54. Propellanes. LXVII. Reactions of 1,6-Bridged [10]annulenes with 4-Methyl-1,2,4-triazoline-3,5-dione[1])

by **Pnina Ashkenazi**[a]), **Emanuel Vogel**[b]), and **David Ginsburg**[a])

[a]) Department of Chemistry, Israel Institute of Technology, Haifa

[b]) Institut für Organische Chemie der Universität, Köln

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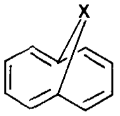
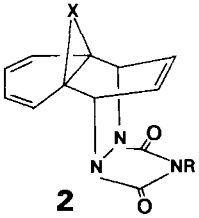
Summary

Reactions of 11-substituted-1,6-methano[10]annulenes and 1,6-methano[10]-annulenes substituted in the aromatic ring with the title dienophile are described.

We have shown that 1,6-methano-, 1,6-oxa-, 1,6-imino-, and 1,6-methylimino-[10]annulene ordinarily give a bis-adduct with 4-methyl-1,2,4-triazoline-3,5-dione (or with the 4-phenyl analog) at a rate much slower than that of dienic or tetraenic propellanes with the same dienophiles [2] [3]. This is not surprising. The annulenes hesitate to lose their aromaticity. When they do and a mono-*Diels-Alder* adduct of type **2** is formed, this is a cyclohexadiene which reacts faster than its aromatic precursor **1**. 11-Substituted-1,6-methano[10]annulenes give mono-adducts but by adding an additional mole of dienophile, the *anti-anti*-bis-adduct may usually be obtained [4].



1 X = CH_2, O, NH, NMe



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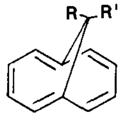

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We studied the reaction of 11,11-disubstituted-1,6-methano[10]annulenes **3**. We show in the *Experimental Part* that with **3**, R = R' = F, CO_2Me, or R = Me, R' = CN, only the mono-adduct is obtained. In several more 11-mono-substituted derivatives of **2**, bis-adducts may be obtained as is also the case with the 11-methylene-derivative.

Among 1,6-methano[10]annulenes substituted in the 2-position **4**, the carbomethoxy [5] and bromo derivatives are attacked in the substituted part of the

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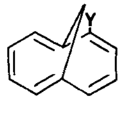
[1]) Part LXVI: [1].

annulene ring, but for the 2-cyano derivative the *anti*-attack is reversed, occurring in the unsubstituted part of the annulene. For 3-substituted derivatives **5**, however, the carbomethoxy- and bromo-derivatives are attacked in the unsubstituted part of the ring but the ^{1}H-NMR. spectrum of the 3-cyano derivative does not permit an unequivocal deduction in this regard.



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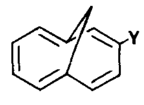

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Experimental Part

General remarks. M.p. are uncorrected. IR. spectra (cm^{-1}) were measured on a *Perkin-Elmer 237* spectrometer. ^{1}H-NMR. spectra were measured on a *T-60* or a *Bruker WP-60* instrument and high-resolution and routine mass spectra on a *Varian MAT-711* spectrometer. 4-Methyl-1,2,4-triazoline-3,5-dione ≡ MTAD, 4-phenyl-1,2,4-triazoline-3,5-dione ≡ PTAD.

General procedure for preparation of mono- or bis-adducts. – One equiv. of the annulene and one equiv. of the dienophile in CH_2Cl_2 (unless stated otherwise) reacted to give the monoadduct. One equiv. of monoadduct and one equiv. of the dienophile in CH_2Cl_2 gave the bis-adduct (temp. and time given below for each compound).

11-Methyliden-1,6-methano-[10]annulene with 2 equiv. of PTAD (r.t., 24 h) afforded the bis-adduct, m.p. 251–252° ($CHCl_3$). – IR. (KBr): 1690, 1500, 1400. – ^{1}H-NMR. ($CDCl_3$): 7.40 (10 arom. H); 6.20 (4 vinylic H); 5.50 (*t*, 4 allylic CHN); 3.25 (*s*, 2 vinylic H). – MS.: 504 (0.5, M^+), 322 (22), 177 (26), 154 (100), 153 (94), 152 (93), 128 (70), 119 (94), 91 (60).

$C_{28}H_{20}N_6O_4$ Calc. N 16.66% Found N 15.37%

Treatment of this substrate with only 1 equiv. of dienophile afforded 50% yield of the bis-adduct and 50% of the starting material was recovered.

11,11-Difluoro-1,6-methano[10]annulene with 2 equiv. of MTAD (r.t., 10 days in the dark), removal of CH_2Cl_2, trituration with hexane dissolved the starting material. Solution in C_6H_6 and precipitation with C_6H_{14} gave the addition product of EtOH (impurity in CH_2Cl_2) to the dienophile. From the filtrate the *mono-adduct* (17% yield), m.p. 123–124° (hexane, in the cold) was obtained. A *retro-Diels-Alder* reaction is observed at the m.p. (red color of dienophile is observed). – IR. ($CHCl_3$): 1770, 1710, 1450. – ^{1}H-NMR. ($CDCl_3$): 6.35 (2 vinylic H); 6.35–5.70 (4 dienic H); 5.15 (2 CHN); 3.00 (*s*, 3 NCH_3). – MS.: 177 (10), 128 (100).

$C_{14}H_{11}F_2N_3O_2$					
	Calc.	C 64.58	H 3.71	F 10.75	N 11.89%
	Found	„ 64.29	„ 3.66	„ 10.86	„ 11.94%

With PTAD (r.t., 5 days in the dark) the *mono-adduct phenyl analog* (38%) was obtained through analogous workup. – IR. ($CHCl_3$): 1770, 1710, 1405. – ^{1}H-NMR. ($CDCl_3$): 7.50 (5 arom. H); 6.50 (*t*, 2 vinylic H); 6.50–5.80 (4 dienic H); 5.30 (2 CHN). – MS.: 177 (47), 128 (6), 120 (100), 119 (76), 93 (23), 91 (32).

11-Bromo-1,6-methano[10]annulene with 1 equiv. of MTAD (r.t., overnight) gave the *mono-adduct* (75%), m.p. 201–202° (benzene/hexane). – IR. ($CHCl_3$): 1780, 1710, 1470, 1410. – ^{1}H-NMR. ($CDCl_3$); 6.55–5.75 (*m*, 6 vinylic + dienic H); 5.10 (*t*, 2 CHN); 3.80 (*s*, 1 cyclopropyl-H); 2.90 (*s*, 3 NCH_3). – MS.: 335 (25, M^+), 333 (16), 254 (96), 220 (32), 197 (97), 169 (80), 141 (100). – M.w.: Calc. 333.0110, 335.0093, Found 333.0044, 335.0106.

$C_{14}N_{12}BrN_3O_2$ Calc. N 12.51% Found N 12.10%

With 2 equiv. of MTAD (r.t., 1 week) gave the *bis-adduct* (70%), m.p. 212–213° (trituration EtOAc). – IR. (KBr): 1770, 1710, 1470. – MS.: 198 (5), 183 (38), 166 (100), 162 (19), 154 (16), 153 (17).

11-Methyl-1,6-methano[10]annulene with 1 equiv. of PTAD (r.t., 5 min) gave the *mono-adduct* (70%), m.p. 174–175° (benzene/hexane). – IR. ($CHCl_3$): 1770, 1720, 1510, 1420. – ^{1}H-NMR. ($CDCl_3$):

7.45 (*s*, 5 arom. H); 6.30 (*t*, 2 vinylic H); 6.30–5.80 (*m*, 4 dienic H); 5.15 (*t*, 2 CHN); 1.80 (*qa*, 1 cyclopropyl-H); 0.50 (*d*, 3 CH_3). – MS.: 331 (6, M^{+}), 156 (35), 155 (56), 141 (100). – M.w.: Calc. 331.1281, Found 333.1281.

$C_{20}H_{17}N_3O_2$ Calc. N 12.68% Found N 12.44%

With 2 equiv. of PTAD (r.t., 7 days) the benzene-insoluble *bis-adduct* was isolated (20%), m.p. 206–207°. This was accompanied by the mono-adduct (42%), isolated by precipitation with hexane from the mother liquor. – IR. ($CHCl_3$): 1770, 1720, 1420. – ^1H-NMR. ($CDCl_3$): 7.45 (*s*, 10 arom. H); 6.30 (*m*, 4 vinylic H); 5.55 (*m*, 4 CHN); 1.75 (*m*, 1 cyclopropyl-H); 1.15 (*s*, 3 CH_3). – MS.: 331 (23), 177 (54), 165 (11), 156 (38), 155 (64), 141 (100), 119 (68).

$C_{28}H_{22}N_6O_4$ Calc. N 16.48% Found N 16.59%

1,6-Methano[10]annulene-11-carboxylic acid with 2 equiv. of PTAD (r.t., 2 days) gave the *bis-adduct* (50%), m.p. 225–227° (trit. acetone) accompanied by some mono-adduct and starting material. – IR. (KBr): 1770, 1720, 1520, 1430. – ^1H-NMR. ($CDCl_3$): 7.50 (10 arom. H); 6.30 (4 vinylic H); 5.70 (4 CHN); 3.70 (1 $CHCO_2H$). – MS.: 322 (5), 186 (16), 177 (32), 141 (100), 128 (47).

$C_{28}H_{20}N_6O_6$ Calc. N 15.55% Found N 15.67%

11-Carbomethoxy-1,6-methano[10]annulene with 1 equiv. of MTAD (r.t., 1 week) gave the *mono-adduct* (36%) and the *bis-adduct* (15%) after separation on a prep. SiO_2-plate with hexane/acetone 1:1.

Mono-adduct, m.p. 161° (benzene/hexane). – IR. ($CHCl_3$): 1770, 1710, 1460, 1400. – ^1H-NMR. ($CDCl_3$): 6.50–6.00 (*m*, 6 vinylic + dienic H); 5.35–5.00 (*m*, 2 CHN); 3.55 (*s*, 3 CO_2CH_3); 2.95 (*s*, 3 NCH_3); 2.55 (*s*, 1 $CHCO_2CH_3$). – MS.: 313 (13, M^{+}), 282 (4), 224 (18), 200 (8), 154 (36), 141 (100). – M.w.: Calc. 313.1062, Found 313.1015.

$C_{16}H_{15}N_3O_4$ Calc. N 13.41% Found N 13.09%

Bis-adduct, m.p. 208–210° (benzene/hexane). – IR. ($CHCl_3$): 1770, 1720, 1460. – ^1H-NMR. ($CDCl_3$): 6.30 (*t*, 2 vinylic H); 6.05 (*t*, 2 vinylic H); 5.55 (*m*, 4 CHN); 3.60 (*s*, 3 CO_2CH_3); 2.90 (*s*, 3 NCH_3); 2.35 (1 $CHCO_2CH_3$). – MS.: 291 (18), 281 (23), 198 (27), 181 (56), 154 (41), 141 (100).

11,11-Dicarbomethoxy-1,6-methano[10]annulene with 1 or 2 equiv. of PTAD (r.t., instantaneously) gave only the *mono-adduct*, m.p. 220° (benzene/hexane) after purification on prep. silica plate with C_6H_6. – IR. ($CHCl_3$): 1740, 1720, 1410. – ^1H-NMR. ($CDCl_3$): 7.40 (*s*, 5 arom. H); 6.15 (*m*, 6 vinylic + dienic H); 5.35 (*t*, 4 CHN); 3.70 (*s*, 3 CO_2CH_3); 3.60 (*s*, 3 CO_2CH_3). – MS.: 259 (9), 228 (86), 199 (100), 183 (5), 171 (24), 140 (39).

$C_{18}H_{17}N_3O_6$ Calc. N 11.32% Found N 11.51%

11-Methyl-11-cyano-1,6-methano[10]annulene with either 1 or 2 equiv. of PTAD (r.t., instantaneously) gave the *mono-adduct* (65%; 80%), m.p. 179–180° by trituration of product with ethyl acetate. – IR. ($CHCl_3$): 1770, 1720, 1510, 1420. – ^1H-NMR. ($CDCl_3$): 7.50 (5 arom. H); 6.60 (*t*, 2 vinylic H); 6.50–5.80 (A_2B_2, 4 dienic H); 5.30 (*t*, 2 CHN); 1.15 (*s*, 3 CH_3). – MS.: 181 (17), 166 (37), 119 (100).

$C_{21}H_{14}N_4O_2$ Calc. N 15.81% Found N 14.98%

2-Bromo-1,6-methano[10]annulene with 2 equiv. of MTAD (r.t., 24 h) gave a mixture of *bis-adduct* (87%) and *mono-adduct* (13%) separated on prep. SiO_2-plate with $CHCl_3$. The *bis-adduct* had m.p. 190–191° ($CHCl_3$). – IR. ($CHCl_3$): 1780, 1720, 1460, 1400. – ^1H-NMR. ($CDCl_3$): 6.60–6.10 (*m*, 4 vinylic H); 5.80 (*m*, 1 CHN); 5.45 (*m*, 2 CHN); 2.95 (*s*, 6 NCH_3); 1.15, 1.10 (*ABqa*, 2 cyclopropyl-H). – MS.: 335 (7), 333 (8), 221 (18), 220 (26), 219 (21), 141 (100).

The *mono-adduct* identical to the above was best prepared (22%) using 0.5 equiv. MTAD (r.t., 24 H). Even under these conditions *bis-adduct* (20%) is formed and recovered annulene (56%) isolated. The *mono-adduct* precipitated from benzene/hexane as an oil. – IR. ($CHCl_3$): 1780, 1710, 1460, 1400. – ^1H-NMR. ($CDCl_3$): 6.50–5.50 (*m*, 6 H, dienic + vinylic H); 3.10 (*t*, 1 CHN); 2.95 (*s*, 3 NCH_3); 1.75, 0.25

(*ABqa*, 2 cyclopropyl-H). – MS.: 335 (8, M^+), 333 (7), 221 (68), 220 (43), 219 (41), 141 (100). – $C_{14}H_{12}BrN_3O_2$ M.w. Calc. 333.0113, 335.0092, Found 333.0116, 335.0033.

The *mono-adduct with* N-*methylmaleimide*, formed by attack of the unsubstituted part of the ring was purified on a prep. SiO_2-plate with C_6H_6, m.p. 145° (benzene/hexane); 26% yield. – IR. ($CHCl_3$): 1780, 1700, 1400, 1400. – ^{1}H-NMR. ($CDCl_3$): 6.40–5.60 (*m*, 5 vinylic H); 3.90 (*m*, 1 allylic H); 3.45 (*m*, 1 allylic H); 3.00 (*m*, 2 CHCO); 2.95 (*s*, 3 NCH_3); 1.90, 0.10 (*ABqa*, 2 cyclopropyl-H). – MS.: 333 (56, M^+), 331 (32), 252 (64), 221 (100), 219 (88). – M.w.:Calc. 331.0208, 333.0188, Found 331.0246, 333.0227.

$C_{16}H_{14}BrNO_2$ Calc. N 4.20% Found N 3.86%

2-Cyano-1,6-methano[10]annulene with 0.5 equiv. of MTAD (r.t., 24 h) gave *mono-adduct* (30%) (with recovered starting material, 70%). The adduct had m.p. 170–171° (benzene/hexane). – IR. ($CHCl_3$): 2210, 1780, 1720, 1710, 1600, 1470, 1400. – ^{1}H-NMR. ($CDCl_3$): 6.90–6.10 (*m*, 5 vinylic H); 5.50 (*t*, 1 CHN); 5.15 (*t*, 1 CHN); 3.10 (*s*, 3 NCH_3); 1.95, 0.00 (*ABqa*, 2 cyclopropyl-H, *J* = 6). – MS.: 280 (1, M^+), 167 (81), 166 (100). – $C_{15}H_{12}N_4O_2$ M.w.:Calc. 280.0959, Found 280.0957.

With 2 equiv. of MTAD (r.t., 24 h) the same *mono-adduct* (60%) was accompanied by *bis-adduct*, separated by fractional crystallization, m.p. 215–217° (ethyl acetate/hexane). – IR. ($CHCl_3$): 1770, 1720, 1420, 1460, 1400. – ^{1}H-NMR. ($CDCl_3$): 6.30 (*m*, 4 vinylic H); 5.80–5.40 (*m*, 3 CHN); 3.00 (*s*, 6 NCH_3); 1.15 (*s*, 2 cyclopropyl-H). – MS.: 198 (8), 167 (89), 166 (100), 139 (30).

With excess N-*methylmaleimide* (in benzene, 140°, 4 days) followed by purification on a prep. SiO_2-plate the starting material (66%) was recovered and *mono-adduct* (6%) was isolated (attack on unsubstituted ring), m.p. 182° (ethyl acetate/hexane). – IR. ($CHCl_3$): 2210, 1780, 1700. – ^{1}H-NMR. ($CDCl_3$): 6.80–5.90 (*m*, 5 vinylic H); 4.15, 3.90 (*d*, 2 allylic H); 2.85 (*s*, 3 NCH_3); 2.75 (*m*, 2 CHCO); 2.10, –0.40 (*ABqa*, 2 cyclopropyl-H). – MS.: 278 (28, M^+), 193 (15), 167 (100). – M.w.:Calc. 278.1055, Found 278.1080.

$C_{17}H_{14}N_2O_2$ Calc. N 10.07% Found N 9.29%

3-Bromo-1,6-methano[10]annulene with 0.5 equiv. of MTAD (r.t., 24 h) gave recovered annulene (66%), *mono-adduct* (34%) and *bis-adduct* (9%) separated on prep. SiO_2-plate with $CHCl_3$. The oily *mono-adduct* separated from benzene/hexane. – IR. ($CHCl_3$): 1780, 1720, 1460, 1400. – ^{1}H-NMR. ($CDCl_3$): 6.50 (*m*, 1 vinylic H); 6.20 (*m*, 4 dienic H); 5.10 (*t*, 2 CHN); 2.95 (*s*, 3 NCH_3); 1.80, 0.00 (*ABqa*, 2 cyclopropyl-H). – MS.: 335 (2, M^+), 333 (2), 254 (12), 221 (51), 219 (52), 157 (10), 141 (100). $C_{14}H_{12}BrN_3O_2$ M.w. Calc. 335.0092, 333.0113,Found 335.0165, 333.0137.

With 2 equiv. of MTAD (r.t., 24 h) the *bis-adduct* was obtained, m.p. 233–235° ($CHCl_3$) after purification as above. – IR. ($CHCl_3$): 1780, 1720, 1470, 1400. – ^{1}H-NMR. ($CDCl_3$): 6.20 (*m*, 3 vinylic H); 5.45 (*m*, 4 CHN); 3.00 (*s*, 3 NCH_3); 2.95 (*s*, 3 NCH_3); 1.05, 1.00 (*ABqa*, 2 cyclopropyl-H). – MS.: 448 (3, M^+), 335 (5), 333 (4), 254 (22), 221 (81), 219 (65), 198 (3), 197 (18), 141 (100). – $C_{17}H_{15}BrN_6O_4$ M.w.:Calc. 448.0318, 446.0034,Found,448.0366, 446.0357.

3-Cyano-1,6-methano[10]annulene with 0.5 equiv. of MTAD (r.t., 24 h) gave unreacted annulene (77%), *mono-adduct* (20%) and *bis-adduct* (3%) separated as above. The *mono-adduct* was an oil, soluble in $CHCl_3$/hexane. – IR. ($CHCl_3$): 2210, 1780, 1710, 1420, 1400. – ^{1}H-NMR. ($CDCl_3$): 7.00 (*m*, 1 H–C(2)); 6.60–6.20 (*m*, 4 vinylic H); 5.20 (*m*, 2 CHN); 2.95 (*s*, 3 NCH_3); 2.10, 0.00 (*ABqa*, 2 cyclopropyl-H, *J* = 6). – MS.: 167 (73), 166 (100).

$C_{15}H_{12}N_4O_2$ Calc. N 19.99% Found N 19.84%

With 2 equiv. of MTAD (r.t., 2 days) a mixture of the same *mono-adduct* (65%) and *bis-adduct* (35%) was obtained. The latter had m.p. 235–236°, insoluble in $CHCl_3$. – IR. ($CHCl_3$): 1780, 1710, 1470, 1440. – ^{1}H-NMR. ($CDCl_3$): 6.80 (*d×d*, 1 CH=CCN); 6.20 (*t*, 2 vinylic H); 4.50 (4 CHN); 3.00 (*d*, 6 NCH_3); 1.10 (*s*, 2 cyclopropyl-H). – MS.: 280 (2), 198 (1), 167 (43), 166 (100).

$C_{18}H_{15}N_7O_4$ Calc. N 24.93% Found N 24.98%

With excess N-*methylmaleimide* (in C_6H_6, 140°, 4 days) and separation on a prep. SiO_2-plate, unreacted annulene (68%) and 2 *mono-adducts* were isolated. The *mono-adduct* formed (3%) by *addition* *to C(2) and C(5) was* an oil. – IR. ($CHCl_3$): 2220, 1780, 1710, 1440, 1390. – ^1H-NMR. ($CDCl_3$): 6.80 (*d*×*d*, 1 CH=CCN); 6.05 (*s*, 4 dienic H); 3.75 (*m*, 2 allylic H); 3.00 (*m*, 2 CHCO); 2.95 (*s*, 3 NCH_3); 1.60–0.25 (*ABqa*, 2 cyclopropyl-H). – MS.: 278 (45, M^+), 193 (33), 167 (100), 140 (17). – M.w.: Calc. 278.1055, Found 278.1063.

$C_{17}H_{14}N_2O_2$ Calc. N 10.07% Found N 9.60%

The *mono-adduct* formed (4%) by *addition to C(7) and C(10)* had m.p. 135–136° (ethyl acetate/hexane). – IR. ($CHCl_3$): 2220, 1780, 1710, 1440, 1390. – ^1H-NMR. ($CDCl_3$): 7.00 (*m*, 1 CH=CCN); 6.60–5.95 (*m*, 4 vinylic H); 3.65 (*m*, 2 allylic H); 2.90 (*s*, 3 NCH_3); 2.70 (*m*, 2 CHCO); 2.20, 0.40 (*ABqa*, 2 cyclopropyl-H). – MS.: 278 (27, M^+), 193 (15), 167 (100), 140 (17). – M.w.: Calc. 278.1055, Found 278.1058.

$C_{17}H_{14}N_2O_2$ Calc. N 10.07% Found N 9.59%

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