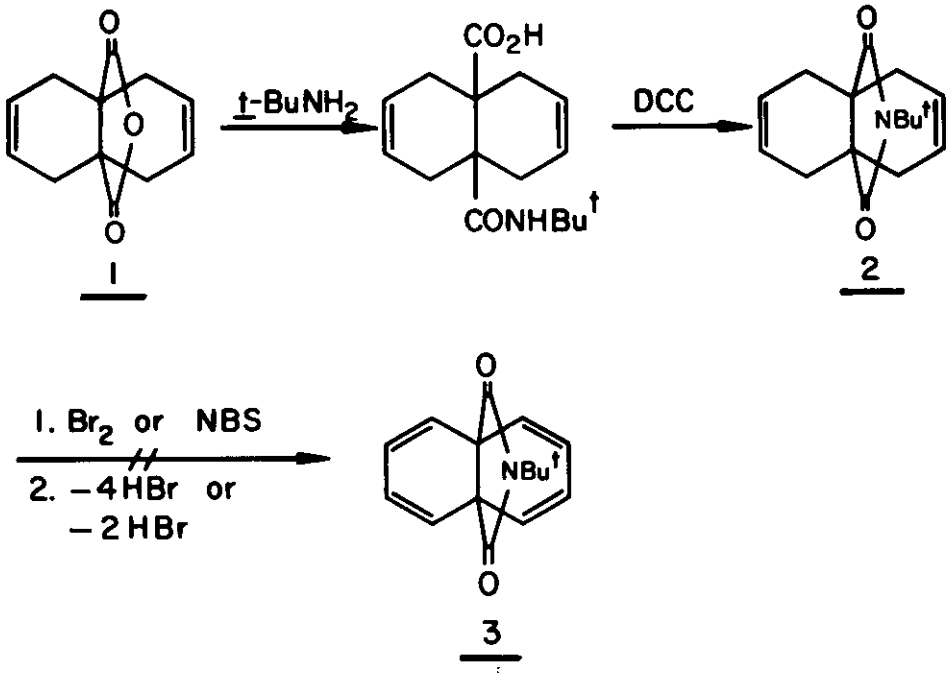
PROPELLANES. LVIII. ATTEMPTED PREPARATION OF 11,13-DIOXO-12-t-BUTYL-12-AZA[4.4.3]-PROPELLA-2,4,7,9-TETRAENE.†

Michael Peled, Jacob Kalo and David Ginsburg*

Department of Chemistry, Israel Institute of Technology, Haifa, Israel

The title compound could not be prepared via intermediates having a dienic oxidation state nor via those with four double bonds as the latter rearrange during reaction.

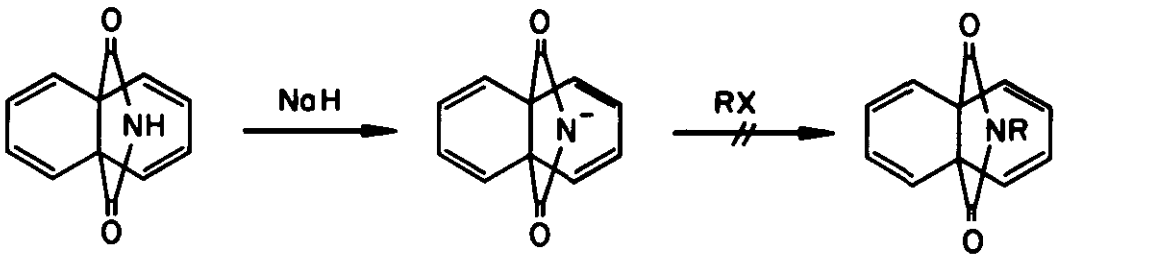
Although it was possible to obtain a t-butylimide 2 from the anhydride 1 and to effect bromination of 2 with either bromine or NBS, it was not possible to find a base effective for dehydrobromination to the tetraenic oxidation state, 3.[1]



† Dedicated to Professor Tetsuji Kametani on the occasion of his retirement.

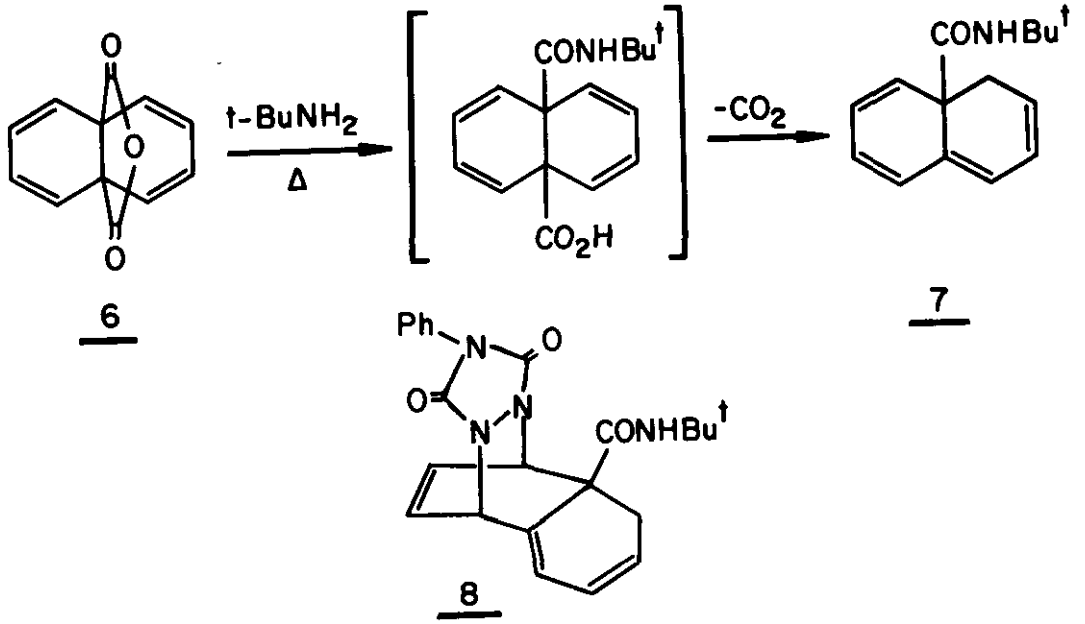
Part LVII. M. Peled and D. Ginsburg, Tetrahedron, in press.

Attempted N-alkylation of 4 using NaH which afforded an equivalent amount of H_2 was unsuccessful when t-BuCl or t-BuBr was used. Ethyl chloroformate or bromoformate and the corresponding benzyl halides also failed to alkylate the imide nitrogen atom. Although 5, R=Me is readily prepared by



4 5 R = t-Bu(≡3), $PhCH_2$, CO_2Et

CH_2N_2 alkylation of 4, analogous treatment of 4 with diazoneopentane was unsuccessful. Alkylation of 4 with isobutene under acidic conditions also failed. Although we usually beware of reacting 6 (due to the tetraenic oxidation state) with amines since such substrates are known to be thermally rearrangement-prone,[2] we turned to such a reaction. But when 6 was heated with t-butylamine although evidently such full-fledged rearrangement did not occur, yet a product was obtained reminiscent of this (scheme 1). The structure 7 was assigned to the product, on the



6 7 8

Scheme 1

basis of spectroscopic evidence. 4-Phenyl-1,2,4-triazoline-3,5-dione (PTD) gave a mono-Diels-Alder product of unproved structure but believed to be 8 rather than the alternative one where addition would have taken place to the conjugated dienic system in the other ring, again on the basis of nmr-evidence.

Experimental

Preparation of 2. - a) A mixture of 1 (900 mg) with water (5 ml) and t-butylamine (5 ml) was heated under reflux for 3 hr. After removal of solvents at the water pump, water (5 ml) was added to the solid residue, 20% HCl (3 ml) was added and the whole was extracted with chloroform (4 x 10 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent was removed. The crude product was crystallized affording the monoacid-monoamide (777 mg; 57%), m.p. 155-156° (hexane). IR($CHCl_3$): 3660, 3500, 3380, 2960, 2900, 1700, 1650, 1580, 1450, 1390, 1360, 1280, 990 cm^{-1}. NMR($CDCl_3$): τ 1.40 (br 5, 1 $CO_2\underline{H}$); 4.30 (s, 4 vinylic H); 7.20-8.00 (br, 8 allylic H), 8.67 (s, 9H, $C(\underline{CH_3})_3$).

b) To a solution of the above acid-amide (554 mg) in THF (15 ml) was added DCC (550 mg) and the whole was stirred magnetically at room temp overnight. AcOH (1 ml) was added and the whole was stirred for 20 min. Some solid was removed by filtration and the solvent was removed from the filtrate at the water pump. The residue was taken up in hexane and some solid was removed by filtration. Purification by column chromatography on neutral alumina (60 g) using EtOAc (1): hexane (9) as eluant gave 2 (250 mg; 50%), m.p. 95-96° (hexane). (Found: N, 5.46. $C_{16}H_{21}NO_2$ requires N, 5.40%). IR($CHCl_3$): 2920, 2820, 1760, 1680, 1450, 1360, 1330, 1310, 1120 cm^{-1}. NMR($CDCl_3$): τ 4.10 (t, 4 vinylic H, J=6 Hz); 7.24-8.10 (m, 8 allylic H); 8.50 (s, 9H, $C(\underline{CH_3})_3$).

Reaction of 6 with t-butylamine. - To a solution of 6 (524 mg) in dry benzene (10 ml) was added t-butylamine (2 ml). The reaction is exothermic and CO_2 is evolved. After 30 min the mixture was filtered and the solvent was removed. Chromatography afforded 7 (411 mg; 68%), m.p. 69-71° (hexane). It is unstable and eventually decomposes at room temp. (Found: M.W. 229.1450. $C_{15}H_{19}NO$ requires M.W. 229.1466). IR(KBr): 3320, 3000, 1660, 1530, 1390, 1360 cm^{-1}. NMR($CDCl_3$): τ 3.5-4.3 (m, 7 vinylic H); 7.05 (m, 2 allylic H); 8.73 (s, 9H, $C(\underline{CH_3})_3$). Irrad at 3.5-4.3 converts the 7.05 multiplet into a singlet. C^{13}-NMR: 28.8 (allylic C); 29.3, $C(\underline{CH_3})_3$; 51.8, 52.2 ($\underline{C}(CH_3)_3$, $\underline{C}O$); 120-144 (8 olefinic C); 171.6 ($\underline{C}ONH$). UV (CH_3CN): λ_{max}, 310 nm (4540). MS: M^+, 229(11); 173(9); 172(3); 149(14); 130(83); 129(100); 128(100).

Reaction of 7 with PTD. - A solution of 7 (410 mg) in CH_2Cl_2 (10 ml) reacted with PTD in excess. After stirring for 30 min at room temp the solvent was removed and the unstable mono-adduct 8 obtained (360 mg; 50%). Sublimation was unsuccessful. (Found: M.W. 404.1851. $C_{23}H_{24}N_4O_3$ requires M.W. 404.1888). IR(KBr): 2950, 1780, 1730, 1670, 1500, 1450 cm^{-1}. NMR($CDCl_3$): τ 2.5

(s, 5 arom H); 3.0-4.7 (m, 2 CHN and 5 vinylic H); 7.1 (m, 2 allylic H); 8.8 (s, 9 $C(CH_3)_3$).

MS: M^+, 404(11); 177(8); 130(11); 129(40); 128(92); 127(13); 119(9).

Structures were assigned on the basis of double resonance experiments.

References

1. J. Kalo and D. Ginsburg, unpublished results.

2. Cf. W. Meckel, Inaugural Dissertation, Köln, 1965.

Received, 9th June, 1980