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# PHENYL MIGRATION IN BICYCLO[5.3.1]UNDECA-1,3,5,8-TETRAENE-8-CARBOXY-N-METHYLANILIDE

## A UNIQUE TRUCE-SMILES TYPE REARRANGEMENT OF AN ANILIDE

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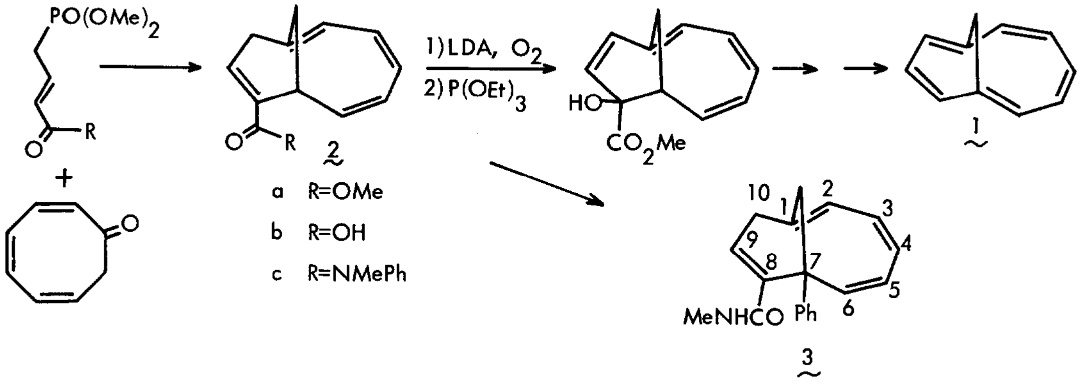
Abstract An unprecedented Truce-Smiles type rearrangement was observed when the dihydro-1,5-methano[10]annulenecarboxy anilide was treated with LDA.

Although loss of aromaticity in 1,5-methano[10]annulene (1) as a result of large distortion of $\pi$-electron system due to the strain in $\sigma$-system has been predicted1), the successful syntheses of 1 and its derivatives by Masamune2) and Scott3) have disclosed the presence of sizable diamagnetic ring current in the peripheral system of 1. In order to facilitate further studies on this interesting molecule, X-ray crystallographic analysis was attempted. However, during preparation of crystalline derivatives suitable for the analysis, we found a unique molecular rearrangement of the Truce-Smiles type occurring with a simple anilide.

1,5-Methano[10]annulene-8-carboxylic acid derivatives were aimed following the Masamune's route2). While several acid derivatives (2) of the dihydroannulene were obtained either from the methylester 2a2) via the carboxylic acid 2b or by the condensation of cyclooctatrienone with 4-(dimethylphosphinyl)-2-butenoic acid derivatives, the next step, aerial oxidation under basic condition, proceeded in the reported direction only with the methyl ester 2a2).



When the corresponding N-methylanilide 2c4) was subjected to the oxidation (LDA/THF, $O_2$ bubbling at -70°C), an isomer 3 was obtained in 75% yield instead of the oxidation product. While PMR spectrum of 3 indicated the presence of MeNHCO (2.58 ppm, 3H, d, J=4.8, singlet after treatment with $D_2O$, and 5.53 ppm, 1H, br.s, exchangeable with $D_2O$) and the absence of the methine signal

(3.82 ppm, 1H br.m for 2c), implying the location of phenyl group at $C_7$. The structure was established by X-ray crystallographic analysis[5] as shown in Fig.

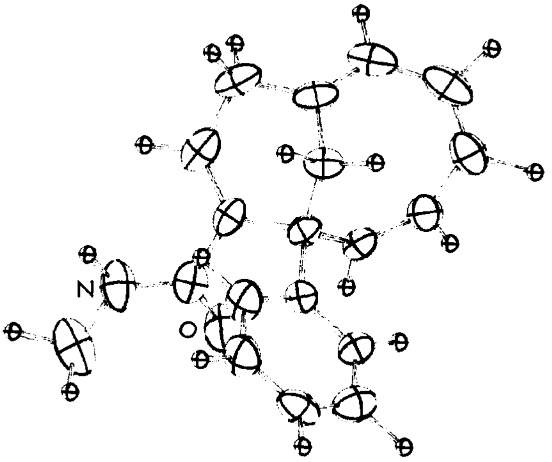
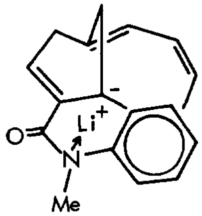


Fig. ORTEP diagram of 3 with 50% probability level of nonhydrogen atoms.

The reaction is the unprecedented Truce-Smiles rearrangement[6] occurring in anilide; the intramolecular nucleophilic attack of a carbanion on ipso position of an anilide. Furthermore, it is remarkable in that the reaction involves a bulky tertiary carbanion and a phenyl group without any additional activating group[7]. The coordination of Li with N[8] may be responsible for LDA to attack the sterically hindered bridge head hydrogen, and to localize negative charge in the resulted double allylic carbanion. Thus the geometry of the transition state can be depicted as shown.



## References and Notes

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4) All compounds reported were homogeneous by TLC and showed PMR, IR and mass spectra consistent with the assigned structures. 2c: colorless needles, m.p. 52-54°C, Mass m/e 277 ($M^+$), 128 (b.p.); IR (KBr) 2980, 2915, 2855, 1641, 1619, 1597, 1500, 1367, 757, 692 $cm^{-1}$; PMR ($CDCl_3$) 1.59 (1H, dd, 11.3, 4.5), 2.37 (1H, dd, 18.0, 4.5), 2.73 (1H, dm, 11.3), 2.75 (1H, dm, 18.0), 3.32 (3H, s), 3.82 (1H, br.m), 5.6-6.1 (6H, m), 6.9-7.35 (5H, m). 3: colorless prisms, m.p. 168-169°C, Mass m/e 277 ($M^+$), 58 (b.p.); IR (KBr) 3430, 3000, 2920, 2885, 1645, 1520, 734, 698 $cm^{-1}$; PMR ($CDCl_3$) 1.92 (1H, dd, 12.0, 2.0), 2.58 (3H, d, 4.8), 2.84 (1H, d, 12.0), 2.88 (1H, dd, 18.0, 4.5), 3.15 (1H, br.d, 18.0), 5.53 (1H, br.s), 5.9-6.2 (4H, m), 6.50 (1H, dm, 12.8), 7.03 (1H, dd, 4.5, 2.4), 7.15-7.35 (5H, m).

5) 3 crystallizes in the monoclinic space group $P2_1/c$ with cell constants a=15.449(4), b=8.234(2), c=12.729(4) Å, β=113.49(3)°, z=4. The structure was solved by MULTAN78 and refined by block-diagonal least square method. Anisotropic temperature factors were given for all nonhydrogen atoms to yield, after introduction of the hydrogen atoms, R=0.078. Final crystallographic coordinates and the structure factor table have been deposited in the Cambridge Crystallographic Data Center.

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