

Synthesis of 2,4-Diaryloxy-6-trinitromethyl-1,3,5-triazines

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Abstract—Reactions of 2,4,6-trichloro-1,3,5-triazine with trinitromethane salts in the presence of phenol and substituted phenols gave previously unknown 2,4-diaryloxy-6-trinitromethyl-1,3,5-triazines. Their yields strongly depend on the nature and position of substituent in the benzene ring of phenol.

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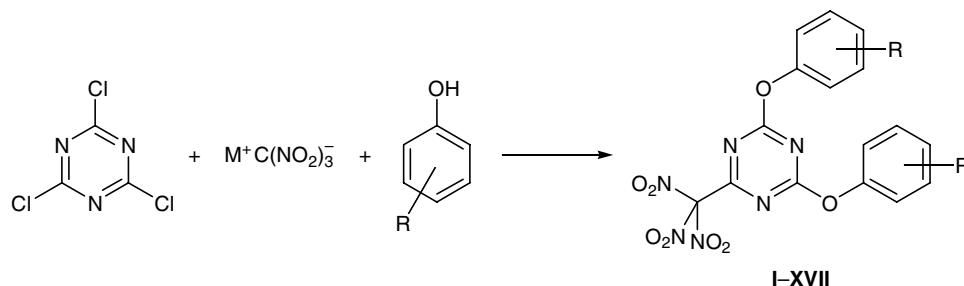
During the last 10–15 years, the chemistry of trinitromethyl derivatives of 1,3,5-triazine has been extensively studied [1]. Several procedures have been proposed for the synthesis of trinitromethyl-1,3,5-triazines having various substituents; these procedures are based on destructive nitration of 1,3,5-triazine derivatives [2, 3] and nucleophilic replacement of already existing trinitromethyl groups [4–6]. Up to now, the only method for the synthesis of aryloxytrinitromethyl-1,3,5-triazines was nucleophilic substitution of the trinitromethyl group in 2-amino(alkoxy)-4,6-bis-(trinitromethyl)-1,3,5-triazines by the action of phenol and substituted phenols [6]. 2,4-Diaryloxy-6-trinitromethyl-1,3,5-triazines were not reported previously. In the present communication we describe a new procedure for the preparation of 2,4-diaryloxy-6-trinitromethyl-1,3,5-triazines, which allows simultaneous introduction of trinitromethyl and aryloxy groups into the 1,3,5-triazine ring.

By treatment of 2,4,6-trichloro-1,3,5-triazine with trinitromethane salts in the presence of phenol and

a series of substituted phenols in acetone at 0–30°C we obtained 2,4-diaryloxy-6-trinitromethyl-1,3,5-triazines **I–XVII** (Scheme 1). The yield of products **I–XVII** does not depend on the nature of cation in the trinitromethane salt but is completely determined by the substituent in the initial phenol: electron-withdrawing substituents (NO_2 , COOCH_3 , Hlg) in the benzene ring of phenol ensure higher yields as compared with unsubstituted phenol and phenols having electron-donor substituents (e.g., methyl group). The position of substituent with respect to the hydroxy group is also important: the yield of 2,4-diaryloxy-6-trinitromethyl-1,3,5-triazines increases in the series *ortho*-substituted phenols $\approx$ unsubstituted phenol $<$ *meta*-substituted phenols $<$ *para*-substituted phenols.

The reaction begins with nucleophilic replacement of one chlorine atom in the 2,4,6-trichloro-1,3,5-triazine molecule by trinitromethyl group. By special experiments we showed that neither 2,4-dichloro-6-phenoxy-1,3,5-triazine (**XVIII**) nor 2-chloro-4,6-diphenoxy-1,3,5-triazine (**XIX**) reacted with potassium

Scheme 1.



I, R = H; **II**, R = *o*-Me; **III**, R = *o*-MeOCO; **IV**, R = *o*-I; **V**, R = *o*-Cl; **VI**, R = *o*-O₂N; **VII**, R = *m*-Me; **VIII**, R = *m*-MeOCO; **IX**, R = *m*-Cl; **X**, R = *m*-O₂N; **XI**, R = *p*-Me; **XII**, R = *p*-*t*-Bu; **XIII**, R = *p*-Cl; **XIV**, R = *p*-Br; **XV**, R = *p*-MeOCO; **XVI**, R = *p*-O₂N; **XVII**, R = 2,4-(O₂N)₂; M = K, Na, Li, NH₄, Me₂NH₂, Et₃NH, Me₄N, Et₃MeN.

trinitromethanide with formation of compound **I** under the conditions ensuring formation of compounds **I–XVII**. Presumably, introduction of the first trinitromethyl group into the 1,3,5-triazine ring is the rate-determining stage of the entire process leading to 2,4-diaryloxy-6-trinitromethyl-1,3,5-triazines. The subsequent steps are considerably faster; after complete consumption of 2,4,6-trichloro-1,3,5-triazine, increase of the reaction time did not result in increased yield of compounds **I–XVII**.

However, some experimental data are difficult to rationalize in terms of nucleophilic replacement of chlorine in 2,4,6-trichloro-1,3,5-triazine by the action of trinitromethanide ion and phenols. First, GLC analysis of the reaction mixtures revealed the presence of small amounts of chlorotrinitromethane (2–4 mol % with respect to 2,4,6-trichloro-1,3,5-triazine). Second, we failed to obtain the corresponding 2,4-diaryloxy-6-trinitromethyl-1,3,5-triazines from a number of phenols having strong electron-donor groups ($R = o\text{-HO}$, $m\text{-HO}$, $p\text{-HO}$, $o\text{-MeO}$, $m\text{-MeO}$, $p\text{-MeO}$, $p\text{-AcNH}$). The reaction was accompanied by fast (at 15–30°C) or slow (at –10 to –15°C) decomposition with gas evolution and formation of cyanuric acid, inorganic salts, and unidentified phenol oxidation products.

However, nucleophilic replacement of the trinitromethyl group in 2-amino-4,6-bis(trinitromethyl)-1,3,5-triazines readily occurs by the action of the same phenols and gives the corresponding 2-amino-4-aryloxy-6-trinitromethyl-1,3,5-triazines in high yields [6]. These data suggest that the reaction of 2,4,6-trichloro-1,3,5-triazine with trinitromethane salts in the presence of various phenols involves formation of radical intermediates.

EXPERIMENTAL

The IR spectra were measured in KBr (except for compound **VII** which was examined as thin film) on an Avatar spectrophotometer. The ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer at 300 MHz using tetramethylsilane as internal reference.

Compounds **XVIII** and **XIX** were synthesized by the procedure described in [7].

2,4-Diaryloxy-6-trinitromethyl-1,3,5-triazines I–XVII (general procedure). Potassium trinitromethanide, 5.67–9.45 g (0.03–0.05 mol), and the corresponding phenol, 0.025–0.04 mol, were added under stirring to a solution of 1.84 g (0.01 mol) of 2,4,6-trichloro-1,3,5-triazine in 13 ml of acetone at 19–22°C. The

mixture was stirred at 19–22°C until 2,4,6-trichloro-1,3,5-triazine disappeared (19–30 h) according to the TLC data (Silufol UV-254 plates). The mixture was filtered, the filtrate was partially evaporated, the residue was poured under stirring into 100 ml of water, and the precipitate was filtered off, washed with propan-2-ol and water, and dried in air. Compound **VII** was isolated by extraction into dichloroethane. The extract was washed with water and dried over sodium sulfate, the solvent was distilled off, and the residue was dried under reduced pressure.

2,4-Diphenoxy-6-trinitromethyl-1,3,5-triazine (I). Yield 32%, mp 82–83°C. IR spectrum, ν , cm^{-1} : 3066, 2876, 1628, 1598, 1574, 1538, 1488, 1466, 1386, 1326, 1288, 1234, 1192, 1164, 1114, 1072, 1022, 1004, 988, 914, 844, 830, 798, 764. ^1H NMR spectrum, δ , ppm: 6.70–7.84 m (10H, H_{arom}). Found, %: C 46.35; H 2.50; N 20.28. $\text{C}_{16}\text{H}_{10}\text{N}_6\text{O}_8$. Calculated, %: C 46.39; H 2.43; N 20.29.

2,4-Bis(2-methylphenoxy)-6-trinitromethyl-1,3,5-triazine (II). Yield 20%, mp 84–86°C. IR spectrum, ν , cm^{-1} : 3028, 2936, 1644, 1600, 1580, 1540, 1496, 1480, 1402, 1334, 1294, 1252, 1184, 1126, 1112, 996, 912, 834, 804, 792, 750, 720. ^1H NMR spectrum, δ , ppm: 2.06 s (6H, CH_3), 6.99–7.25 m (8H, H_{arom}). Found, %: C 48.87; H 3.19; N 19.00. $\text{C}_{18}\text{H}_{14}\text{N}_6\text{O}_8$. Calculated, %: C 48.82; H 3.24; N 19.04.

Dimethyl 2,2'-[6-trinitromethyl-1,3,5-triazine-2,4-diylidioxy]dibenzoate (III). Yield 25%, mp 134–136°C (decomp.). IR spectrum, ν , cm^{-1} : 3032, 1726, 1638, 1630, 1598, 1578, 1550, 1472, 1464, 1456, 1392, 1304, 1280, 1214, 1138, 1096, 1076, 1014, 813, 796, 764. ^1H NMR spectrum, δ , ppm: 3.72 s (6H, OCH_3), 7.30–8.00 m (8H, H_{arom}). Found, %: C 45.34; H 2.58; N 15.76. $\text{C}_{20}\text{H}_{14}\text{N}_6\text{O}_{12}$. Calculated, %: C 45.29; H 2.66; N 15.85.

2,4-Bis(2-iodophenoxy)-6-trinitromethyl-1,3,5-triazine (IV). Yield 24%, mp 119–121°C (decomp.). IR spectrum, ν , cm^{-1} : 3040, 1632, 1604, 1596, 1570, 1556, 1546, 1516, 1464, 1444, 1386, 1338, 1292, 1270, 1242, 1212, 1126, 1096, 1050, 1032, 998, 912, 840, 826, 794, 758. ^1H NMR spectrum, δ , ppm: 6.98–7.91 m (8H, H_{arom}). Found, %: C 28.77; H 1.26; N 12.63. $\text{C}_{16}\text{H}_8\text{I}_2\text{N}_6\text{O}_8$. Calculated, %: C 28.85; H 1.21; N 12.62.

2,4-Bis(2-chlorophenoxy)-6-trinitromethyl-1,3,5-triazine (V). Yield 23%, mp 64–66°C. IR spectrum, ν , cm^{-1} : 2916, 1634, 1600, 1572, 1556, 1512, 1484, 1464, 1394, 1332, 1296, 1220, 1210, 1108, 1066, 1000, 914,

868, 842, 794, 760, 726. ^1H NMR spectrum, δ , ppm: 7.18–7.39 m (8H, H_{arom}). Found, %: C 39.72; H 1.69; N 17.44. $\text{C}_{16}\text{H}_8\text{Cl}_2\text{N}_6\text{O}_8$. Calculated, %: C 39.77; H 1.67; N 17.39.

2,4-Bis(2-nitrophenoxy)-6-trinitromethyl-1,3,5-triazine (VI). Yield 34%, mp 170–172°C (decomp.). IR spectrum, ν , cm^{-1} : 3116, 2872, 1638, 1600, 1566, 1534, 1458, 1396, 1362, 1352, 1330, 1296, 1276, 1208, 1172, 1154, 1112, 1090, 1004, 960, 916, 884, 868, 858, 836, 798, 780, 750, 708. ^1H NMR spectrum, δ , ppm: 7.48–8.19 m (8H, H_{arom}). Found, %: C 38.04; H 1.70; N 22.21. $\text{C}_{16}\text{H}_8\text{N}_8\text{O}_{12}$. Calculated, %: C 38.11; H 1.60; N 22.22.

2,4-Bis(3-methylphenoxy)-6-trinitromethyl-1,3,5-triazine (VII). Yield 40%, viscous liquid. IR spectrum, ν , cm^{-1} : 2932, 1640, 1632, 1606, 1580, 1544, 1530, 1494, 1474, 1396, 1350, 1338, 1294, 1248, 1234, 1162, 1012, 996, 944, 828, 796. ^1H NMR spectrum, δ , ppm: 2.25 s (6H, CH_3), 6.95–7.12 m (8H, H_{arom}). Found, %: C 48.77; H 3.26; N 19.07. $\text{C}_{18}\text{H}_{14}\text{N}_6\text{O}_8$. Calculated, %: C 48.82; H 3.24; N 19.04.

Dimethyl 3,3'-[6-trinitromethyl-1,3,5-triazine-2,4-diylldioxy]dibenzoate (VIII). Yield 54%, mp 114–116°C. IR spectrum, ν , cm^{-1} : 3078, 3000, 2954, 1726, 1628, 1596, 1572, 1544, 1462, 1446, 1384, 1288, 1270, 1184, 1108, 1076, 988, 928, 906, 868, 832, 798, 760. ^1H NMR spectrum, δ , ppm: 3.84 s (6H, OCH_3), 7.44–7.86 m (8H, H_{arom}). Found, %: C 45.31; H 2.71; N 15.83. $\text{C}_{20}\text{H}_{14}\text{N}_6\text{O}_{12}$. Calculated, %: C 45.29; H 2.66; N 15.85.

2,4-Bis(3-chlorophenoxy)-6-trinitromethyl-1,3,5-triazine (IX). Yield 52%, mp 78–80°C. IR spectrum, ν , cm^{-1} : 3110, 3080, 2880, 1634, 1628, 1602, 1590, 1580, 1570, 1550, 1542, 1520, 1510, 1482, 1468, 1440, 1388, 1354, 1336, 1296, 1274, 1242, 1208, 1168, 1108, 1080, 1012, 996, 930, 854, 828, 796, 780, 728. ^1H NMR spectrum, δ , ppm: 7.20–7.42 m (8H, H_{arom}). Found, %: C 39.81; H 1.63; N 17.42. $\text{C}_{16}\text{H}_8\text{Cl}_2\text{N}_6\text{O}_8$. Calculated, %: C 39.77; H 1.67; N 17.39.

2,4-Bis(3-nitrophenoxy)-6-trinitromethyl-1,3,5-triazine (X). Yield 59%, mp 160–162°C (decomp.). IR spectrum, ν , cm^{-1} : 3140, 3125, 1640, 1606, 1580, 1565, 1542, 1464, 1390, 1358, 1284, 1245, 1216, 1115, 1086, 1000, 946, 834, 796, 740. ^1H NMR spectrum, δ , ppm: 7.71–8.12 m (8H, H_{arom}). Found, %: C 38.14; H 1.62; N 22.31. $\text{C}_{16}\text{H}_8\text{N}_8\text{O}_{12}$. Calculated, %: C 38.11; H 1.60; N 22.22.

2,4-Bis(4-methylphenoxy)-6-trinitromethyl-1,3,5-triazine (XI). Yield 49%, mp 124–126°C

(decomp.). IR spectrum, ν , cm^{-1} : 3030, 2980, 1638, 1600, 1584, 1542, 1514, 1472, 1396, 1292, 1228, 1200, 1176, 1118, 1102, 1028, 996, 914, 844, 792. ^1H NMR spectrum, δ , ppm: 2.27 s (6H, CH_3), 7.13 s (8H, H_{arom}). Found, %: C 48.84; H 3.27; N 19.10. $\text{C}_{18}\text{H}_{14}\text{N}_6\text{O}_8$. Calculated, %: C 48.82; H 3.24; N 19.04.

2,4-Bis(4-tert-butylphenoxy)-6-trinitromethyl-1,3,5-triazine (XII). Yield 50%, mp 165–167°C (decomp.). IR spectrum, ν , cm^{-1} : 3062, 2962, 2904, 2870, 1628, 1596, 1574, 1540, 1508, 1466, 1388, 1326, 1288, 1270, 1204, 1174, 1112, 1086, 1014, 988, 918, 840, 798. ^1H NMR spectrum, δ , ppm: 1.26 s (18H, CH_3), 7.13 d and 7.30 d (8H, H_{arom} , $J = 6.9$ Hz). Found, %: C 54.82; H 5.02; N 15.90. $\text{C}_{24}\text{H}_{26}\text{N}_6\text{O}_8$. Calculated, %: C 54.75; H 4.98; N 15.96.

2,4-Bis(4-chlorophenoxy)-6-trinitromethyl-1,3,5-triazine (XIII). Yield 56%, mp 105–107°C. IR spectrum, ν , cm^{-1} : 3056, 2976, 2960, 2908, 2872, 1614, 1608, 1578, 1550, 1514, 1466, 1396, 1344, 1316, 1276, 1210, 1184, 1120, 1096, 1024, 998, 980, 968, 900, 860, 824, 812, 782. ^1H NMR spectrum, δ , ppm: 7.25 d and 7.43 d (8H, H_{arom} , $J = 7.5$ Hz). Found, %: C 39.73; H 1.66; N 17.42. $\text{C}_{16}\text{H}_8\text{Cl}_2\text{N}_6\text{O}_8$. Calculated, %: C 39.77; H 1.67; N 17.39.

2,4-Bis(4-bromophenoxy)-6-trinitromethyl-1,3,5-triazine (XIV). Yield 60%, mp 126–128°C. IR spectrum, ν , cm^{-1} : 3072, 1640, 1608, 1592, 1580, 1538, 1490, 1412, 1388, 1296, 1266, 1196, 1176, 1076, 1022, 1000, 940, 908, 832, 808, 792, 728. ^1H NMR spectrum, δ , ppm: 7.18 d and 7.57 d (8H, H_{arom} , $J = 7.9$ Hz). Found, %: C 33.65; H 1.40; N 14.63. $\text{C}_{16}\text{H}_8\text{Br}_2\text{N}_6\text{O}_8$. Calculated, %: C 33.59; H 1.41; N 14.69.

Dimethyl 4,4'-[6-trinitromethyl-1,3,5-triazine-2,4-diylldioxy]dibenzoate (XV). Yield 58%, mp 158–159°C (decomp.). IR spectrum, ν , cm^{-1} : 3064, 2964, 1726, 1632, 1602, 1580, 1554, 1510, 1460, 1444, 1388, 1290, 1238, 1216, 1200, 1168, 1124, 1024, 1000, 956, 912, 864, 848, 828, 812, 794, 768, 720, 696. ^1H NMR spectrum, δ , ppm: 3.83 s (6H, OCH_3), 7.34 d and 8.00 d (8H, H_{arom} , $J = 8.2$ Hz). Found, %: C 45.25; H 2.69; N 15.89. $\text{C}_{20}\text{H}_{14}\text{N}_6\text{O}_{12}$. Calculated, %: C 45.29; H 2.66; N 15.85.

2,4-Bis(4-nitrophenoxy)-6-trinitromethyl-1,3,5-triazine (XVI). Yield 65%, mp 169–170°C (decomp.). IR spectrum, ν , cm^{-1} : 3118, 3088, 1612, 1540, 1488, 1338, 1288, 1254, 1238, 1210, 1200, 1164, 1108, 1014, 990, 954, 914, 860, 842, 818, 798. ^1H NMR spectrum, δ , ppm: 7.52 d and 8.30 d (8H, H_{arom} , $J = 8.6$ Hz). Found, %: C 38.08; H 1.56; N 22.15. $\text{C}_{16}\text{H}_8\text{N}_8\text{O}_{12}$. Calculated, %: C 38.11; H 1.60; N 22.22.

2,4-Bis(2,4-dinitrophenoxy)-6-trinitromethyl-1,3,5-triazine (XVII). Yield 27%, mp 102–105°C. IR spectrum, ν , cm^{-1} : 3128, 3100, 2892, 1636, 1604, 1576, 1546, 1488, 1454, 1386, 1354, 1292, 1256, 1228, 1132, 1094, 1072, 1000, 920, 904, 852, 832, 792, 744, 724, 712. ^1H NMR spectrum, δ , ppm: 7.92 d and 8.70 d (4H, H_{arom} , $J = 8.7$ Hz), 8.90 s (2H, H_{arom}). Found, %: C 32.37; H 1.06; N 23.49. $\text{C}_{16}\text{H}_6\text{N}_{10}\text{O}_{16}$. Calculated, %: C 32.34; H 1.02; N 23.57.

Reactions of 2,4-dichloro-6-phenoxy-1,3,5-triazine (XVIII) and 2-chloro-4,6-diphenoxy-1,3,5-triazine (XIX) with potassium trinitromethanide. Trinitromethane potassium salt, 7.56 g (0.04 mol), was added to a solution of 0.01 mol of compound XVIII or XIX in 13 ml of acetone under stirring at 19–22°C. The mixture was stirred for 48 h at 19–22°C, the precipitate was filtered off and washed with acetone on a filter, the filtrate was partially evaporated, the residue was poured into 100 ml of water, and the precipitate was filtered off and washed with water. No compound I was detected by TLC among the products.

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