Bull. Chem. Soc. Jpn., ***69***, 2249—2252 (1996) 2249

Novel Reaction between 3,4,5,6-Tetrachloro-1,2-benzoquinone and Bis-azomethines

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(Received January 16, 1996)

3,4,5,6-Tetrachloro-1,2-benzoquinone (*o*-CHL) reacted with *N*,*N*′-dicyclohexyl-1,2-ethanediimine **1a** to give a transient condensation product, which underwent [4+2]cycloaddition reaction with another molecule of **1a**. In a different manner, utilizing *N*,*N*′-diaryl-1,2-ethanediimines **1b,c** as a dienophile led to an initial production of substituted *o*-CHL, followed by a [4+2]cycloaddition reaction with another molecule of **1b,c**. A similar behavior was observed on the reaction of *N*,*N*′-di(alkyl/aryl)-*p*-xylenediimines **1a—f** with the same acceptor.

Our main research topic deals with the synthesis of new heterocyclic and fused-heterocyclic compounds via donor–acceptor interactions.[1—6]

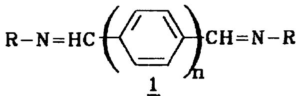
We recently reported that *N*,*N*′-diaryl-1,2-ethane- and -*p*-xylenediimines as well as *N*,*N*′-dicyclohexyldiimine derivatives, reacted with tetracyanoethylene (TCNE) to give pyrrole, imidazolidine, and quinoline derivatives.[7]

It has been reported that simple 1,2-benzoquinones produce normal Diels–Alder adducts in which the quinone reacts as a carbon diene,[8—12] and proved to be the most reactive diene ever studied.[13] The presence of four chlorine atoms led to a much higher yield of the product.[9] Also, the α-dicarbonyl structure of 1,2-quinones provides a useful varient from the diene system, which has also been the subject of several Diels–Alder studies.[14]

In spite of extensive studies that have been carried out concerning the cycloaddition reactions between 1,2-quinones and a variety of dienophile systems,[15] the reaction with imines as dienophiles has not been reported.

As a part of our continued interest concerning the cycloaddition reactions,[16—18] we now report on our studies involving the reaction of *N*,*N*′-di(alkyl/aryl)-1,2-ethanediimine **1a—c** as well as *N*,*N*′-di-(alkyl/aryl)-*p*-xylenediimine **1d—f** as a dienophile with *o*-chloranil as a diene (Fig. 1).

The addition of *N*,*N*′-dicyclohexyldiimine **1a** to *o*-CHL in dry ethyl acetate at room temperature gave a colored solution (transient charge-transfer CT-complex) that slowly changed to a brown solution. The chromatographic purification of the reaction mixture afforded **2a** (Fig. 2).



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a) n=0, R=cyclohexyl
b) n=0, R=$-C_6H_4-CH_3$-p
c) n=0, R=$-C_6H_4-Cl$-p
d) n=1, R=cyclohexyl
e) n=1, R=$-C_6H_4-CH_3$-p
f) n=1, R=$-C_6H_4-Cl$-p

Fig. 1.

A plausible mechanism for the formation of **2a** is shown in Fig. 3; it suggests an initial formation of a CT-complex, followed by the formation of an adduct **7**. The formation of **10** may be expected based on the role played by water (possibly from moist air or a solvent).

The reactions of the diimines with *o*-CHL under dry conditions have been reinvestigated, and no reactions occurred. This is further evidence concerning the important role played by moist air or water in a solvent in the formation of the obtained reaction products. A cycloaddition reaction between the condensation intermediate **10** and **1a** yielded **2a**. In a recent study, the hydrolysis of imines under the same conditions was reported.[19]

On the other hand, the diimines **1b**, **c** underwent a cycloaddition reaction with *o*-CHL in a different manner, forming the final products **3d**, **c** (Fig. 4).

Evidently, the higher basicity of the nitrogen atom in **1a** relative to **1b**, **c**, as well as the lese sterically hindered radical centre **6**($\overline{O}$–C$^\bullet$), compared with the other radical intermediate **11** ($\overline{O}$–CO–C$^\bullet$–Cl), enhance the recombination between the cation and the anion radical pair **6** to form a condensation intermediate **10**, followed by a cycloaddition reaction to finally form **2a**; however, it proceeded in **11** (Fig. 4) between the donor cation radical and the C–Cl radical followed by the elimination of the HCl forming the substitution intermediate **14**, which finally underwent a cycloaddition reaction to give **3b**, **c**.

In an attempt to expand this chemistry, a series of di(alkyl/aryl)-*p*-xylenediimines **1d—f** were employed to study the effect of the *p*-phenylene group on the course of the reaction. Similar results were obtained in case of both *N*,*N*′-dicyclohexyl and diaryl derivatives, evidencing the absence of any role played by the *p*-phenylene group.

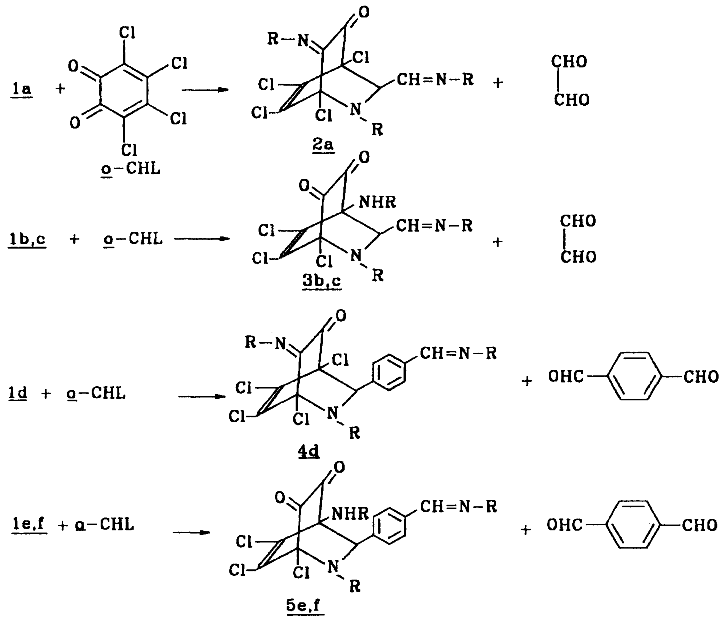

Fig. 2.

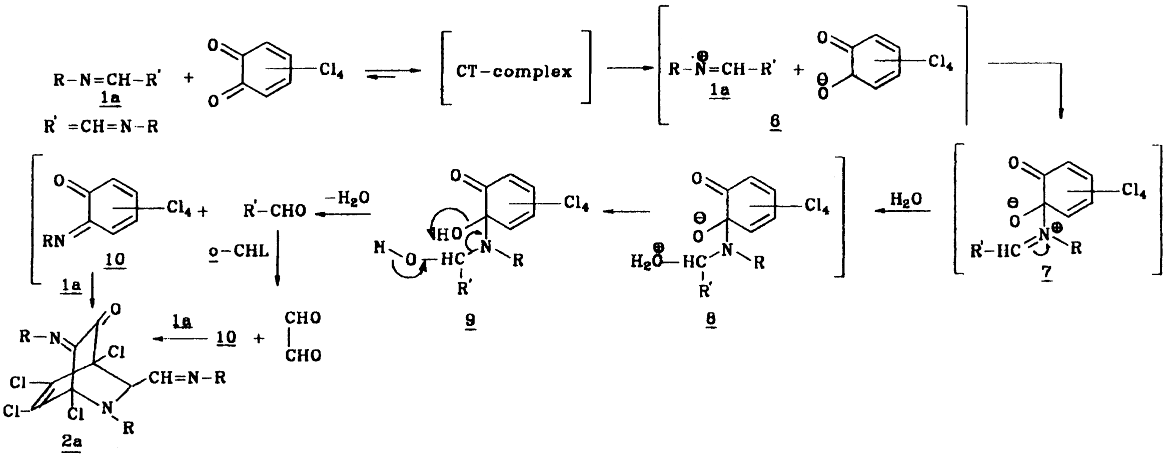

Fig. 3.

As can be seen from Figs. 3 and 4, the proposed mechanism depends on the initial formation of CT-complexes. A series of Diels–Alder cycloaddition reactions initiated by CT complex formation on different diene-dienophile components have recently been published.[18)]

The structural elucidation of reaction products **2**—**5** was based on analytical as well as spectral data. Besides the IR and ^{1}H NMR spectral data, the ^{13}C NMR spectra are in agreement with the proposed structures, and, hence, confirm the regiochemistry of reaction products **2**—**5**.

In conclusion, *o*-CHL reacts with diimines **1a**—**f** as a diene, and behaves differently with both *N*,*N*′-dicyclohexyl and *N*,*N*′-diaryldiimines. Also, only one azomethine group is involved in the cycloaddition reaction.

Experimental

The melting points were uncorrected. IR: Shimadzu 470 spectrophotometer using KBr pellets. ^{1}H NMR, AM-400 (400.134 MHz) and ^{13}C NMR AM-400 (100.164 MHz) using TMS as the internal reference; the chemical shifts are reported in δ (ppm) from TMS. MS: Finnigan MAT 8430 spectrometer at 70 eV. Elemental analysis: Microanalytical unit at Cairo University.

Materials: *o*-CHL (Merck), *N*,*N*′-di(alkyl/aryl)-1,2-ethanediimines **1a**—**c** were synthesized according to Refs. 20 and 21. *N*,*N*′-Di(alkyl/aryl)-*p*-xylenediimines **1d**—**f** were prepared by the condensation of 0.01 mol of *p*-terephthalaldehyde with 0.02 mol of substituted amines. Ethyl acetate (B.D.H) was purified following Vogel,[22)] then dried and distilled.

Preparative TLC was performed on Merck silica-gel 60 PF254 (1 mm).

Reaction of *o*-CHL with Diimines 1a—f. General Procedure: To a solution of *o*-CHL (1 mmol) in dry ethyl acetate (20 ml) was added a solution of diimine **1a**—**f** (1 mmol) in dry ethyl acetate (20 ml); the reaction mixture was then stirred at room temperature for 3 d (the reaction was followed by TLC). The reaction mixture turned from red to brown color after 3 h. The concentration and chromatographic separation on preparative TLC using toluene : ethyl acetate (10 : 1) as an eluent afforded pure reaction products **2**—**5** as the slowest migrating zone, whereas the fastest migrating zone contained terephthalaldehyde in the case of **1d**—**f**.

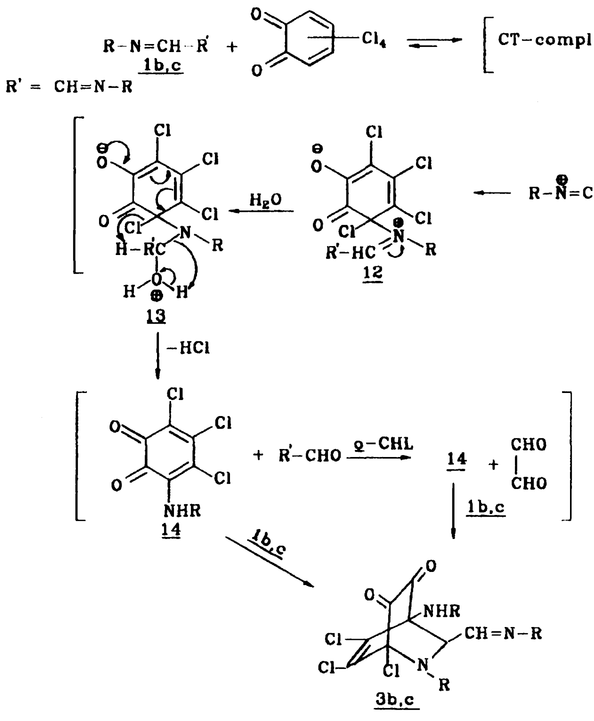

Fig. 4.

2a: Yield 251 mg (46%), mp 264—265 °C, colorless crystals (from ethanol). ^{1}H NMR (CDCl$_3$) $\delta = 1.10$—2.30 (m, 33H, Ali-H), 3.08—3.10 (d, 1H, cyclic-H), and 8.38—8.40 (d, 1H, CH=N). ^{13}C NMR (CDCl$_3$) $\delta = 185.18$ (C=O), 140.28 (CH=N), 138.18 (C=N), 130.88, 129.79, (Cl-C=C-Cl), 58.66 (CO-C-Cl), 56.18 (=C-C-Cl), 54.20, 54.08, 53.88 (-C-N), 43.88 (C-CH=N), 30.16, 30.08, 29.60, 26.60, 25.98, 24.38, 23.86, 21.01, and 20.49 (cyclohexyl carbon). IR (KBr) $\overline{\nu} = 2995$—2890 (Ali-CH), 1680 (CO), and 1610 cm^{-1} (C=N). MS (70 eV) *m/z* (%) 551 (4), 550 (12), 549 (8), 548 (18), 547 (M$^+$; 38), 546 (100), 513 (18), 344 (44), 273 (24), 172 (10), and 98 (12). Found: C, 56.89; H, 6.42; N, 7.63; Cl, 25.90%. Calcd for $C_{26}H_{35}Cl_4N_3O$ (M, 547.394): C, 57.05; H, 6.44; N, 7.68; Cl, 25.91%.

3d: Yield 270 mg (49%), mp 270—272 °C, colorless crystals (from ethanol). ^{1}H NMR (CDCl$_3$) $\delta = 2.20$ (s, 9H, 3CH$_3$), 3.47—3.50 (d, 1H, cyclic-H), 7.25—7.70 (m, 13H, Ar-H, NH), and 8.39—8.42 (d, 1H, CH=N). ^{13}C NMR (CDCl$_3$) $\delta = 186.20$, 185.88 (C=O), 150.23, 148.90, 148.63 (Ar-C-N-), 140.70 (CH=N), 132.18, 131.83 (Cl-C-Cl), 130.90, 129.87, 129.18, 129.08, 128.93, 128.66, 128.50, 127.94, 127.64 (Ar-C), 52.80 (C-Cl), 48.60 (C-NH), 34.18 (CH-Ar), 21.13, 21.06, and 20.90 (3CH$_3$). IR (KBr) $\overline{\nu}=3200$ (NH), 3090—3010 (Ar-CH), 2985—2890 (Ali-CH), 1680 (CO), and 1600 cm^{-1} (Ar-C=C, C=N). MS (70 eV) *m/z* (%) 556 (12), 555 (20), 554 (28), 553 (M$^+$; 100), 552 (30), 551 (18), 484 (12), 397 (18), 361 (24), 333 (30), 306 (26), 199 (24), and 92 (18). Found: C, 62.89; H, 4.45; N, 7.56; Cl, 19.40%. Calcd for $C_{29}H_{24}Cl_3N_3O_2$ (M, 552.887): C, 63.00; H, 4.38; N, 7.60; Cl, 19.24%.

3c: Yield 252 mg (41%), mp 215—217 °C, colorless crystals (from acetonitrile). ^{1}H NMR (CDCl$_3$) $\delta = 3.36$—3.42 (d, 1H, cyclic-H), 7.42—7.80 (m, 13H, Ar-H, NH), and 8.36—8.38 (d, 1H, CH=N). IR (KBr) $\overline{\nu} = 3260$ (NH), 3049—3008 (Ar-CH), 2980—2965 (Ali-CH), 1680 (CO), and 1602 cm^{-1} (Ar-C=C, C=N). MS (70 eV) *m/z* (%) 620 (4), 619 (12), 618 (28), 617 (40), 616 (48), 615 (62), 614 (M$^+$; 100), 613 (40), 612 (20), 611 (10), 610 (8), 578 (4), 577 (6), 465 (14), 451 (18), 433 (16), 187 (10), and 151 (4). Found: C, 50.73; H, 2.33; N, 6.68; Cl, 34.52%. Calcd for $C_{26}H_{15}Cl_6N_3O_2$ (M, 614.141): C, 50.85; H, 2.46; N, 6.84; Cl, 34.64%.

4d: Yield 300 mg (48%), mp 218—219 °C, colorless crystals (from ethanol). ^{1}H NMR (CDCl$_3$) $\delta = 1.15$—2.50 (m, 33H, Ali-H), 3.35 (s, 1H, cyclic-H), 7.30—7.60 (m, 4H, Ar-H), and 8.40 (s, 1H, CH=N). ^{13}C NMR (CDCl$_3$) $\delta = 186.88$ (C=O), 140.30 (CH=N), 139.26 (C=N), 130.16, 129.98 (Cl-C=C-Cl), 129.81, 128.66, 128.28, 127.74 (Ar-C), 57.16 (CO-C-Cl), 56.74 (=C-C-Cl), 54.17, 53.90, 52.18 (-C-N), 45.60 (CH-Ar), 30.80, 29.88, 28.98, 28.73, 27.32, 26.09, 24.30, 23.62, and 23.18 (cyclohexyl carbons). IR (KBr) $\overline{\nu}=3038$—3000 (Ar-CH), 2995—2885 (Ali-CH), 1685 (CO), and 1600 cm^{-1} (C=N). MS (70 eV) *m/z* (%) 627 (8), 626 (20), 625 (32), 624 (60), 623 (M$^+$; 100), 622 (58), 621 (20), 592 (32), 591 (20), 556 (14), 488 (24), 360 (16), 334 (10), 298 (18), 200 (14), 186 (40), 125 (4), and 98 (12). Found: C, 61.59; H, 6.10; N, 6.65; Cl, 22.70%. Calcd for $C_{32}H_{39}Cl_4N_3O$ (M, 623.492): C, 61.65; H, 6.30; N, 6.74; Cl, 22.74%.

5e: Yield 308 mg (49%), mp 270—271 °C, pale yellow crystals (from ethanol). ^{1}H NMR (CDCl$_3$) $\delta = 2.20$ (s, 3H, 3CH$_3$), 3.50 (s, 1H, cyclic-H), 7.15—7.50 (m, 17H, Ar-H, NH), and 8.35 (s, 1H, CH=N). ^{13}C NMR (CDCl$_3$) $\delta = 187.10$, 186.88 (C=O), 150.18, 148.97, 148.00 (3Ar-C-N), 140.20 (CH=N), 138.18, 136.35, 133.98, 134.81, 133.77, 132.20, 131.83, 131.50, 130.65, 130.43, 129.78, 128.52, 128.04, 127.18, 127.04 (Ar-C+2Cl-C=C-Cl), 52.60 (C-Cl), 48.40 (C-NH), 35.18 (CH-Ar), 20.13, 20.00, and 19.89 (3CH$_3$). IR (KBr) $\overline{\nu} = 3220$ (NH), 3025—3005 (Ar-CH), 2995—2980 (Ali-CH), 1680 (CO), and 1600 cm^{-1} (Ar-C=C, C=N). MS (70 eV) *m/z* (%) 631 (12), 630 (24), 629 (100), 628 (M$^+$; 8), 627 (20), 593 (40), 592 (44), 470 (12), 496 (14), 433 (38), 432 (30), 335 (14), 334 (12), 227 (16), 120 (20), 107 (14), and 72 (16). Found: C, 66.75; H, 4.41; N, 6.63; Cl, 16.73%. Calcd for $C_{35}H_{28}Cl_3N_3O_2$ (M, 628.984): C, 66.84; H, 4.49; N, 6.68; Cl, 16.91%.

5f: Yield 248 mg (36%), mp 235—237 °C, colorless crystals (from ethanol). ^{1}H NMR (CDCl$_3$) $\delta = 3.45$ (s, 1H, cyclic-H), 7.20—

7.50 (m, 17H, Ar–H and NH), and 8.35 (s, 1H, CH=N). IR (KBr) $\overline{\nu}$=3200 (NH), 3112—3060 (Ar–CH), 2990—2975 (Ali–CH), 1680 (CO), and 1610 cm^{-1} (Ar–C=C, C=N). MS (70 eV) *m*/*z* (%) 696 (5), 699 (8), 694 (20), 693 (28), 692 (42), 691 (60), 690 (M$^+$; 100), 689 (58), 688 (40), 687 (30), 686 (16), 685 (30), 654 (12), 653 (16), 652 (22), 646 (40), 518 (32), 482 (18), 446 (16), 200 (4), and 92 (14). Found: C, 55.53; H, 2.59; N, 6.25; Cl, 30.75%. Calcd for $C_{32}H_{19}Cl_6N_3O_2$ (M, 690.239): C, 55.68; H, 2.77; N, 6.09; Cl, 30.82%.

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