p-Fluorophenylmercuric chloride (VIII) was obtained by analogy with (VI) from fluorobenzene in 75% yield, mp 280°C [8].

CONCLUSIONS

The reaction of difluoronitroacetic acid with mercuric oxide in aromatic hydrocarbons proceeds by mercuration of the aromatic ring and formation of arylmercury salts of difluoronitroacetic acid. Aryl derivatives of mercuric chloride are obtained in the case of fluorochloronitroacetic acid.

LITERATURE CITED

1. G. A. Razuvaev, N. S. Vasilevskaya, and L. A. Nikitina, Tr. Khim. Khim. Tekhnol., 3, 38 (1960).
2. P. E. Aldrich, US Patent No. 30043859 (1962); Chem. Abstr., 57, 14944 (1962).
3. A. V. Fokin, V. A. Komarov, A. F. Kolomets, A. I. Rapkin, and T. M. Pomarina, Izv. Akad. Nauk SSSR, Ser. Khim., 707 (1978).
4. T. N. Srivastava and M. M. J. Pande, J. Indian Chem. Soc., 60, No. 10, 914 (1983).
5. B. Deacon and S. F. Taylor Brion, Austral. J. Chem., 34, 30 (1981).
6. I. V. Martynov, V. K. Brel', L. V. Postnova, and B. I. Martynov, Izv. Akad. Nauk SSSR, Ser. Khim., 2832 (1984).
7. T. J. Logan, J. Org. Chem., 28, 1129 (1963).
8. F. Whitemore, Organic Mercury Compounds [Russian translation], Izd. ONTI, Leningrad (1938), pp. 145, 153, 159.

CHLORINATION OF 3,6-DI-TERT-BUTYL-o-BENZOQUINONE BY SULFURYL CHLORIDE

V. A. Garnov, V. I. Nevodchikov, G. A. Abakumov,
V. K. Cherkasov, L. G. Abakumova, and Yu. A. Kurskii

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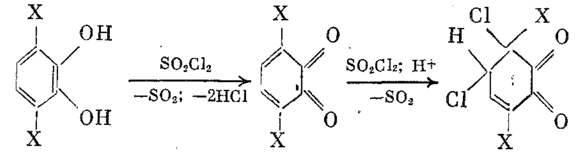
In order to expand the range of sterically hindered o-benzoquinones, we studied the chlorination of 3,6-di-tert-butyl-o-benzoquinone (I) by SO_2Cl_2. Ershov et al. have shown that the reactions of HCl with (I) [1] or of Cl_2 and 3,6-di-tert-butylpyrocatechol (II) [2] cannot introduce two chlorine atoms. However, Peratoner [3] established that the reaction of two equivalents of SO_2Cl_2 with pyrocatechol in absolute ether in the cold leads to the formation of 4,5-dichloropyrocatechol. In the present work, we have shown that under analogous conditions, (II) gives 5,6-dichloro-3,6-di-tert-butyl-3-cyclohexene-1,2-dione (III):



(II) (I) (III)

(1)

Here and subsequently, X = t-Bu.

The action of diethylamine on (III) in pentane gives 4-chloro-3,6-di-tert-butyl-o-benzoquinone (IV) [1], which reacts with one equivalent of SO_2Cl_2 in the presence of HCl to give 4,5,6-trichloro-3,6-di-tert-butyl-3-cyclohexene-1,2-dione (V). Upon treatment with amine, dione (V) is converted to 4,5-dichloro-3,6-di-tert-butyl-o-benzoquinone (VI):

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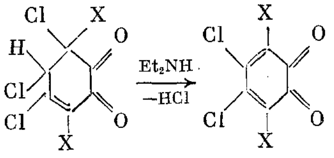


(V) (VI)

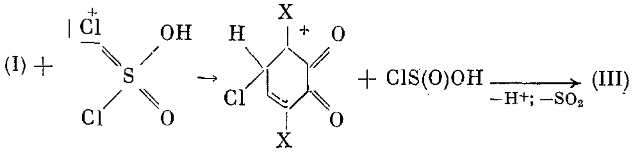
(2)

The structures of (III)-(VI) were established by IR and PMR spectroscopy. The IR spectrum of (III) has two bands in the C=O stretching region at 1680 and 1743 cm^{-1}. The band at 1680 cm^{-1} is characteristic for a keto group conjugated with a double bond, while the band at 1743 cm^{-1} is characteristic for a keto group of a cyclohexanone whose frequency is elevated due to the electrostatic interaction with the α-chlorine atom. The IR spectrum of (V) shows stretching bands for two different carbonyl groups at 1695 and 1752 cm^{-1}. Products (IV) and (VI) have bands in the C=O stretching region at 1680 and 1695 cm^{-1}, respectively, which are typical for o-benzoquinones.

These spectral data are in accord with the chemical properties of these compounds. Benzoquinones (IV) and (VI), similar to all o-quinones, are reduced by Na or Tl to paramagnetic o-semiquinones and then to disodium or dithallium derivatives of the corresponding pyrocatechols, while (III) and (V) react more slowly with thallium to form dechlorination products, namely, o-semiquinones (I) and (IV) and then dithallium derivatives of pyrocatechols.

Dione (III) is formed not only by reaction (1) but also by the treatment of (I) with SO_2Cl_2 in the presence of small amounts of HCl, hydrochloric or sulfuric acids, or (II). We should note that hydrochloric acid is capable of accelerating reaction (1) more than HCl, which indicates protic catalysis. Compounds (I) and (IV) do not react with SO_2Cl_2 in the absence of acids.

These results indicate that the role of acids lies in the protonation of SO_2Cl_2 providing for electrophilic attack of the species formed on the quinone.



(3)

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in Vaseline mull, while the PMR spectra were taken on a Tesla BS-487C spectrometer in CCl_4 with TMS as the internal standard. The melting points were not corrected. The product yields in all steps were close to quantitative.

5,6-Dichloro-3,6-di-tert-butyl-3-cyclohexene-1,2-dione (III). a) A sample of 25 mmoles SO_2Cl_2 was added with cooling to a solution of 10 mmoles (II) [4] in 15 ml ether. The solution was stirred until the color of (I) disappeared and a large portion of (III) had precipitated. The reaction mixture was filtered, and the filtrate was washed with water, aq. sodium carbonate, and again with water until neutral and dried over Na_2SO_4. Ether was removed, and the combined product was recrystallized from heptane to yield light-yellow crystals, mp 153°C. Found: C 57.69; H 6.92; Cl 24.34%. Calculated for $C_{14}H_{20}Cl_2O_2$: C 57.73; H 6.94; Cl 24.34%. IR spectrum (ν, cm^{-1}): 1680 s, 1743 s. PMR spectrum (δ, ppm): 1.25 s (9H), 1.41 s (9H), 5.10 d (1H, J = 6.4 Hz), 6.83 d (1H, J = 6.4 Hz).

b) A sample of 15 mmoles SO_2Cl_2 was added to a solution of 10 mmoles (I) [5] in ether and then one drop of concentrated hydrochloric acid was added. The solution was maintained with occasional agitation until the color of (I) had completely disappeared. The product was isolated as in procedure a.

4-Chloro-3,6-di-tert-butyl-o-benzoquinone (IV). A sample of 12 mmoles Et_2NH was added to a solution of 10 mmoles (III) in pentane. The precipitate was removed, and the filtrate was maintained for 1 h, washed with water until neutral, and dried over Na_2SO_4. After removal of pentane, the product was recrystallized from heptane to yield dark cherry-red crystals, mp 50°C. Found: C 66.01; H 7.50; Cl 13.89%. Calculated for $C_{14}H_{19}ClO_2$: C 65.99; H 7.53; Cl 13.92%. IR spectrum (ν, cm^{-1}): 1680 S. PMR spectrum (δ, ppm): 1.25 s (9H), 1.40 s (9H), 6.66 s (1H).

4,5,6-Trichloro-3,6-di-tert-butyl-3-cyclohexene-1,2-dione (V) was obtained according to procedure b for the synthesis of (III) as light-yellow crystals, mp 86°C. Found: C 51.67; H 5.84; Cl 32.70%. Calculated for $C_{14}H_{19}Cl_3O_2$: C 51.63; H 5.89; Cl 32.65%. IR spectrum (ν, cm^{-1}): 1695 s, 1752 s. PMR spectrum (δ, ppm): 1.37 s (9H), 1.40 s (9H), 4.83 s (1H).

4,5-Dichloro-3,6-di-tert-butyl-o-benzoquinone (VI) was obtained according to the method used to obtain (IV) as dark rasberry-red crystals, mp 48°C. Found: C 58.09' H 6.29; Cl 24.51%. Calculated for $C_{14}H_{18}Cl_2O_2$: C 58.13; H 6.29; Cl 24.52%. IR spectrum (ν, cm^-): 1695 s. PMR spectrum (δ, ppm): 1.41 s.

CONCLUSIONS

1. A study of the chlorination of 3,6-di-tert-butylpyrocatechol and its corresponding quinone and 4-chloro-3,6-di-tert-butyl-o-benzoquinone by sulfuryl chloride showed that this method may serve as a preparative method for obtaining 4-chloro-3,6-di-tert-butyl-o-benzoquinone and 4,5-dichloro-3,6-di-tert-butyl-o-benzoquinone.

2. A mechanism was established for the reaction of 4-X-3,6-di-tert-butyl-o-benzoquinone (X = H, Cl) with SO_2Cl_2 involving the protonation of SO_2Cl_2.

LITERATURE CITED

1. I. A. Novikova, V. B. Vol'eva, N. L. Komisarova, N. S. Belostotskaya, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim, 2110 (1981).
2. V. B. Vol'eva, I. A. Novikova, N. S. Belostotskaya, É. V. Dzhuaryan, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1416 (1985).
3. Peratoner, Gazz. Chim Ital., 28, 222 (1898).
4. N. S. Belostotskaya, N. L. Komissarova, É. V. Dzhuaryan, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1594 (1972).
5. N. L. Komissarova, N. S. Belostotskaya, É. V. Dzhuaryan, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1380 (1973).