Unusual Base-induced Ring-opening Reactions of the Bis-tosylhydrazones of Dibenzobicyclo[2.2.2]octadiene-2,3-dione and Acenaphthenequinone

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Summary Unusual KOH-induced ring-opening reactions of the bis-tosylhydrazones of dibenzobicyclo[2.2.2]octadiene-2,3-dione and acenaphthenequinone are described.

For our work on strained cycloalkynes, we needed the triazoles (**1**) and (**2**) as precursors of dibenzobarrelyne and acenaphthyne. It has been well documented that treatment of the bis-hydrazones of α-diketones by base or acid gives 1-(*p*-tolylsulphonylamino)triazoles in good yields,[1,2] and so we treated the bis-tosylhydrazones, (**4**) and (**13**),† with potassium hydroxide in the expectation of obtaining (**1**) and (**2**). We report the anomalous ring opening reactions of (**4**) and (**13**).

Heating (**4**) with an excess of potassium hydroxide at 110 °C in ethylene glycol evolved nitrogen gas vigorously. Work-up of the mixture gave the anthracenes, (**10**) (51%) and (**11**) (10%), unexpectedly, along with a good yield of toluene-*p*-sulphinic acid.‡[3] Diazomethanes like (**5**) have previously been assumed to be the intermediates for sulphoamidotriazoles. In the present case, it seems that the sulphoamidotriazole from (**5**) loses potassium toluene-*p*-sulphinate to give the nitrene intermediate, which undergoes a ring-opening reaction yielding the bis-diazomethane (**6**). Another possible way to (**6**) may involve the direct loss of potassium toluene-*p*-sulphinate from (**5**). Compound (**6**) may then cyclise to (**7**), which eliminates nitrogen with concurrent C–C bond cleavage yielding (**9**). Compound (**9**) must undergo dehydrocyanation and dehydrogenation to give (**10**) and (**11**).

Since oxidation of hydrazones by lead tetra-acetate gives diazomethanes,[4] the oxidation of the bis-hydrazone (**8**)† by lead tetraacetate was attempted in order to generate (**6**). The oxidation proceeded quickly in methylene chloride at room temperature but gave (**10**) and (**11**) in poor yields. Thus, although the major product of this reaction is the diacetate (**12**),[5] the result suggests the formation of (**10**) and (**11**) from (**6**).

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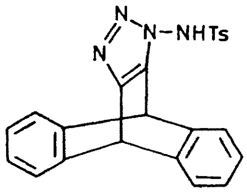
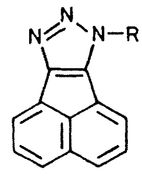
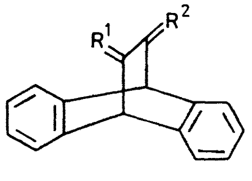
† Satisfactory analytical and spectroscopic data were obtained for all new compounds.

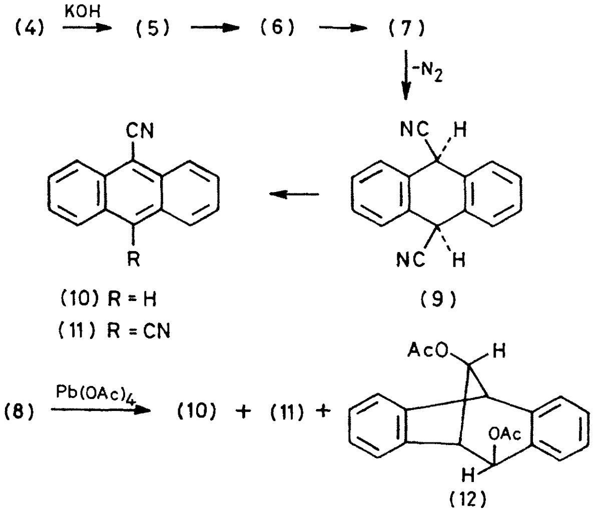
‡ Yields based on isolated materials.


(1)


(2) R = NHTs
(3) R = $\ddot{N}$:


(4) R^1=R^2=N–NHTs
(5) R^1=N_2, R^2=N–N(K)Ts
(6) R^1=R^2=N_2
(7) R^1, R^2=N–N=N–N
(8) R^1=R^2=N–NH_2

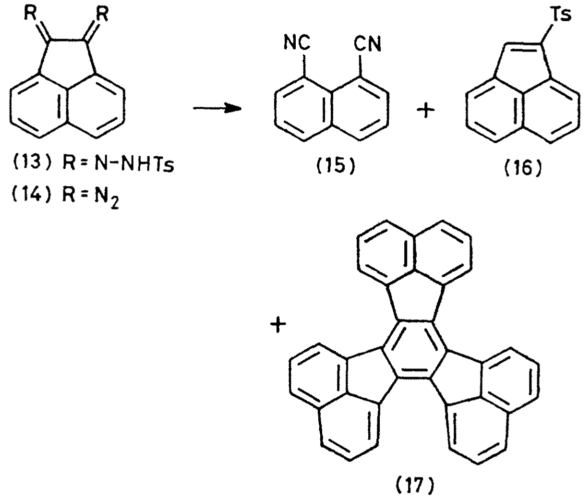
Ts = $O_2SC_6H_4Me$-*p*

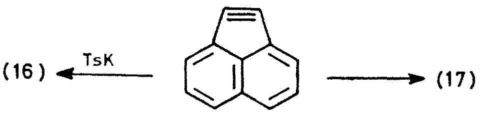

$(4) \xrightarrow{KOH} (5) \longrightarrow (6) \longrightarrow (7) \xrightarrow{-N_2} (9) \longrightarrow (10)$

(10) R = H
(11) R = CN
(9)

$(8) \xrightarrow{Pb(OAc)_4} (10) + (11) + (12)$

(12)


(13) R = N-NHTs
(14) R = N_2
(15)
(16)
(17)


$(16) \xleftarrow{TsK}$ $\longrightarrow (17)$

Heating (13) with potassium hydroxide at 100 °C in ethylene glycol also evolved nitrogen and afforded (15) (39%), (16)† (4%), and (17) [11%, m p 385 °C (lit[6] m p 387 °C)] together with some other products in low yields ‡§ The formation of (16) can be explained by a mechanism similar to that described for the formation of (10) and (11) The formation of (16) and (17) suggests the generation of acenaphthyne, possibly by loss of two molecules of nitrogen from (3) or (14)[7]

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§ Heating (13) in boiling acetic acid gave (16) (m p 167—168 °C) as the major product

[1] T L Gilchrist and G E Gymer, *Adv Heterocycl Chem* , 1974, **16**, 33, and references cited therein

[2] The only exception is the formation of diphenylacetylene from the bis-hydrazone of benzil W R Bamford and T S Stevens, *J Chem Soc* , 1952, 4735

[3] Another abnormal reaction encountered for the attempted construction of the five-membered ring fused to this ring system is the quantitative formation of dibenzobicyclo[2 2 2]octadien 2 one from its semicarbazone by oxidation with selenium dioxide, conditions under which semicarbazones usually give good yields of selenadiazoles I Lalezari, A Shafiee, and M Yalpani, *J Org Chem* , 1971, **36**, 2836

[4] E Ciganek, *J Org Chem* , 1965, **30**, 4198, D M Gale, W J Middleton, and C G Krespan, *J Am Chem Soc* , 1965, **87**, 657

[5] S G Cristol, F P Parungo, D E Plorde, and K Schwarzenbach, *J Am Chem Soc* , 1965, **87**, 2870

[6] K Dziewonski, *Ber* , 1903, **36**, 962

[7] If this is the case, the reaction corresponds to the formation of diphenylacetylene from the bis-tosylhydrazone of benzil (ref 2) The generation of acenaphthyne from 1-diazoacenaphthen-2-one was postulated J I G Cadogan, R J Scott, and N H Wilson, *J Chem Soc , Chem Commun* , 1974, 902 Attempts to generate acenaphthyne by conventional methods were unsuccessful K Rasheed, *Tetrahedron*, 1966, **22**, 2957

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