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UNUSUAL CYCLOADDITION BEHAVIOR OF 2-SUBSTITUTED NORBORNADIENES WITH TRIAZOLINEDIONES

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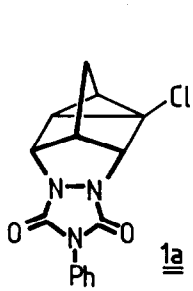
SUMMARY: 2-Chloronorbornadiene affords with 4-phenyltriazolinedione the homocycloadduct (1a) regioselectively as major product, along with small yields of the (2+2)-cycloadduct (2a), the dipolar rearrangement product (3a), and the ring insertion product (4a), while 2-trimethylsilyloxynorbornadiene leads to the ene-product (7c).

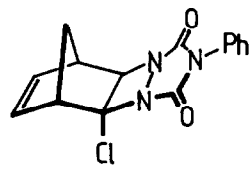
The usual cycloaddition course of norbornadienes with dienophiles is homo-Diels-Alder reaction.[1] It was of interest to explore whether electronic or steric factors of substituents in the 2-position of norbornadiene, e.g. 2-chloro and 2-trimethylsilyloxy groups, could promote cycloaddition of the (2+2)-type[2] and with dipolar rearrangement.[3] Moreover, it was of interest to assess the regioselectivity of the homocycloaddition of these 2-substituted norbornadienes, since such data is still scarce to date. Herein we report our preliminary results.

While the parent norbornadiene gives essentially quantitatively the homocycloaddition product with MTAD and PTAD, the 2-chloro derivative gave with PTAD a complex product mixture in low yield (30%). Running the reaction in CH_2Cl_2 at 0°C for 36-48 h, followed by silica gel chromatography (10:1 ratio of adsorbant to substrate) and eluting with 8:2 methylene chloride/ether afforded besides the expected homoadduct (1a) as major product (ca. 20%), the (2+2)-adduct (2a), the dipolar rearrangement product (3a) and the unusual ring insertion product (4a). Such diversity in cycloaddition modes for triazolinedione dienophiles has not been so far reported.

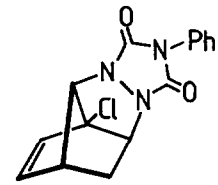
All products gave satisfactory elemental composition for the $C_{15}H_{12}ClN_3O_2$ empirical formula by combustion analysis and their structures are consistent with the IR and ^1H- and ^{13}C-NMR spectral data (cf. Table I). For cycloadduct (4a) it was necessary to run an X-ray structure determination[4], which confirmed beyond any reasonable doubt the proposed structure of this unusual ring insertion product with PTAD. A possible mechanism for the formation of urazole (4a) is given in Eq.1. Thus, exo-attack by PTAD on 2-chloro-norbornadiene gives directly the dipolar intermediate (5). Alternatively this intermediate could be formed indirectly via an aziridinium ion.[2a] Fragmentation of the norbornyl



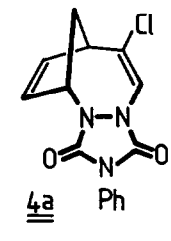
1a



2a



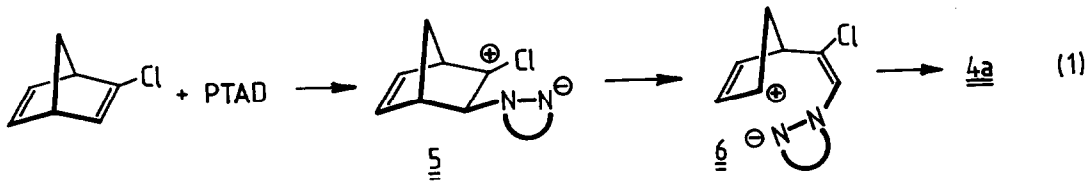
3a



4a

skeleton at the C_3-C_4 bond into the dipolar intermediate (6) and subsequent cyclization would lead to product (4a). Wagner-Meerwein shift of the C_1-C_6 bond in (5) and dipolar collapse would afford the rearranged urazole (3a)[3]. Finally, direct cyclization of dipole (5) gives the (2+2)-adduct (2a). This complex dienophilic behavior of a dienic substrate towards PTAD appears to be unprecedented.

Clearly, 2-chloro substitution of the norbornadiene substrate does promote competitive cycloaddition routes leading to the dipolar rearrangement product (3a) and the (2+2)-cycloaddition product (2a), but in low yields (ca. 2% each, cf. Table I). It was, therefore, of interest to probe whether other factors, e.g. solvent polarity, temperature or TAD-substituents could divert a larger fraction of the substrate towards these cycloaddition modes and away from the homo-Diels/Alder reaction. While solvent and temperature effects were negligible on the product distribution, e.g. besides dichloromethane, acetonitrile was tried at temperatures between 0°-60°C, an electron-withdrawing substituent on the TAD did afford larger yields of dipolar rearrangement product (3b) at the expense of the homocycloadduct (1b). For example, with 4(p-nitrophenyl)-1,2,4-triazolin-3,5-dione (NPTAD) (cf. Table I) the yield of rearranged urazole (3b) is doubled, but it is still very low (ca. 4%). On the other hand, an electron-donating substituent, e.g. 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) enhances the homocycloaddition product. Thus, with MTAD no rearranged urazole (3c) nor (2+2)-adduct (2c) could be detected, only the homocycloadduct (1c) in 29% yield (Table I). Both with NPTAD nor MTAD the novel insertion product (4b,c) was not observed under similar conditions as with PTAD. Furthermore, it is important to point out that all the cycloaddition reactions with the TAD's were regioselective, but the low yield of isolated products must be kept in mind, since the major course of action in the cycloaddition of 2-chloronorbornadiene with TAD leads to intractable, undefined material. Thus, in the homoreaction only (1) was formed and no (1'). Presumably steric factors exerted by chlorine dictate this choice. In the dipolar rearrangement only (3) and none of the alternatives (3') [resulting from TAD attack at the chlorine-substituted double bond but at the C_3-position] or (3'') and (3''') [due to TAD attack on the unsubstituted double bond respectively at the C_5 and C_6-positions] were observed.



5 6

The (2+2)-process led only to (2), from attack at the chlorine-substituted double bond, and no (2'), from attack at the unsubstituted double bond. If the dipolar and (2+2)-routes involve a common dipolar intermediate such as (5), a likely reason why the alternative products (3'), (3'') and (3''') and (2'), respectively are not formed is that the dipole (5) is the most stable choice.

The cycloaddition of the 2-trimethylsilyloxynorbornadiene with MTAD was disappointing because the silatropic ene-reaction leading to 5-(4-methylurazolyl)norbornen-6-one (7c) was the predominant course (ca. 81%). Only traces of homocycloadduct (8c) were detected. Product (7c) was too labile for rigorous purification and characterization.

It seems to us important to search for other dienic substrates which could display the diverse cycloaddition behavior as observed here for 2-chloronorbornadiene towards reactive dienophiles such as TAD. Through such studies we should be able to learn about the competitive nature of these cycloaddition modes.

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REFERENCES AND FOOTNOTES:

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1. Cookson, R. C.; Gilani, J. S. H.; Stevens, I. D. R. J. Chem. Soc. C 1967, 1905.

2. a. Seymour, C. A.; Greene, F. D. J. Am. Chem. Soc. 1980, 102, 6384.
b. Adam, W.; De Lucchi, O. Tetrahedron Lett. 1981, 22, 929.

3. a. Adam, W.; De Lucchi, O. Angew. Chem. Int. Ed. Engl. 1980, 19, 762.
b. Adam, W.; De Lucchi, O. and Erden, I. J. Am. Chem. Soc. 1980, 102, 4806.

4. The details of the X-ray analysis will be published separately by Dr. K. Peters.

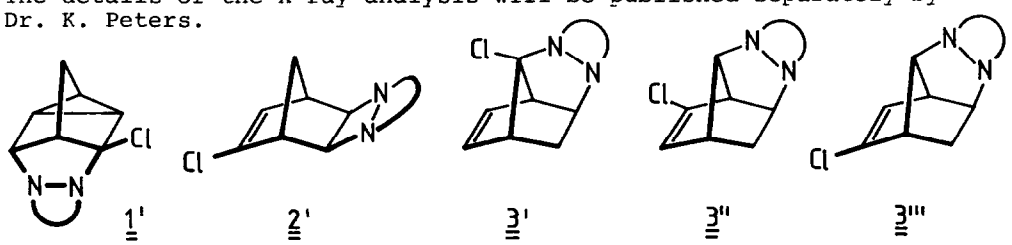

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TABLE I: Yields, physical constants and spectral data of the products formed in the cycloaddition of 2-substituted norbornadienes with 4-substituted triazolinediones (TAD).

Urazole[a]	Yield (%)	mp (°C) solvent (shape)	90 MHz ^{1}H-NMR ($CDCl_3$, Me_4Si) δ (ppm)[b] ^{13}C-NMR ($CDCl_3$, Me_4Si) δ (ppm)[c]	IR (KBr) ν (cm^{-1})
(1a)	20	220-221 ethanol (prisms)	1.86 and 2.11 (2H, H_7, AB system, J_{AB}=12.3 Hz); 2.07 (2H, $H_{1,6}$, m); 2.53 (1H, H_4, m); 4.62 (1H, H_5, m, $J_{4,5}$=2.7 Hz, $J_{5,6}$=0.5 Hz); 4.68 (1H, H_3, d, $J_{3,4}$=2.7 Hz); 7.46 (5H, C_6H_5, m). 24.16, 26.23, 28.84, 43.04, 44.93, 66.24, 70.30, 125.79, 128.52, 129.31, 131.68.	3060, 2940, 1765, 1700, 1490, 1410, 1330, 1270, 1220, 1130, 865, 815, 770, 700, 650.
(1b)	14	243-244 acet one (prisms)	1.88 and 2.18 (2H, H_7, AB system, $J_{A,B}$=12.3 Hz); 2.10 (2H, $H_{1,6}$, m); 2.60 (1H, H_4, m); 4.65 (1H, H_5, m); 4.72 (1H, H_3, d, $J_{3,4}$=2.7 Hz); 7.80-8.45 (4H, C_6H_4, AA'BB' system).	3130, 3100, 3010, 2950, 2880, 1800, 1780, 1725, 1600, 1530, 1500, 1400, 1355, 1270, 1130, 860, 850, 820, 770.
(1c)	29	122-123 CH_2Cl_2/ether (prisms)	1.83 and 2.12 (2H, H_7, AB system, J_{AB}=12.3 Hz); 2.02 (2H, $H_{1,6}$, m); 2.43 (1H, H_4, m); 3.10 (3H, CH_3, s); 4.53 (1H, H_5, m); 4.57 (1H, H_3, d, $J_{3,4}$=2.4 Hz).	3080, 3000, 2940, 2870, 1780, 1710, 1460, 1400, 1325, 1280, 1215, 1200, 1020, 950, 840, 770.
(2a)	2	202-203 ethanol (needles)	2.10 and 2.65 (2H, H_7, AB system, J_{AB}=10.2 Hz); 3.38 (2H, $H_{1,4}$, m); 4.32 (1H, H_3, m); 6.25 (2H, $H_{5,6}$, m); 7.50 (5H, C_6H_5, m). 44.42(t); 45.46(d); 51.92(d); 74.89(d); 92.73(s); 125.59(d); 128.81(d); 129.33(d); 131.40(s); 134.94(d); 137.27(d); 156.84(s); 161.14(s).	3000, 1790, 1730, 1600, 1500, 1405, 1320, 1240, 1140, 1025, 970, 780, 750, 720, 690.
(2b)	2	196-197 acetone (prisms)	2.15 and 2.62 (2H, H_7, AB system, J_{AB}=10.2 Hz); 3.42 (2H, $H_{1,4}$, m); 4.37 (1H, H_3, m); 6.28 (2H, $H_{5,6}$, m); 7.85-8.53 (4H, C_6H_4, AA'BB' system).	3120, 3075, 2980, 1790, 1730, 1610, 1600, 1525, 1500, 1385, 1340, 1250, 1125, 1040, 855, 780, 760, 715.
(3a)	2	214-215 ethanol (prisms)	1.67 (1H, H_{7endo}, ddd, $J_{7,7}$=12.3 Hz, $J_{1,7endo}$=5.4 Hz, $J_{4,7endo}$= 1.5 Hz); 2.23 (1H, H_{7exo}, dd, $J_{1,7exo}$=5.4 Hz); 3.20 (1H, H_4, br.s); 4.55 (2H, $H_{1,3}$, m); 6.00 (1H, H_6, dd, $J_{5,6}$=6.6 Hz, $J_{4,6}$=1.4 Hz); 6.45 (1H, H_5, dd, $J_{4,5}$=3.6 Hz); 7.45 (5H, C_6H_5, m). 37.31(t); 43.44(d); 62.15(d); 78.74(s); 84.14(d); 125.85(d); 128.45(d); 129.21(d); 130.58(d); 131.70(s); 138.67(d); 156.78(s); 157.49(s).	3090, 3040, 2990, 2940, 1770, 1710, 1590, 1500, 1400, 1290, 1260, 1230, 1125, 1095, 820, 735, 700, 690.
(3b)	4	222-224 acetone (prisms)	1.68 (1H, H_{7endo}, ddd, $J_{7,7}$=12.0 Hz, $J_{1,7endo}$=5.1 Hz, $J_{4,7endo}$= 1.5 Hz); 2.23 (1H, H_{7exo}, dd, $J_{1,7exo}$=5.1 Hz); 3.22 (1H, H_4, br.s); 4.55 (2H, $H_{1,3}$, m); 6.00 (1H, H_6, dd, $J_{5,6}$=6.0 Hz, $J_{4,6}$=1.5 Hz); 6.47 (1H, H_5, dd, $J_{4,5}$=3.6 Hz); 7.60-8.30 (4H, C_6H_4, AA'BB' system).	3120, 3090, 2990, 1780, 1715, 1590, 1515, 1490, 1400, 1340, 1125, 1090, 850, 810, 760, 735.
(4a)	2	153-154 ethanol (plates)	2.15 (1H, H_{7endo}, d, $J_{7,7}$=13.2 Hz); 2.43 (1H, H_{7exo}, dt, $J_{1,7exo}$= $J_{4,7exo}$=6.3 Hz); 3.58 (1H, H_1, br.d); 5.38 (1H, H_4, ddd); 6.22 (2H, $H_{5,6}$, narrow AB system split into d, $J_{5,6}$=5.4 Hz; $J_{1,6}$=3.0 Hz, $J_{4,5}$=2.7 Hz); 6.98 (1H, H_3, d, $J_{1,3}$=1.5 Hz); 7.48 (5H, C_6H_5, m). 39.45(t) ; 51.40(d); 60.17(d); 119.32(d); 122.32(s); 125.39(d); 128.29(d); 129.11(d); 130.11(d); 131.14(s); 136.51(d); 147.89(s); 150.01(s).	3080, 2990, 2930, 2860, 1775, 1720, 1655, 1590, 1500, 1490, 1410, 1305, 1275, 1145, 1065, 830, 755, 735.
(7c)	81	200-203 ethanol (plates)	2.27 and 2.53 (2H, H_7, AB system, J_{AB}=10.3 Hz); 3.07 (4H, CH_3 + H_4, s); 3.52 (1H, H_1, br.s); 4.08 (1H, H_3, d, $J_{3,4}$=3.3 Hz); 6.30 (1H, dd, $J_{5,6}$=6.0 Hz, J=3.0 Hz); 6.67 (1H, dd, J=3.0 Hz); 8.00 (1H, N-H, br.s).	3100, 3020, 2980, 2960, 2860, 2800, 1780, 1760, 1700, 1490, 1400, 1375, 1320, 1290, 1250, 1190, 1140, 1050, 990, 950, 860, 815, 760, 620.

a) The index letters a, b and c refer to 4-phenyl, 4(p-nitro)phenyl and 4-methyl substitution, respectively of the urazole moiety. b) Numbering of protons refers to the norbornene skeleton. c) 22.6 MHz or 100.1 MHz.

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