml) was added benzophenone (0.54 g, 0.30 mmol) and the mixture heated to reflux for 1 h under nitrogen. *Benzophenone 2,6-dimethylphenylhydrazone* (0.7 g, 79%) separated on cooling and crystallised from methanol as colourless needles, m.p. 113—114.5 °C, $\nu_{max.}$ 3 300, 1 580, 1 550, 1 480, 1 320, 1 270, 1 230, 1 120, 1 970, 1 030, 920, 780, and 720 cm^{-1}; δ 7.7—6.8 (13 H, m) and 2.3 (6 H, s) (Found: C, 83.65; H, 6.8; N, 9.3. $C_{21}H_{20}N_2$ requires C, 83.95; H, 6.7; N, 9.35%).

Reaction of Benzophenone 2,6-Dimethylphenylhydrazone with Benzeneseleninic Anhydride.—To a solution of benzophenone 2,6-dimethylphenylhydrazone (50 mg, 0.18 mmol) in dry THF (15 ml) was added BSA (60 mg, 0.17 mmol) and the solution stirred at 50 °C for 18 h under argon. Work up gave diphenyl diselenide (28.8 mg, 61%), recovered starting material (5 mg, 10%), and benzophenone (29.6 mg, 97%). All products were identical (m.p.) with authentic samples.

Reactions giving Cholestan-3-one as Product.—(*a*) Cholestanone phenylhydrazone (50 mg, 0.105 mmol) in THF (5 ml) with BSA (37.8 mg, 0.105 mmol) afforded cholestanone

TABLE 2

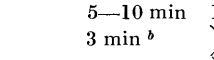
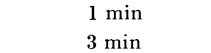
Reaction of aldehydo-derivatives with $(PhSeO)_2O$

Aldehyde	Derivative	Reaction conditions [a]	Product [b] Yield (%)	Yield of deriv. from hydrazide with (1) [c]	Yield of ketoazo deriv. from hydrazide with NBS
2-Furaldehyde	Phenylhydrazone	45 min	C_4H_3O-2-CON=NPh [d] 87	92	65
	p-Nitrophenylhydrazone	35 min	C_4H_3O-2-CON=$NC_6H_4NO_2$-*p* [d] 70 (64)	95 (86)	78 (64)
	Tosylhydrazone	2 h	2-Furaldehyde 88		
Benzaldehyde	Phenylhydrazone	1 h	PhCON=NPh 73 (67)	85	80
	p-Nitrophenylhydrazone	1 h	PhCON=$NC_6H_4NO_2$-*p* 76 (72)	99	79
2-Naphthaldehyde	Phenylhydrazone	30 min	$C_{10}H_7$-2-CON=NPh [e] 69 (49)	72	47
	p-Nitrophenylhydrazone	20 min	$C_{10}H_7$-2-CON=$NC_6H_4NO_2$-*p* [e] 90 (89)	89 (80)	70 (57)
	Tosylhydrazone	30 min	2-Naphthaldehyde 99 (87)		
	Oxime	20 min	2-Naphthaldehyde 94 (81)		
Isobutyraldehyde	Tosylhydrazone	45 min [f]	Isobutyraldehyde 71		
Cinnamaldehyde	Tosylhydrazone	40 min [f]	Cinnamaldehyde 91		
Crotonaldehyde	Tosylhydrazone	45 min [f]	Crotonaldehyde 68		
n-Heptaldehyde	Tosylhydrazone	30 min [f]	n-Heptaldehyde 89		
Valeraldehyde	Tosylhydrazone	30 min [f]	Valeraldehyde 92		

[a] 1 equiv. of BSA 40—50 °C in dry THF. [b] Recrystallised yield in parentheses. [c] 1 equiv. of BSA at 50 °C in dry THF. [d] C_4H_3O ≡ furyl. [e] $C_{10}H_7$ ≡ naphthyl. [f] At room temp.

TABLE 3

Oxidation of other nitrogenous compounds with $(PhSeO)_2O$ [a]

Starting material	Reaction conditions	Product	Yield (%)
PhNHNHPh	5—10 min	PhN=NPh	99
	3 min [b]		95
	1 min		96 [c]
PhNHOH	3 min	PhNO	89
4-Phenyl-1,2,4-triazolidine-3,5-dione	5—10 min	4-Phenyl-1,2,4-triazoline-3,5-dione	72 [d]

[a] Equivalent of BSA in dry THF at room temperature [b] Reaction carried out on neat starting material. [c] Estimated by u.v. spectroscopy. [d] Trapped as the ergosterol acetate adduct.

(25.9 mg, 64%), m.p. 127—129 °C (from ethanol; 21.1 mg, 52%) (lit.,[13] 128—129 °C).

(*b*) Cholestanone *p*-nitrophenylhydrazone (50 mg, 0.096 mmol) in THF (5 ml) with BSA (34.5 mg, 0.096 mmol) afforded cholestanone (35.2 mg, 95%), m.p. 128—130 °C (from ethanol; 30.8 mg, 83%).

(*c*) Cholestanone tosylhydrazone (50 mg, 0.090 mmol) in THF (5 ml) with BSA (32 mg, 0.090 mmol) afforded cholestanone (33.7 mg, 97%), m.p. 129—130 °C (from ethanol; 30.2 mg, 87%).

(*d*) Cholestanone oxime (50 mg, 0.125 mmol) in THF (5 ml) with BSA (45 mg, 0.125 mmol) afforded cholestanone (40 mg, 83%), m.p. 129—130 °C (from ethanol; 30 mg, 60%).

(*e*) Cholestanone semicarbazone (50 mg, 0.11 mmol) in THF (5 ml) with BSA (39.6 mg, 0.11 mmol) afforded cholestanone (34.5 mg, 83%), m.p. 127—129 °C (from ethanol; 27.9 mg, 67%).

Reactions giving Cholest-4-en-3-one as Product.—(*a*) Cholest-4-en-3-one phenylhydrazone (50 mg, 0.105 mmol) in THF (5 ml) with BSA (37.8 mg, 0.105 mmol) afforded cholest-4-en-3-one (23.0 mg, 57%), m.p. 77—79 °C (from ethanol; 16.1 mg, 40%) (lit.,[14] m.p. 78 °C).

(*b*) Cholest-4-en-3-one *p*-nitrophenylhydrazone (50 mg, 0.096 mmol) in THF (5 ml) with BSA (34.5 mg, 0.096 mmol) afforded cholest-4-en-3-one (20.8 mg, 56.5%), m.p. 77—79 °C (from ethanol; 14.4 mg, 41%).

(*c*) Cholest-4-en-3-one tosylhydrazone (50 mg, 0.091 mmol) in THF (5 ml) with BSA (33 mg, 0.091 mmol) afforded cholest-4-en-3-one (30.1 mg, 86%), m.p. 79—80 °C (from ethanol; 25.8 mg, 74%).

(*d*) Cholest-4-en-3-one oxime (50 mg, 0.125 mmol) in THF (5 ml) with BSA (45 mg, 0.125 mmol) afforded cholest-4-en-3-one (46.1 mg, 96%), m.p. 79—80 °C (from ethanol; 38.4 mg, 80%).

(*e*) Cholest-4-en-3-one semicarbazone (50 mg, 0.11 mmol) in THF (5 ml) with BSA (41 mg, 0.11 mmol) afforded cholest-4-en-3-one (36.7 mg, 85%), m.p. 77—79 °C (from ethanol; 30.8 mg, 71%).

Cholesta-1,4-dien-3-one from Cholesta-1,4-dien-3-one p-*Nitrophenylhydrazone.*—Cholesta-1,4-dien-3-one *p*-nitrophenylhydrazone (3.5 g, 6.77 mmol) in THF (25 ml) with BSA (2.45 g, 6.8 mmol) afforded diphenyl diselenide (1.0 g, 47%) and cholesta-1,4-dien-3-one (1.79 g, 73%), m.p. 109—111 °C (from methanol), $\lambda_{max.}$ 241 nm (ε 14 400) [lit.,[15] $\lambda_{max.}$ 245 nm (ε 14 500)]; $\nu_{max.}$ 1 670, 1 625, 1 605, 1 290, 1 240, 895, and 810 cm^{-1}; $[\alpha]_D^{23}$ +26.9° (*c* 1.0) (lit.,[15] $[\alpha]_D$ +28°).

Preparation of 1α,2α-Epoxycholesta-1,4,6-trien-3-one from Cholesta-1,4,6-trien-3-one p-*Nitrophenylhydrazone.*—Cholesta-1,4,6-trien-3-one *p*-nitrophenylhydrazone (100 mg, 0.19 mmol) in THF (10 ml) with BSA (70 mg, 0.19 mmol) was stirred at 40 °C in the dark for 18 h. P.l.c. afforded a brown oil (84 mg) R_F 0.04—0.30 which was subjected to further chromatography [alumina, benzene–ethyl acetate (95 : 5)] to afford an orange oil (71.3 mg) which crystallised on standing in methanol at 0 °C for 2 days to afford cholesta-1,4,6-trien-3-one (51.3 mg, 74%) m.p. 60—69 °C, homogeneous by t.l.c., u.v., and i.r. (lit.,[16] 82—83 °C); $\lambda_{max.}$ 226 (ε 12 700), 256 (9 700), and 302 nm (7 350) [lit.,[17] $\lambda_{max.}$ 224 (ε 10 700), 258 (8 300), and 300 nm (12 860)]. Cholesta-1,4,6-trien-3-one was dissolved in methanol (2.8 ml) and treated with methanolic sodium hydroxide (10%, 0.019 ml) and hydrogen peroxide (30%, 0.13 ml) and the solution allowed to stand at room temperature overnight. Cooling to −40 °C afforded a brown solid (50 mg, 68%), m.p. 85—97 °C. P.l.c. [benzene–ethyl acetate (95 : 5)] afforded 1α,2α-epoxycholesta-1,4,6-trien-3-one (31.1 mg, 43%), m.p. 104—106 °C (from methanol–acetone) (lit.,[18] 105–107 °C), $\lambda_{max.}$ 291 nm (ε 18 500) [lit., [18] $\lambda_{max.}$ 292 nm (ε 19 600)], $[\alpha]_D^{22}$ +195.9° (*c* 0.40) (lit.,[18] $[\alpha]_D$ +200°).

Reactions of Aldehyde Tosylhydrazones with Benzeneselenic Anhydride.—(*a*) 2-Furaldehyde tosylhydrazone (50 mg, 0.19 mmol) in THF (5 ml) with BSA (69 mg, 0.19 mmol) afforded 2-furaldehyde (16.0 mg, 88%), identical (i.r.) with an authentic sample.

(*b*) 2-Naphthaldehyde tosylhydrazone (50 mg, 0.15 mmol) in THF (5 ml) with BSA (52 mg, 0.14 mmol) afforded 2-naphthaldehyde (24.0 mg, 99%), m.p. 58—60 °C (from ethanol; 22.6 mg, 87%) (lit.,[19] 57—58 °C).

(*c*) Dry nitrogen was bubbled through isobutyraldehyde tosylhydrazone (0.5 g, 2.2 mmol) in diglyme (5 ml) and BSA (0.75 g, 2.1 mmol) at room temperature. The volatile products were condensed in a tube cooled to −78 °C using solid carbon dioxide–acetone. Isobutyraldehyde (101.4 mg, 71%), n_D^{23} 1.371 6 (authentic material n_D^{22} 1.372 1) was obtained as a colourless liquid, identical (n.m.r.) with an authentic sample.

(*d*) Cinnamaldehyde tosylhydrazone (100 mg, 033 mmol). in THF (1 ml) with BSA (120 mg, 0.33 mmol) afforded cinnamaldehyde (40 mg, 91%), identical (n.m.r. and i.r.) with authentic material.

(*e*) Crotonaldehyde tosylhydrazone (100 mg, 0.44 mmol) in THF (1 ml) with BSA (160 mg, 0.44 mmol) afforded crotonaldehyde (16.5 mg, 68%), identical (n.m.r.) with authentic material.

(*f*) Heptaldehyde tosylhydrazone (100 mg, 0.35 mmol) in THF (1 ml) with BSA (126 mg, 0.35 mmol) afforded heptaldehyde (35.5 mg, 89%), identical (i.r. and n.m.r.) with authentic material.

(*g*) Valeraldehyde tosylhydrazone (100 mg, 0.39 mmol) in THF (1 ml) with BSA (140 mg, 0.39 mmol) afforded valeraldehyde (31.6 mg, 92%), identical (n.m.r.) with authentic material.

Reactions of Aldehyde Phenylhydrazones with Benzeneseleninic Anhydride.—(*a*) Benzaldehyde phenylhydrazone (50 mg, 0.25 mmol) in THF (5 ml) with BSA (91 mg, 0.25 mmol) afforded benzoylazobenzene (39.0 mg, 73%), m.p. 28—29 °C (from ethanol at −78 °C; 35.7 mg, 67%) (lit.,[8] 29—30 °C), $\nu_{max.}$ 3 100, 1 705, 1 605, 1 590, 1 500, 1 450, 1 250, 1 000, 765, 730, and 700 cm^{-1}; $\lambda_{max.}^{EtOH}$ 441 (ε 120) and 286 nm (10 900); δ 5.6—6.2 (5 H, m) and 7.6—8.2 (5 H, m); M^+, 212 (M^+ + 2) [lit.,[8] m.p. 30 °C; $\lambda_{max.}^{EtOH}$ 443 (ε 121) and 288 (13 400)].

(*b*) 2-Naphthaldehyde phenylhydrazone (50 mg, 0.20 mmol) in THF (5 ml) with BSA (73 mg, 0.20 mmol) afforded 2-naphthoylazobenzene (36.5 mg, 69%), m.p. 53—56 °C (from ethanol at −78 °C; 25.5 mg, 49%), $\nu_{max.}$ 3 050, 1 700, 1 620, 1 600, 1 500, 1 180, 1 040, 830, and 700 cm^{-1}; $\lambda_{max.}^{CHCl_3}$ 492 (ε 96) and 288 nm (17 800); δ 7.2—8.6 (12 H, m); *m/e* 260 (M^+ + 2).

(*c*) 2-Furaldehyde phenylhydrazone (50 mg, 0.27 mmol) in THF (5 ml) with BSA (97 mg, 0.27 mmol) afforded 2-*furoylazobenzene* (46.8 mg, 87%) as a deep red oil, $\nu_{max.}$ 3 100, 1 700, 1 570, 1 510, 1 460, 1 400, 1 300, 1 150, 1 040, 780, and 700 cm^{-1}; $\lambda_{max.}^{CHCl_3}$ 494 (ε 134) and 301 nm (11 800); δ 7.2—7.5 (3 H, m) and 7.5—8.2 (5 H, m); M^+, 202 (M^+ + 2) (Found: C, 66.05; H, 4.0; N, 13.86. $C_{11}H_8N_2O_3$ requires C, 66.0; H, 4.05; N, 14.0%).

Reactions of Aldehyde p-*Nitrophenylhydrazones with Benzeneseleninic Anhydride.*—(*a*) Benzaldehyde *p*-nitro-

phenylhydrazone (50 mg, 0.21 mmol) in THF (5 ml) with BSA (78 mg, 0.21 mmol) afforded benzoylazo-*p*-nitrobenzene (40.2 mg, 76%), m.p. 99—100 °C (from ethanol, 38.1 mg, 72%), $\nu_{max.}$ 3 100, 1 705, 1 605, 1 580, 1 530, 1 505, 1 350, 1 260, 1 180, 1 110, 1 000, 880, 860, 760, 720, and 700 cm^{-1}; $\lambda_{max.}^{CHCl_3}$ 460 (ε 153) and 286 (23 800); δ 7.2—7.6 (4 H, m) and 7.8—8.5 (5 H, m); M^+, 257 ($M^+ + 2$) [lit.,[8] m.p. 99—100 °C; $\lambda_{max.}$ 458 (ε 141) and 284 nm (24 500)] (Found: C, 61.1; H, 3.6; N, 16.55. Calc. for $C_{13}H_9N_3O_3$: C, 61.2; H, 3.55; N, 16.45%).

(*b*) 2-Naphthaldehyde *p*-nitrophenylhydrazone (50 mg, 0.17 mmol) in THF (5 ml) with BSA (62 mg, 0.17 mmol) afforded 2-*naphthoylazo*-p-*nitrobenzene* (47.2 mg, 90%), m.p. 141—142 °C (from ethanol; 46.7 mg, 89%); $\nu_{max.}$ 3 050, 1 700, 1 630, 1 505, 1 520, 1 350, 1 260, 1 180, 1 010, 870, 780, and 700 cm^{-1}; $\lambda_{max.}^{CHCl_3}$, 498 (ε 160) and 286 nm (25 500); δ 7.2—8.4 (11 H, m); M^+, 307 ($M^+ + 2$) (Found: C, 66.9; H, 3.65; N, 13.7. $C_{17}H_{11}N_3O_3$ requires C, 66.9; H, 3.65; N, 13.75%).

(*c*) 2-Furaldehyde *p*-nitrophenylhydrazone (50 mg, 0.22 mmol) in THF (5 ml) with BSA (78 mg, 0.22 mmol) afforded 2-*furoylazo*-p-*nitrobenzene* (37.0 mg, 70%), m.p. 187—189 °C (from ethanol; 33.8 mg, 64%); $\nu_{max.}$ 3 100, 1 700, 1 610, 1 570, 1 400, 1 310, 1 110, 1 050, 1 010, 870, 780, and 700 cm^{-1}; $\lambda_{max.}^{CHCl_3}$ 466 (ε 190) and 287 nm (23 500); δ 4.5 (1 H, dd, *J* 5 and 3 Hz), 5.2—5.7 (2 H, m) and 5.8—6.4 (4 H, m); M^+ 245, ($M^+ + 2$) (Found: C, 53.75; H, 3.0; N, 17.05. $C_{11}H_7N_3O_4$ requires C, 53.9; H, 2.9; N, 17.15%).

2-*Naphthaldehyde from* 2-*Naphthaldehyde Oxime*.—2-Naphthaldehyde oxime (50 mg, 0.29 mmol) in THF (5 ml) with BSA (105 mg, 0.29 mmol) afforded 2-naphthaldehyde (42.8 mg, 94%), m.p. 59—60 °C (from ethanol; 36.8 mg, 81%).

Preparation of N′-*Phenylfurohydrazide*.—To a solution of phenylhydrazine (216 mg, 2 mmol) in ethanol (4 ml) containing pyridine (0.2 ml) was added furoyl chloride (260 mg, 2 mmol) and the solution heated to its boiling point. Water (2 ml) was added and the mixture allowed to crystallise to give N′-*phenylfurohydrazide* (350 mg, 86%), m.p. 142—145 °C (from ethanol–water), $\nu_{max.}$ 3 240 and 1 630 cm^{-1} (Found: C, 65.05; H, 4.95; N, 13.7. $C_{11}H_{10}N_2O_2$ requires C, 65.35; H, 5.0; N, 13.85%).

Preparation of N′-p-*Nitrophenylfurohydrazide*.—To a solution of *p*-nitrophenylhydrazine (153 mg, 1 mmol) in hot ethanol (2 ml) containing pyridine (0.1 ml) was added furoyl chloride (130 mg, 1 mmol). The reaction mixture was allowed to stand for 5 min at 50—60 °C then water (0.5 ml) was added to give, on cooling N′-p-*nitrophenylfurohydrazide* (170 mg, 69%), m.p. 179—180 °C (from ethanol–water), $\nu_{max.}$ 3 230 and 1 650 cm^{-1} (Found: C, 53.55; H, 3.7; N, 17.0. $C_{11}H_9N_3O_4$ requires C, 53.45; H, 3.65; N, 17.0%).

Preparation of N′-*Phenyl*-2-*naphthohydrazide*.—To a solution of phenylhydrazine (216 mg, 2 mmol) in ethanol (4 ml) containing pyridine (0.2 ml) was added 2-naphthoyl chloride (380 mg, 2 mmol) and the solution heated to reflux for 5 min. Water (0.5 ml) was added and the mixture allowed to crystallise to give N′-*phenyl*-2-*naphthohydrazide* (347 mg, 62%), m.p. 185—186 °C, $\nu_{max.}$ 3 200 and 1 650 cm^{-1} (Found: C, 77.85; H, 5.4; N, 10.65. $C_{17}H_{14}N_2O$ requires C, 77.85; H, 5.4; N, 10.7%).

Preparation of N′-p-*Nitrophenyl*-2-*naphthohydrazide*.—To a solution of *p*-nitrophenylhydrazine (153 mg, 1 mmol) in hot ethanol (2 ml) containing pyridine (0.1 ml) was added 2-naphthoyl chloride (190 mg, 1 mmol) and the solution heated to reflux for 5 min. Water (0.5 ml) was added and the mixture allowed to crystallise to give N′-p-*nitrophenyl*-2-*naphthohydrazide* (234 mg, 72%), m.p. 246—248 °C (from ethanol–water), $\nu_{max.}$ 3 200 and 1 630 cm^{-1} (Found: C, 65.9; H, 4.2; N, 13.5. $C_{17}H_{13}N_3O_3$ requires C, 66.45; H, 4.25; N, 13.65%).

Oxidation of Hydrazo-compounds with Benzeneseleninic Anhydride.—(*a*) N′-Phenylbenzohydrazide (50 mg, 0.25 mmol) in THF (1.5 ml) with BSA (90 mg, 0.25 mmol) for 10 min afforded benzoylazobenzene (42.5 mg, 85%) as an oil, identical (i.r., m.s., n.m.r.) with previous samples.

(*b*) N′-*p*-Nitrophenylbenzohydrazide (50 mg, 0.20 mmol) in THF (2 ml) with BSA (73 mg, 0.20 mmol) for 10 min afforded benzoylazo-*p*-nitrobenzene (49.5 mg, 99%), m.p. 98—99 °C (from ethanol), identical with previously prepared samples (t.l.c., m.p., and i.r.).

(*c*) N′-Phenylfurohydrazide (50 mg, 0.25 mmol) in THF (1.5 ml) with BSA (90 mg, 0.25 mmol) for 10 min afforded furoylazobenzene (46 mg, 92%) as an oil, identical (i.r., n.m.r., and m.s.) with previously prepared samples.

(*d*) N′-*p*-Nitrophenylfurohydrazide (50 mg, 0.20 mmol) in THF (1.5 ml) with BSA (73 mg, 0.20 mmol) for 10 min afforded 2-furoylazo-*p*-nitrobenzene (47.4 mg, 95%), m.p. 187—189 °C (from ethanol; 43.0 mg, 86%) identical with other previously prepared samples (t.l.c., i.r.) and diphenyl diselenide (17.4 mg, 27%), m.p. 61—63 °C (lit.,[20] 63 °C).

(*e*) N′-Phenylnaphthohydrazide (50 mg, 0.20 mmol) in THF (2 ml) with BSA (76 mg, 0.21 mmol) for 10 min afforded naphthoylazobenzene (36 mg, 72%) as an oil, identical (i.r., n.m.r., and m.s.) with previously prepared samples.

(*f*) N′-*p*-Nitrophenylnaphthohydrazide (50 mg, 0.16 mmol) in THF (2 ml) with BSA (64 mg, 0.19 mmol) for 10 min afforded naphthoylazo-*p*-nitrobenzene (44.5 mg, 89%), m.p. 141—142 °C (from ethanol; 40 mg, 80%), identical with previously prepared samples (m.p., t.l.c., and i.r.).

(*g*) Hydrazobenzene (92 mg, 0.50 mmol) in dry THF (2 ml) with BSA (180 mg, 0.50 mmol) afforded azobenzene [21,22] (91 mg, 99%).

Oxidation of Hydroxylamines with Benzeneseleninic Anhydride.—(*a*) Phenylhydroxylamine (109 mg, 1 mmol in THF (5 ml) with BSA (360 mg, 1 mmol) afforded diphenyl diselenide (85.9 mg, 28%), m.p. 61—63 °C and nitrosobenzene [22,23] (98.1 mg, 91%), m.p. 65—67 °C.

(*b*) t-Butylhydroxylamine (38.4 mg, 0.431 mmol) in THF (1 ml) was mixed with BSA (200 mg, 0.556 mmol) in THF (7 ml) and the solution made up to exactly 10.0 ml with THF. The transmission of the solution at 685 nm was measured and the yield of 2-methyl-2-nitrosopropane (96%) estimated from the calculated extinction coefficient.

Preparation of 4-*Phenyl*-1,2,4-*triazoline*-3,5-*dione and Trapping with Ergosterol Acetate*.—To a solution of 4-phenyl-1,2,4-triazolidine-3,5-dione (50 mg, 0.28 mmol) in THF (2 ml) containing ergosterol acetate (112 mg, 0.25 mmol) was added BSA (180 mg, 0.5 mmol) and the suspension stirred at room temperature until a deep red colour developed (3—4 min). P.l.c. [methylene chloride–light petroleum (50 : 50)] afforded the adduct (120.1 mg, 78%), m.p. 172—174 °C (from ethanol; 111 mg, 72%) (lit.,[9] 173—175 °C), $[\alpha]_D^{22}$ −114° (*c* 1.0) {lit.,[9] $[\alpha]_D$ −118° (*c* 0.98)}; δ 7.25 (5 H, m), 6.2 (2 H, m), and 5.1 (2 H, m).

p-*Nitrophenylhydrazine with Benzeneseleninic Anhydride*.—To *p*-Nitrophenylhydrazine (153 mg, 1 mmol) in THF (5 ml) at 0 °C was added BSA (360 mg, 1 mmol) and the suspension stirred with cooling for 20 min. P.l.c. afforded

(*a*) diphenyl diselenide (90.1 mg, 32%), m.p. 61—63 °C (*b*) nitrobenzene (32.8 mg, 27%), identical (i.r. and u.v.) with authentic material, and (*c*) phenyl *p*-nitrophenyl selenide (113 mg, 63%), m.p. 57—58.5 °C (from methylene chloride–light petroleum) (lit.,[24] 58 °C), $\lambda_{max.}$ (ε 3 800) and 346 nm (100) [lit.,[25] $\lambda_{max.}$ 275 (ε 3 980) and 340 nm (1 000)]; δ 8.1—7.1 (m); *m/e* 279.

p-*Nitrophenylhydrazine with an Excess of Benzeneseleninic Anhydride*.—*p*-Nitrophenylhydrazine (76 mg, 0.50 mmol) in THF (5 ml) was added to a stirred suspension of BSA (350 mg, 1 mmol) in THF (2 ml) at room temperature during 40 min. P.l.c. afforded (*a*) diphenyl diselenide (69.5 mg, 22%), m.p. 61—63 °C, (*b*) nitrobenzene (44.7 mg, 72%), $\lambda_{max.}$ 260 nm (ε 8 000) [lit.,[26] $\lambda_{max.}$ 260 nm (ε 8 100)], and (*c*) phenyl *p*-nitrophenyl selenide (22.5 mg, 16%), m.p. 57—58.5 °C (from methylene chloride–light petroleum), identical with previously prepared samples.

We thank the Beit Trust for a Fellowship (to D. J. L.) and Dr. N. J. Cussans for the e.s.r. experiment.

[9/863 *Received*, 5*th June*, 1979]

REFERENCES

[1] (*a*) I. Bhatnagar and M. V. George, *J. Org. Chem.*, 1967, **32**, 2252; (*b*) T. L. Ho and C. M. Wong, *ibid.*, 1974, **39**, 3453; (*c*) G. Rosini, *ibid.*, 1974, **39**, 3504; (*d*) S. R. Maynez, L. Pelavin, and G. Erker, *ibid.*, 1975, **40**, 3302; (*e*) B. P. Chandrasekhar, S. V. Sunthankar, and S. Q. Telang, *Chem. and Ind.*, 1975, 87; (*f*) C. E. Sacks and P. L. Fuchs, *Synthesis*, 1976, 456; (*g*) T. L Ho and G. A. Olah, *Synthesis*, 1976, 611; (*h*) G. A. Olah, J. Welch, G. K. S. Prakash, and T. L. Ho, *Synthesis*, 1976, 808; (*i*) G. A. Olah and J. Welch, *Synthesis*, 1976, 809 and references therein.

[2] (*a*) C. H. Depuy and B. W. Ponder, *J. Amer. Chem. Soc.*, 1959, **81**, 4629; (*b*) H. Alper and J. T. Edward, *J. Org. Chem.*, 1967, **32**, 2938; (*c*) J. W. Bird and D. G. M. Diaper, *Canad. J. Chem.*, 1969, **47**, 145 and references therein; (*d*) S. H. Pines, J. M. Chemerda, and M. A. Kozlowski, *J. Org. Chem.*, 1966, **31**, 3446; (*e*) E. J. Corey and J. E. Richman, *J. Amer. Chem. Soc.*, 1970, **92**, 5276; (*f*) G. H. Timms and E. Wildsmith, *Tetrahedron Letters*, 1971, 195; (*g*) J. K. Sugden, *Chem. and Ind.*, 1972, 680; (*h*) A. McKillop, J. D. Hunt, R. D. Naylor, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1971, **93**, 4918; (*i*) G. A. Olah and T. L. Ho, *Synthesis*, 1976, 610.

[3] (*a*) C. H. Gleason and G. W. Holden, *J. Amer. Chem. Soc.*, 1950, **72**, 1751; (*b*) E. P. Oliveto, H. L. Herzog, L. Weber, M. E. Tully, and E. B. Hershberg, *J. Org. Chem.*, 1956, **21**, 795; (*c*) H. L. Herzog, C. C. Payne, M. A. Jevnik, D. Gould, E. L. Shapiro, E. P. Oliveto, and E. B. Hershberg, *J. Amer. Chem. Soc.*, 1955, **77**, 4781; (*d*) P. A. Diassi, J. Fried, R. M. Palmere, and E. F. Sabo, *J. Amer. Chem. Soc.*, 1961, **83**, 4249.

[4] Preliminary communications: D. H. R. Barton, D. J. Lester, and S. V. Ley, *J.C.S. Chem. Comm.*, 1977, 445; 1978, 276.

[5] D. H. R. Barton, J. C. Coll, J. F. McGarrity, and D. A. Widdowson, *J.C.S. Perkin I*, 1973, 1565.

[6] D. H. R. Barton, R. H. Hesse, M. M. Pechet, and E. Rizzardo, *J. Amer. Chem. Soc.*, 1973, **95**, 2748.

[7] D. H. R. Barton, S. V. Ley, P. D. Magnus, and M. N. Rosenfeld, *J.C.S. Perkin I*, 1977, 567.

[8] H. Boch, *Ber.*, 1966, **99**, 3337.

[9] D. H. R. Barton, T. Shiori, and D. A. Widdowson, *J.C.S. Chem. Comm.*, 1970, 939.

[10] T. G. Back, *J.C.S. Chem. Comm.*, 1978, 278.

[11] M. R. Czarney, *J.C.S. Chem. Comm.*, 1976, 81.

[12] C. S. Marvel and W. M. Sperry, *Org. Synth.*, Coll. Vol. 1, 1948, p. 95.

[13] R. Willstätter and E. W. Mayer, *Ber.*, 1908, **41**, 2199.

[14] O. Diels and E. Abderhalden, *Ber.*, 1904, **37**, 3092.

[15] L. F. Fieser and M. Fieser, ' Steroids,' Reinhold, New York, 1951, p. 28.

[16] C. Djerassi, G. Rosenkranz, J. Romo, St. Kaufmann, and J. Pataki, *J. Amer. Chem. Soc.*, 1950, **72**, 4534.

[17] M. Fiser, M. A. Romero, and L. F. Fieser, *J. Amer. Chem. Soc.*, 1955, **77**, 3305.

[18] B. Pelc and E. Kodicek, *J. Chem. Soc.* (*C*), 1971, 1568.

[19] J. W. Williams, *Org. Synth.*, Coll. Vol. **3**, 1955, p. 626.

[20] K. Krafft and R. E. Lyons, *Ber.*, 1894, **27**, 1761.

[21] R. J. W. LeFèvre and C. V. Worth, *J. Chem. Soc.* 1951 1814.

[22] H. E. Ungenade, ' Organic Electronic Spectral Data,' Wiley, London, 1967, p. 457.

[23] G. H. Coleman, C. M. McCloskey, and F. A. Stuart, *Org. Synth.*, Coll. Vol. **3**, 1955, p. 668.

[24] L. Chierici and R. Passerini, *Boll. Sci. Fac. Chim. Bologna*, 1954, **12**, 56.

[25] Ref. 22, p. 293.

[26] Ref. 22. p. 53.