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Unusual Reaction of Tetrachlorocyclopentadienone Dimer with Secondary Amines

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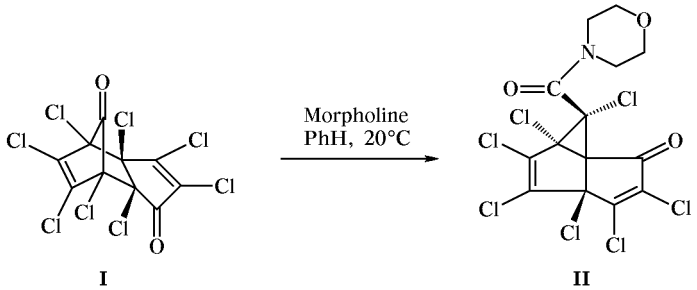
Abstract—Tetrachlorocyclopentadienone dimer reacts with secondary amines to afford unusual products, tricyclic 6-oxo-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalene-1-carboxamide derivatives.

While studying the reaction of [2 + 4]-cycloadduct **I** derived from tetrachlorocyclopentadiene [1] with morpholine under the conditions reported previously [2] for analogous reactions of a series of functionally substituted 2,3-dichloro-2-cyclopentenones, we have revealed formation of an unusual product, tricyclic compound **II** (Scheme 1). Its structure was determined on the basis of spectral data, including X-ray analysis. Other secondary amines, such as diethylamine, dimethylamine, *N*-methylpiperazine, and dipropylamine reacted with dimer **I** in a similar way. Apart from the corresponding tricyclic compounds (**III**, **V**, **VII**, and **VIII**) we isolated minor products arising from partial (compound **VI**) and complete aromatization (**IV** and **IX**) (Scheme 2). The reaction of diketone **I** with dipropylamine afforded exclusively compound **VII**.

Undoubtedly, the most interesting in the above reactions are possible mechanistic aspects of the formation of tricyclic structures **II**, **III**, **V**, **VII**, and **VIII**. It was primarily expected that secondary amine would add (Ad_NE) at the α,β-dichlorocyclopentenone fragment of diketone **I** since an analogous reaction pattern is typical of monomeric 2,3-dichlorocyclopentenones [3, 4]. However, the reaction with amine followed the 1,2-addition pattern at the activated and spatially more accessible carbonyl group with subsequent regioselective cleavage of the bridging bond in anion **A** to generate allylic carbanion **B** which is stabilized due to the presence of chlorine. The isomerization of **B** into carbanion **C** is completed by closure of three-membered ring (Scheme 3).

Presumably, the observed difference in the product composition is explained in terms of different sizes and nucleophilicities of the amines used. In the reactions with sterically unhindered amines, e.g., diethylamine and dimethylamine, closure of the three-membered ring is accompanied by replacement of chlorine at the double bond in **I** by Et_2N or Me_2N group, which is typical of 2,3-dichlorocyclopentenones [3]. Enamino ketone **D** thus formed undergoes aromatization [5] with elimination of carbon(II) oxide and two chlorine atoms to afford the corresponding 3-amino-

Scheme 1.



I **II**

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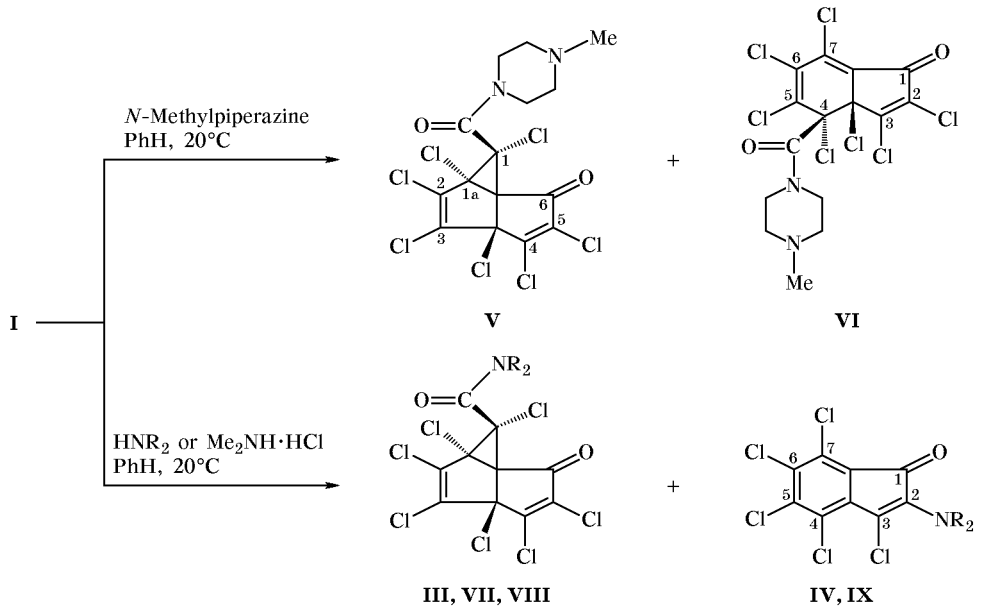
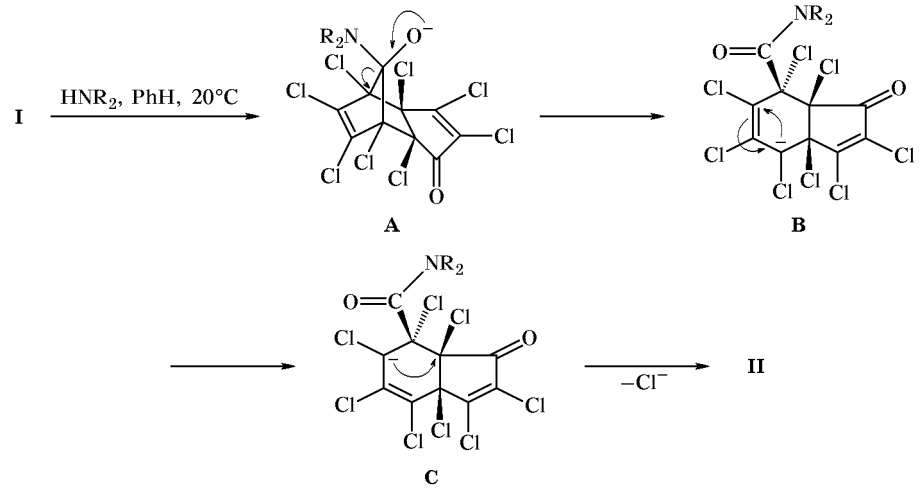
Scheme 2.



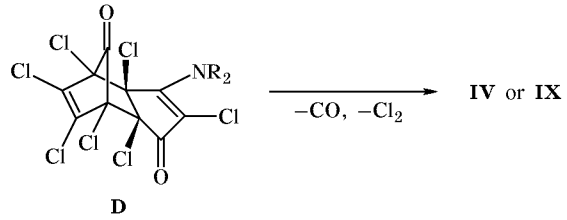
III, **IV**, R = Et; **VII**, R = Pr; **VIII**, **IX**, R = Me.

Scheme 3.



perchloroindenones **IV** and **IX** (Scheme 4). In the reaction with *N*-methylpiperazine we isolated dihydroindenone derivative **VI** as a minor product. It could be formed via partial generation of intermediate aminal **E** in which anchimeric assistance to recyclization through epoxide **F** is possible (Scheme 5; for analogous reaction with MeOH, see [6]).

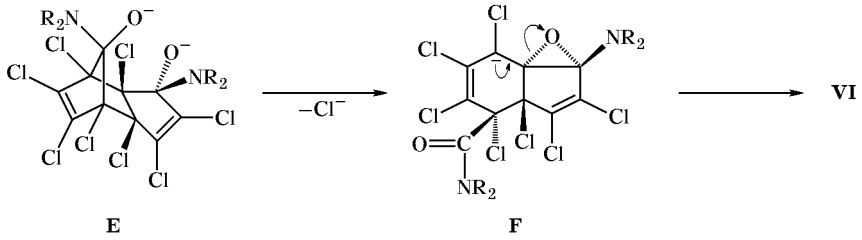
Scheme 4.



EXPERIMENTAL

The IR spectra of samples dispersed in mineral oil were recorded on UR-20 and Specord M-80 spectrophotometers. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-300 instrument at 300.13 and 75.47 MHz, respectively, from solutions in

Scheme 5.



$CDCl_3$. The mass spectra (electron impact, 70 eV) were run on a Varian MAT CH-5 instrument. Silufol UV-254/366 plates were used for thin-layer chromatography; spots were visualized by calcination or treatment with iodine vapor and subsequent wetting with water. The products were isolated by column chromatography on silica gel L 100/160 μm (Chemapol) with a sorbent-to-substrate weight ratio of (30–60):1. Freshly distilled solvents were used as eluents.

Reaction of tetrachlorocyclopentadienone dimer (I) with amines (*typical procedure*). A solution of 3–4 equiv of appropriate secondary amine in 3 ml of benzene was added to a solution of 0.5 g (0.57 mmol) of diketone **I** in 5 ml of benzene, and the mixture was stirred at room temperature until the initial compound disappeared (according to TLC, eluent ethyl acetate–petroleum ether, 1:5). The mixture was diluted with chloroform, washed with a saturated solution of sodium chloride, dried over $MgSO_4$, and evaporated, and the residue was ground with ethyl acetate–petroleum ether (1:10). The product was purified by recrystallization or column chromatography on silica gel.

(1*R,1a*R*,3a*R**,6a*S**)-*N*,*N*-Diethyl-1,1a,2,3,3a,4,5-heptachloro-6-oxo-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalene-1-carboxamide (III).** Yield 50%. Colorless crystals, mp 174–176°C (from ethyl acetate–petroleum ether, 1:10). IR spectrum, ν, cm^{-1}: 1590, 1610 (C=C); 1660 (C=O, amide); 1740 (C=O, ketone). ^1H NMR spectrum, δ, ppm: 1.09 t and 1.22 t (6H, $2CH_3$, $^3J_1$ = 7.1, $^3J_2$ = 7.0 Hz), 3.14 d.q and 3.63 d.q (1H, CH_2N, ^3J = 7.0, ^2J = –14 Hz), 3.25 d.q and 3.43 d.q (1H, CH_2N, ^3J = 7.1, ^2J = –14 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.68, 12.89 ($2CH_3$); 40.39, 44.68 (NCH_2); 49.51 (C^{6a}); 60.38, 60.94 (C^{1a}, C^1); 76.46 (C^{3a}); 127.68 (C^5); 136.78, 136.89 (C^2, C^3); 157.37 (C^4); 159.27 (C=O, amide); 179.58 (C^6). Mass spectrum, *m*/*z*: 477, 475, 473, 471, 469 $[M]^+$ (base peak), 462, 460, 458, 456, 454 $[M - CH_3]^+$, 440, 438, 436, 434 $[M - Cl]^+$, 414, 412, 410, 408 $[M - Cl - C_2H_4]^+$, 100 $[Et_2NC{\equiv}O]^+$, 72 $[Et_2N]^+$. Found, %: C 35.16; H 2.10; Cl 51.86; N 2.60. $C_{14}H_{10}Cl_7NO_2$. Calculated, %: C 35.59; H 2.13; Cl 52.53; N 2.96.

2,4,5,6,7-Pentachloro-3-diethylamino-1*H*-inden-1-one (IV). Yield ~10%. Dark red needles, mp 188–190°C (from ethyl acetate–petroleum ether, 1:10). IR spectrum, ν, cm^{-1}: 1460, 1580 (C=C); 1695 (C=O). ^1H NMR spectrum, δ, ppm: 1.22 t (6H, CH_3, *J* = 7.1 Hz), 3.56 q (4H, CH_2, *J* = 7.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.67 (CH_3), 46.85 (NCH_2), 113.55 (C^2), 124.98 (C^{3a}), 127.83 (C^7, C^{7a}), 135.28 (C^4), 136.57 (C^5), 137.84 (C^6), 159.98 (C^3), 181.77 (C^1).

(1*R,1a*R**,3a*R**,6a*S**)-1,1a,2,3,3a,4,5-Heptachloro-1-(4-methyl-1-piperazinylcarbonyl)-1,1a,-3a,6-tetrahydrocyclopropa[*c*]pentalen-6-one (V).** Yield 35% (overall yield 57% with triene **VI**). Colorless crystals, mp 208.5–210°C (from ethyl acetate–petroleum ether, 1:10). IR spectrum, ν, cm^{-1}: 1596, 1604 (C=C); 1660 (C=O, amide), 1748 (C=O, ketone). ^1H NMR spectrum, δ, ppm: 2.20 d.t (1H, *J* = 12.0, 2.9 Hz) and 2.34 d.t (1H, 5′-H_2, *J* = 10.4, 2.6 Hz), 2.29 s (3H, CH_3), 2.6 d (2H, 3′-H_2), 3.14 t (1H, *J* = 10.6 Hz) and 3.34 t (1H, 2′-H_2, *J* = 10.1, 3.7 Hz), 3.81 d (1H, *J* = 13.4 Hz) and 3.98 d (1H, 6′-H_2, *J* = 13.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 42.80 and 47.86 (NCH_2), 45.62 (CH_3), 49.38 (C^{6a}), 53.75 and 53.97 ($C^{2'}$, $C^{6'}$), 59.59 and 60.46 (C^1, C^{1a}), 76.26 (C^{3a}), 127.87 (C^5), 136.56 and 136.62 (C^3, C^2), 157.29 (C^4), 158.45 (C=O, amide), 179.48 (C^5). Found, %: C 35.90; H 2.20; Cl 48.94; N 5.20. $C_{15}H_{11}Cl_7N_2O_2$. Calculated, %: C 36.07; H 2.22; Cl 49.69; N 5.61.

(3a*S,4*S**)-2,3,3a,4,5,6,7-Heptachloro-4-(4-methyl-1-piperazinylcarbonyl)-3a,4-dihydro-1*H*-inden-1-one (VI).** Yield 22%. Red crystals, mp 202–204°C (decomp.; from ethyl acetate–petroleum ether, 1:10). IR spectrum, ν, cm^{-1}: 1460, 1584, 1612 (C=C); 1660 (C=O, amide), 1700 (C=O, ketone). ^1H NMR spectrum, δ, ppm: 2.31 s (3H, CH_3), 2.56 m (4H, 5′-H_2, 3′-H_2), 3.58 t (4H, 2′-H_2, 6′-H_2, *J* = 4.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 46.02 (CH_3),

51.48 and 55.19 (NCH_2), 53.85 (C^{3a}), 77.20 (C^4), 124.95 (C^2), 127.93 (C^{7a}), 128.01 (C^7), 135.53 (C^5), 136.19 (C^6), 137.78 (C^3), 159.19 (C=O, amide), 181.25 (C^1).

(1*R,1a*R**,3a*R**,6a*S**)-*N*,*N*-Dipropyl-1,1a,2,3,3a,-4,5-heptachloro-6-oxo-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalene-1-carboxamide (VII).** Yield 30%. Colorless crystals, mp 153–155°C (from ethyl acetate–petroleum ether, 1:10). IR spectrum, ν, cm^{-1}: 1460, 1560, 1600 (C=C); 1656 (C=O, amide); 1748 (C=O, ketone). ^1H NMR spectrum, δ, ppm: 0.86 t (3H, *J* = 7.4 Hz) and 0.91 t (3H, CH_3, *J* = 7.4 Hz), 1.52 m (2H) and 1.72 m (2H, CH_2), 2.87 m (1H), 3.15 m (1H), 3.24 m (1H) and 3.40 m (1H, NCH_2). ^{13}C NMR spectrum, δ_C, ppm: 11.18 and 11.37 (CH_3), 19.63 and 20.94 (CH_2), 48.09 and 52.25 (NCH_2), 49.41 (C^{6a}), 60.21 and 60.85 (C^{1a}, C^1), 76.28 (C^{3a}), 127.56 (C^5), 136.67 and 136.67 (C^2, C^3), 157.24 (C^4), 159.27 (C=O, amide), 179.46 (C^6).

Reaction of tetrachlorocyclopentadienone dimer (I) with dimethylamine hydrochloride. Dimethylamine hydrochloride, 0.3 g (3.68 mmol), was added to a suspension of 0.19 g (3.45 mmol) of KOH in 5 ml of benzene, the mixture was stirred for 15 min, a solution of 0.5 g (1.15 mmol) of diketone **I** in 3 ml of benzene was added dropwise, and the mixture was stirred at room temperature until initial diketone **I** disappeared (TLC, ethyl acetate–petroleum ether, 1:5). The mixture was treated as described above, and the product was subjected to chromatographic separation in a column charged with silica gel (eluent ethyl acetate–petroleum ether, 1:5) to isolate 0.14 g (28%) of compound **VIII** and 0.08 g (20%) of indenone **IX** (overall yield 48%).

(1*R,1a*R**,3a*R**,6a*S**)-*N*,*N*-Dimethyl-1,1a,2,3,3a,-4,5-heptachloro-6-oxo-1,1a,3a,6-tetrahydrocyclopropa[*c*]pentalene-1-carboxamide (VIII).** Colorless crystals, mp 170–172°C (from ethyl acetate–petroleum ether, 1:10). IR spectrum, ν, cm^{-1}: 1588, 1608 (C=C); 1660, 1664, 1668 (C=O, amide); 1744 (C=O, ketone). ^1H NMR spectrum, δ, ppm: 2.93 s (3H) and 3.11 s (3H, $2CH_3$). ^{13}C NMR spectrum, δ_C, ppm: 36.02 and 39.01 (NCH_3), 48.97 (C^{6a}), 59.61 and 60.66 (C^{1a}, C^1), 76.46 (C^{3a}), 127.81 (C^5), 136.65 and 136.81 (C^2, C^3), 157.30 (C^4), 159.41 (C=O, amide), 179.40 (C^6).

2,4,5,6,7-Pentachloro-3-dimethylamino-1*H*-inden-1-one (IX). Dark red needles, mp 200–202°C (from ethyl acetate–petroleum ether, 1:10); published data [7]: mp 198.5–199.5°C. IR spectrum, ν, cm^{-1}: 1460, 1588 (C=C); 1696 (C=O). ^1H NMR spectrum, δ, ppm: 3.01 m (6H, $2CH_3$). ^{13}C NMR spectrum, δ_C, ppm: 43.90 (NCH_3), 109.96 (C^2), 124.80 (C^{3a}), 127.75 (C^7), 128.11 (C^{7a}), 135.52 (C^4), 136.07 (C^5), 137.63 (C^6), 161.02 (C^3), 181.13 (C^1). Found, %: C 38.80; H 1.70; Cl 50.93; N 4.25. $C_{11}H_6Cl_5NO$. Calculated, %: C 38.25; H 1.75; Cl 51.32; N 4.05.

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REFERENCES

1. Newcomer, J.S. and McBee, E.T., *J. Am. Chem. Soc.*, 1949, vol. 71, p. 946.
2. Akhmetvaleev, R.R., Akbutina, F.A., Ivanova, N.A., and Miftakhov, M.S., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2001, p. 1417.
3. Tolstikov, G.A., Ismailov, S.A., Prishchepova, E.V., and Miftakhov, M.S., *Zh. Org. Khim.*, 1991, vol. 27, p. 2334.
4. Tolstikov, G.A., Ismailov, S.A., Prishchepova, E.V., and Miftakhov, M.S., *Zh. Org. Khim.*, 1991, vol. 27, p. 2539.
5. Chertanova, L.F., Akbutina, F.A., Torosyan, S.A., Khalilov, L.M., and Miftakhov, M.S., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1997, p. 1979.
6. Weil, E.D. and Linder, J., *J. Org. Chem.*, 1963, vol. 28, p. 2218.
7. McBee, E.T., Stoffer, J.Q., and Braendlin, H.P., *J. Am. Chem. Soc.*, 1962, vol. 84, p. 4540.