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BIS(2-THIENYL)ETHYLENE GIVES [4 + 2] CYCLOADDUCTS BY RADICAL ION PAIRS

Teresa Varea, Belén Abarca, Rafael Ballesteros, and Gregorio Asensio*

Departamento de Química Orgánica. Facultad de Farmacia. Universidad de Valencia.
Avda. Blasco Ibáñez, 13. 46010-Valencia, Spain

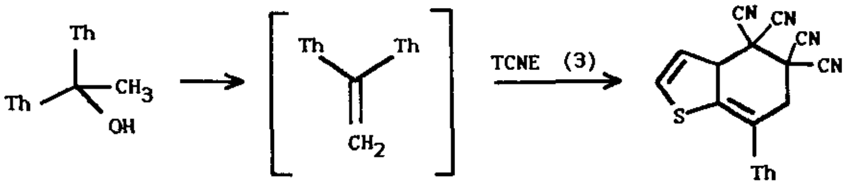
Abstract- 1,1-Bis(2-thienyl)ethanol reacts at room temperature in the absence of light with electron-deficient alkenes such as TCNE or DDQ to give quantitatively [4 + 2] cycloadducts derived from 1,1-bis(2-thienyl)ethylene. The process was monitored by esr and it is shown that it is the first example of a cycloaddition involving a heterocyclic ring that occurs through the formation of intermediate radical ion pairs. Fragmentation of the DDQ adduct constitutes a straightforward new route to the 4,5-dicyanobenzo[b]thiophene skeleton.

The Diels-Alder reaction is a [4 + 2] cycloaddition, a thermally allowed, six electron process. The substitution pattern on the reacting diene and dienophile as well as the reaction conditions modifies the course of the reaction in the sense of proceeding in a concerted fashion[1] or stepwise *via* biradicals[2] or zwitterionic[3] intermediates. On the other hand, the initial formation of diene-dienophile electron donor-acceptor (EDA) complexes was first suggested to be important in the context of cycloadditions between arenes and dienophiles.[4] The photochemical promotion of cycloaddition reactions, both [4 + 2] as well as [2 + 2] are known. The violation of the Woodward-Hoffmann rules for such a [4s + 2s] stereoselective photochemical process has been explained by considering the direct involvement of the CT excited state of the EDA complex.

Tetracyanoethylene (TCNE) is a strong electron acceptor which gives typical cycloaddition reactions with π-electron donors[5] as well as the EDA complex formation.[6] The dipole moment of the transition state in the thermal cycloaddition of α-methylstyrene or 1,1-diphenylethylene to TCNE is assumed to be larger than either that of the corresponding EDA complex or cycloadduct.[7] This is due, in some extent, to the contribution of a zwitterionic structure.[8] To our knowledge, the involvement of radical ion pairs as intermediates[9] in Diels Alder reactions has been ascertained only in one instance when studying the reaction of *trans*-2,3-bis(dimethylaminomethylene)norbornane, a high-lying HOMO diene, with TCNE, a low lying LUMO dienophile.

We wish to report now that 1,1-bis(2-thienyl)ethanol (1) when it is mixed with TCNE (3) at room temperature affords in quantitative yield a white crystalline compound identified as the cycloadduct 4 (see Scheme 1). The formation of 4 is easily understood as a [4+2] cycloaddition of

1,1-bis(2-thienyl)ethylene (2), formed by dehydration of the alcohol (1), and TCNE (3). The reaction is unusually fast since it takes place in less than 15 minutes and it does not need any source of heat or light to be promoted. Other vinylthiophenes participate in Diels-Alder reactions to give aromatic cycloadducts under rather drastic conditions.[10]



1 2 4

Th = 2-Thienyl

Scheme 1

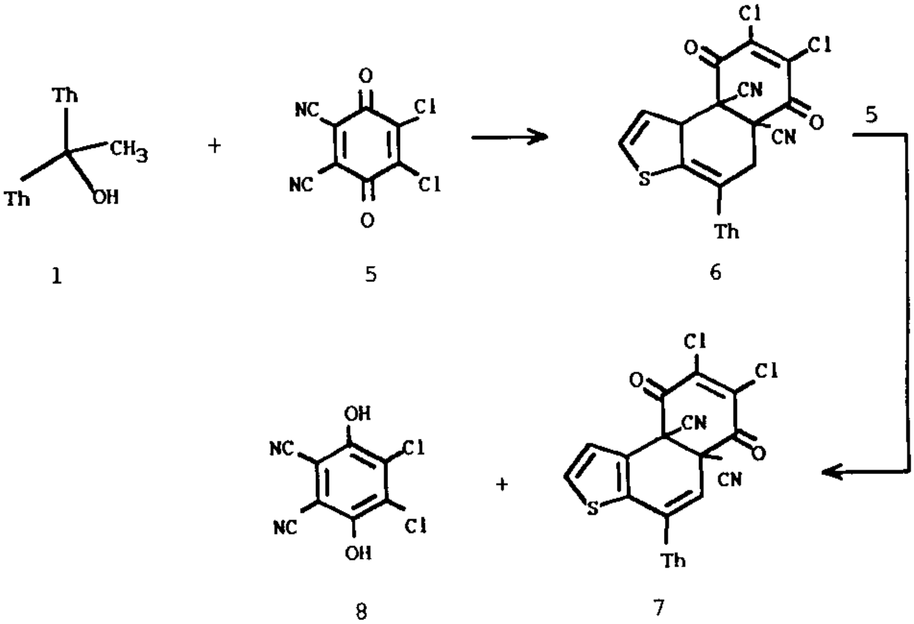
To get a deep insight into the mechanism of the cycloaddition, compound (1) and TCNE (3) dissolved in methylene chloride were mixed and the resulting solution was examined by esr showing a very strong signal (g = 2.0069, H = 3428.3) whose intensity decreased with the formation of cycloadduct (4). This strongly suggests that the reaction occurs by electron transfer through a mechanism of radical ion pairs as shown in Scheme 2.

$$\underline{2} + \underline{3} \xrightarrow{ET} \left[\underline{2}^{\oplus\odot} + \underline{3}^{\ominus\odot} \right] \longrightarrow \underline{4}$$

Scheme 2

When we essayed the equimolecular reaction of alcohol (1) with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (5) the formation of 0.5 equivalents of the unsaturated aromatic cycloadduct (7) and 0.5 equivalents of the hydroquinone (8) was observed to take place. Complete regioselectivity was observed since the chlorine substituted olefinic double bond does not participate at all as dienophile. The unreacted alcohol (1) was converted into 1,1-bis(2-thienyl)ethylene (2). Further addition to the reaction mixture of one equivalent of DDQ (5) resulted in the complete transformation of the reagents into the unsaturated cycloadduct (7). All the above observations are readily rationalized by assuming the initial formation of the intermediate adduct (6) that is subsequently oxidized by 5 (see Scheme 3). The dehydrogenation of hydroaromatic compounds by DDQ

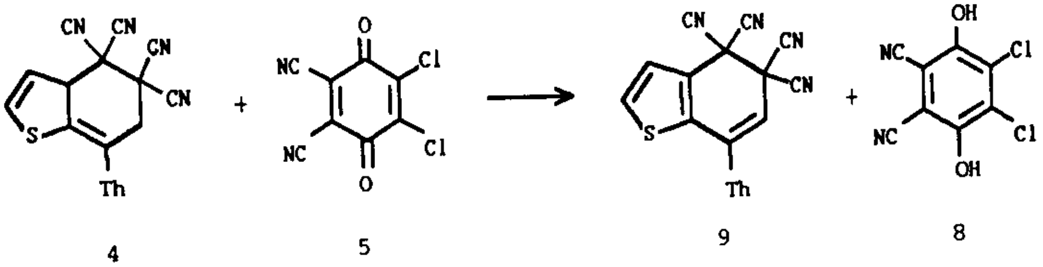
(5) is well documented in the literature.[11] The reaction of 1 with 5 was also monitored by esr. An unresolved signal was detected at 100°K suggesting also the participation of radical ion pairs as intermediates. However no definitive conclusion can be reached in this case since the mixtures of 5 and 8 have been found actives in the esr.[11] Other electron deficient olefins such as acrylonitrile, methyl acrylate and dimethyl acetylenedicarboxylate did not react with 1 under similar conditions.



Th = 2-Thienyl

Scheme 3

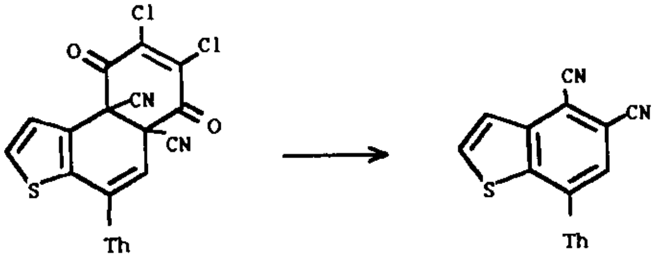
Based on the above results we treated the cycloadduct (4) with one equivalent of DDQ (5) giving rise to the aromatization to yield compound (9) in quantitative yield (see Scheme 4).



Th = 2-Thienyl

Scheme 4

Cycloadduct (7) is an unstable compound which in the process of purification was transformed in a new product identified by nmr and elemental analysis as the benzothiophene (10) (see Scheme 5). Diels-Alder adducts derived from heptafulvalenes and DDQ have been shown to yield dicyanoazulenes by a formally similar process.[12]



7

10

Th = 2-Thienyl

Scheme 5

Alcohol (1) is a stable compound in the dark and it is noteworthy that it undergoes very fast dehydration in the presence of TCNE (3) or DDQ (5). The dehydration reaction is not directly related to the formation of the cycloadduct since, as shown above, the olefin (2) is also generated in 50% yield in the equimolecular reaction of 1 and 5. Compound (2) is unstable and polymerizes rapidly when *non*-crystalline[13] and, for this reason, from the synthetic point of view the route reported herein to the heterocyclic skeletons 4, 7, 9, and 10 is advantageous since it avoids handling the precursor olefin giving quantitative yields.

EXPERIMENTAL

^1H and ^{13}C nmr spectra were recorded in a Brucker WP-80 SY or AC-200 spectrometer. Melting points are uncorrected and were determined with a Kofler hot-stage apparatus. Esr spectra were measured in a Brucker ER 200 equipment.

Reaction of 1,1-bis(2-thienyl)ethanol (1) with TCNE. To a solution of 1 (0.21 g, 1 mmol) in 10 ml of methylene chloride, TCNE (0.128 g, 1 mmol) was added at room temperature with vigorous stirring. Immediately, the solution became dark. After 15 min, the solvent was evaporated, and the resulting solid was washed with CCl_4 and recrystallized from chloroform. Cycloadduct (4) was obtained (0.31 g, 98%), mp 148°C. Anal. Calcd for $C_{16}H_8N_4S_2$: C, 59.98; H, 2.51; N, 17.48; S, 20.01. Found: C, 59.98; H, 2.41; N, 17.47; S, 20.23. ^1H Nmr ($CDCl_3$): 3.58 (m, 2H), 4.67 (m, 1H), 5.80 (dd, J = 6 and 2 Hz, 1H), 6.62 (dd, J = 6 and 2 Hz, 1H), 7.00 (m, 2H), 7.35 (t, J = 3 Hz, 1H). ^{13}C Nmr ($CDCCl_3$):

37.34(t), 39.26(s), 41.08(s), 55.46(d), 107.61(s), 110.32(s), 110.64(s), 116.16(d), 117.53(s), 126.89(d), 127.45(d), 127.71(d), 129.86(s), 132.21(d), 138.30(s).

Reaction of 1,1-bis(2-thienyl)ethanol (1) with DDQ. DDQ (0.456 g, 2 mmol) was added at room temperature with vigorous stirring to a solution of alcohol (1) (0.21 g, 1 mmol) in methylene chloride (10 ml). Immediately the solution became dark and a solid appeared. After 15 min with stirring, the suspension was filtered. The resulting solid was identified as the hydroquinone (8) (0.225 g, 49 % based on DDQ) by conversion into the corresponding diacetate,[14] mp 180°C. ^{13}C Nmr (DMSO-d_6) : 101.41(s), 113.66(s), 129.22(s), 150.89(s). The solvent of the filtrate was evaporated and the solid residue washed with CCl_4. After filtration, cycloadduct (7) was obtained (0.40 g, 97% based on the alcohol). ^1H Nmr (CD_3COCD_3): 5.87 (s, 1H), 6.72 (dd, J = 3.5 and 4.5 Hz, 1H), 6.87 (d, J = 5.5 Hz, 1H), 7.07 (m, 2H), 7.48 (d, J = 5.5 Hz, 1H). ^{13}C Nmr ($DCCl_3$): 54.86(s), 110.05(d), 112,37(s), 126.14(s), 126.56(s), 126.71(d), 128.17(d), 128.37(d), 128.58(d), 129.86(d), 133.28(s), 134.67(s), 135.46(s), 136.78(s), 176.96(s), 178.04(s).

The purification of 7 by column chromatography (silica gel) with chloroform as eluent, gave rise to benzo[b]thiophene (10). mp 206-208°C. Anal. Calcd for $C_{14}H_6N_2S_2$: C, 63.13; H, 2.27; N, 10.52; S, 24.08. Found: C, 63.27; H, 2.29; N, 10.23; S, 24.20. ^1H Nmr ($CDCl_3$): 7.28 (dd, J = 5 and 3.7 Hz, 1H), 7.61 (dd, J = 1 and 5 Hz, 1H), 7.73 (dd, J = 1 and 3.7 Hz, 1H), 7.75 (d, J = 5.6 Hz, 1H), 7.85 (s, 1H), 7.93 (d, J = 5.6 Hz, 1H). ^{13}C Nmr ($CDCl_3$): 108.64(s), 113.18(s), 115.02(s), 116.05(s), 123.53(d), 125.76(d), 128.40(d), 128.85(d), 129.03(d), 133.57(d), 135.13(s), 138.88(s), 141.66(s), 142.25(s).

Oxidation of cycloadduct 4 by DDQ. To a solution of 4 (0.32 g, 1 mmol) in 10 ml of methylene chloride, DDQ (0.22 g, 1 mmol) was added at room temperature with vigorous stirring. Immediately the solution became dark and a solid precipitated. After 5 min stirring the suspension was filtered. The precipitate was identified as the hydroquinone 8 (0.2 g) by conversion into the corresponding diacetate,[14] mp 180°C (ethanol). The liquid phase was evaporated to yield compound (9) (0.304 g, 96 %), mp 150°C (decomp.). ^1H Nmr ($DCCl_3$): 5.90 (s, 1H), 7.05 (dd, J = 4 and 5 Hz, 1H), 7.25-7.50 (m, 3H), 7.58 (d, J = 5 Hz, 1H). ^{13}C Nmr ($DCCl_3$): 41.59(s), 106.26(d), 109.17(s), 109.68(s), 123.26(s), 126.38(d), 128.49(d), 129.37(d), 131.23(d), 134.95(s), 135.70(s), 143.79(s).

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REFERENCES

1. T. L. Gilchrist and R. C. Storr, 'Organic Reactions and Orbital Symmetry', 2nd. edition, Cambridge University Press, 1979, p. 114.
2. J. Sauer and R. Sustmann, Angew. Chem. Int. Ed. Engl., 1980, 19, 779.
3. R. Gompper, Angew. Chem. Int. Ed. Engl., 1969, 9, 312.
4. S. Fukuzumi and J. K. Kochi, Tetrahedron, 1982, 38, 1035, and references cited therein.
5. A. J. Fatiadi, Synthesis, 1987, 749.
6. J. E. Frey, A. M. Andrews, D. G. Ankoviac, D. N. Beaman, L. E. Du Pont, T. E. Elsner, S. R. Lang, M. A. Oosterbaan Zwart, R. E. Seagle, and L. A. Torreano, J. Org. Chem., 1990, 55, 606.
7. Y. Uosaki, M. Nakahara, and J. Osugi, Bull. Chem. Soc. Jpn., 1981, 54, 2569.
8. Y. Uosaki, M Nakahara, and J. Osugi, Bull. Chem. Soc. Jpn., 1982, 55, 41.
9. M. Dern, H. G. Korth, G. Kopp, and R. Sustmann, Angew. Chem. Int. Ed. Engl., 1985, 24, 337.
10. B. Abarca, R. Ballesteros, E. Enríquez, and G. Jones, Tetrahedron, 1985, 41, 2435; 1987, 43 269; B. Abarca, R. Ballesteros, and C. Soriano, Tetrahedron, 1987, 43, 991.
11. D. Walker and J. D. Hiebert, Chem. Rev., 1967, 67, 153.
12. S. Kuroda, M. Funamizu, Y. Kitahara, Tetrahedron Lett., 1975, 1973.
13. L. Kaper and T. J. de Boer, Spectrochimica Acta 26A, 1970, 2155.
14. Beilstein's Handbuch der Organischen Chemie, 4th. edition, 1918, vol. X, p. 551.

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