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Transformation of Trinitromethyl Group into Cyano: A New Synthesis of 1,3,5-Triazinecarbonitriles

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Abstract—1,3,5-Triazine-2-carbonitriles were synthesized by reactions of 2-trinitromethyl-1,3,5-triazines with triphenylphosphine.

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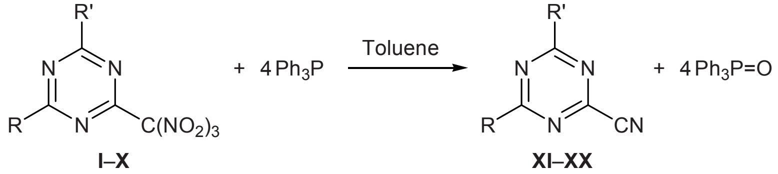
Up to now, only two kinds of transformations of the trinitromethyl group in trinitromethyl derivatives of 1,3,5-triazines have been reported: substitution by the action of nucleophilic reagents [1–4] and denitration to dinitromethyl-1,3,5-triazine salts [5–7]. We have revealed a novel transformation of the trinitromethyl group into cyano in the reaction of trinitromethyl-1,3,5-triazines with triphenylphosphine. A few examples of reactions of mononitro compounds with phosphines and phosphites are known. These are synthesis of 1,3-benzodioxole-5-carbonitrile from 5-nitromethyl-1,3-benzodioxole and tributylphosphine in the presence of azobis(isobutyronitrile) (AIBN) [8], reaction of α-chloro(bromo)-α-nitrotoluene with triethyl phosphite with formation of benzonitrile and phenylnitrometane [9], formation of benzonitrile and 3,4-diphenyl-1,2,5-oxadiazole *N*-oxide in the reaction of α-bromo-α-nitrotoluene with triphenylphosphine [10], and preparation of octanenitrile from 1-bromo-1-nitrooctane and triphenylphosphine [11]. Reactions of geminal polynitro compounds with phosphines and phosphites were not reported.

4,6-Substituted 2-trinitromethyl-1,3,5-triazines **I**–**X** reacted with triphenylphosphine in toluene to give the corresponding 4,6-substituted 1,3,5-triazine-6-carbonitriles **XI**–**XX** and triphenylphosphine oxide (Scheme 1). Here, it was necessary to use four equivalents of triphenylphosphine to achieve complete conversion of the initial trinitromethyl derivative.

In the IR spectra of triazinecarbonitriles **XI**–**XX** we observed a very weak absorption band at 2255–2248 cm^{-1} due to stretching vibrations of the cyano group. The low intensity of this band results from conjugation with the 1,3,5-triazine ring. The ^{1}H NMR spectra of these compounds contained signals from protons in the substituents on C^4 and C^6.

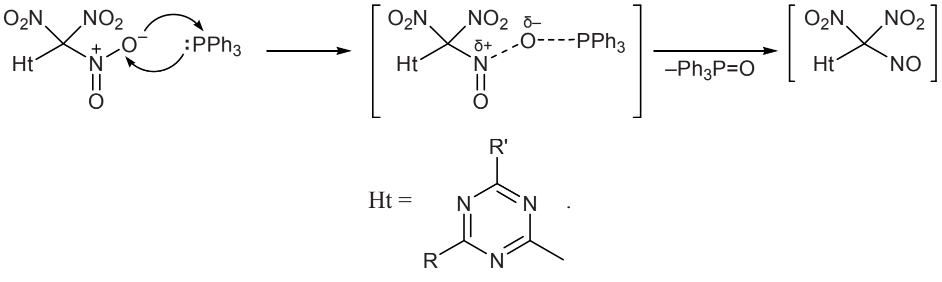
We believe that the transformation of trinitromethyl-1,3,5-triazines **I**–**X** into 1,3,5-triazinecarbonitriles **XI**–**XX** includes three consecutive reactions. The process begins with biphilic [12] attack by triphenylphosphine on the oxygen atom of one nitro group in the trinitromethyl moiety of **I**–**X** (Scheme 2). Partial conjugation between the lone electron pair on the phosphorus atom in triphenylphosphine and π-electron systems of the aromatic rings reduces its nucleophilicity. As a result, electron transfer from the oxygen atom to *d* orbitals of the phosphorus atom becomes predomi-

Scheme 1.



I, **XI**, R = R′ = MeO; **II**, **XII**, R = R′ = *i*-PrO; **III**, **XIII**, R = R′ = 3-MeOCOC$_6$H$_4$O; **IV**, **XIV**, R = MeO, R′ = pyrrolidin-1-yl; **V**, **XV**, R = MeO, R′ = morpholino; **VI**, **XVI**, R = Me$_2$N, R′ = 3-O$_2$NC$_6$H$_4$O; **VII**, **XVII**; R = Me$_2$N, R′ = 4-MeC$_6$H$_4$O; **VIII**, **XVIII**, R = pyrrolidin-1-yl, R′ = PhO; **IX**, **XIX**, R = pyrrolidin-1-yl, R′ = morpholino; **X**, **XX**, R = R′ = Me$_2$N.

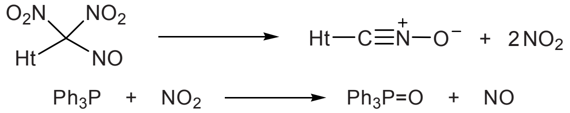
Scheme 2.



nating, and the biphilic attack becomes mostly electrophilic. Here, the transition state is similar to that assumed for the reactions with tertiary amines [12].

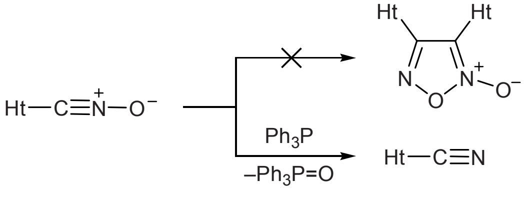
Elimination of triphenylphosphine oxide with formation of dinitro(nitroso)methyl-1,3,5-triazine is likely to be the rate-determining stage since only initial trinitromethyl derivatives **I**–**X** and 1,3,5-triazinecarbonitriles **XI**–**XX** can be detected in the reaction mixture (TLC data). The dinitro(nitroso)methyl derivative thus formed (cf. [13]) quickly loses two nitro groups (as nitrogen dioxide) to afford 1,3,5-triazinecarbonitrile oxide (Scheme 3).

Scheme 3.



The reaction with nitrogen dioxide requires 2 equiv of triphenylphosphine (a part of NO_2 has no time to react with triphenylphosphine, so that it evolves as brown vapor over the surface of toluene) [14, 15]. The next step is fast reaction of 1,3,5-triazinecarbonitrile oxide with the fourth molecule of triphenylphosphine with formation of triphenylphosphine oxide and final 1,3,5-triazinecarbonitrile **XI**–**XX** (Scheme 4); the rate of this reaction is higher than the rate of dimerization of 1,3,5-triazinecarbonitrile oxide to 3,4-bis(1,3,5-triazin-2-yl)-1,2,5-oxadiazole *N*-oxide [16] (the latter was not detected in the reaction mixture by TLC). The proposed scheme is the most consistent with our experimental results and available published data on the mechanisms of particular reaction steps.

Scheme 4.



Thus we have described a novel procedure for the synthesis of 1,3,5-triazinecarbonitriles having alkoxy, aroxy, and amino substituents in the ring via transformation of the corresponding trinitromethyl-1,3,5-triazines by the action of triphenylphosphine. Undoubtedly, studies on reactions of triphenylphosphine with trinitromethyl derivatives of the aromatic, aliphatic, and heterocyclic series attract strong interest.

EXPERIMENTAL

The progress of reactions was monitored by thin-layer chromatography on Silufol UV-254 plates. The IR spectra were recorded on an Avatar spectrophotometer from samples pelleted with KBr or thin films (**XI**–**XIII**). The ^{1}H NMR spectra were measured on a Bruker AM-300 spectrometer (300 MHz) using tetramethylsilane as internal reference. Compounds **I**–**III** were prepared according to the procedure reported in [17], and 1,3,5-triazines **IV**–**X** were synthesized as described in [4].

4,6-Substituted 1,3,5-triazine-2-carbonitriles XI–XX (*general procedure*). Triphenylphosphine, 10.48 g (0.04 mol), was added in portions over a period of 1–1.5 h to a solution of 0.01 mol of trinitromethyl-1,3,5-triazine **I**–**X** in 40 ml of toluene under stirring at 20–25°C. The mixture was stirred at 20–25°C until the initial 1,3,5-triazine disappeared (~0.5 h), the precipitate was filtered was filtered off, the solvent was distilled off from the filtrate under reduced pressure, and the residue was subjected to column chromatography on silica gel using dichloroethane as eluent to isolate 1,3,5-triazinecarbonitriles **XI**–**XX**.

4,6-Dimethoxy-1,3,5-triazine-2-carbonitrile (XI). Yield 65%, light yellow oily substance. IR spectrum, ν, cm^{-1}: 3012, 2954, 2927, 2887, 2852, 2252, 1564, 1535, 1517, 1469, 1403, 1367, 1251, 1236, 1211, 1105, 1078, 1058, 987, 923, 819, 715, 698. ^{1}H NMR spectrum, δ, ppm: 4.12 s (6H, OCH_3). Found, %: C 43.30; H 3.75;

N 33.64. $C_6H_6N_4O_2$. Calculated, %: C 43.38; H 3.64; N 33.72.

4,6-Diisopropoxy-1,3,5-triazine-2-carbonitrile (XII). Yield 63%, light yellow oily substance. IR spectrum, ν, cm^{-1}: 2985, 2939, 2877, 2252, 1560, 1535, 1494, 1411, 1375, 1321, 1228, 1182, 1145, 1095, 1035, 902, 819. ^1H NMR spectrum, δ, ppm: 1.44 d (12H, CH_3, $J = 7.4$ Hz), 5.37 m (2H, OCH). Found, %: C 53.97; H 6.42; N 25.12. $C_{10}H_{14}N_4O_2$. Calculated, %: C 54.04; H 6.35; N 25.21.

Dimethyl 3,3′-(6-cyano-1,3,5-triazine-2,4-diyldioxy)dibenzoate (XIII). Yield 59%, light yellow substance. IR spectrum, ν, cm^{-1}: 3077, 3002, 2954, 2846, 2254, 1724, 1591, 1548, 1486, 1444, 1371, 1295, 1268, 1224, 1201, 1105, 1076, 1020, 1002, 938, 879, 815, 796, 761, 727, 690, 676. ^1H NMR spectrum, δ, ppm: 3.94 s (6H, OCH_3); 7.32 d, 7.48 t, 7.79 s, and 7.96 d (8H, C_6H_4). Found, %: C 59.21; H 3.51; N 13.85. $C_{20}H_{14}N_4O_6$. Calculated, %: C 59.12; H 3.47; N 13.89.

4-Methoxy-6-(pyrrolidin-1-yl)-1,3,5-triazine-2-carbonitrile (XIV). Yield 74%, mp 87–89°C. IR spectrum, ν, cm^{-1}: 3031, 2985, 2956, 2927, 2885, 2248, 1602, 1567, 1506, 1473, 1457, 1371, 1342, 1243, 1226, 1182, 1160, 1120, 1074, 970, 914, 869, 802, 721, 541, 526. ^1H NMR spectrum, δ, ppm: 1.93 t (4H, CH_2CH_2, $J = 4.5$ Hz), 3.52 t (4H, CH_2NCH_2, $J = 4.5$ Hz), 3.91 s (3H, OCH_3). Found, %: C 52.76; H 5.47; N 34.15. $C_9H_{11}N_5O$. Calculated, %: C 52.67; H 5.40; N 34.13.

4-Methoxy-6-morpholino-1,3,5-triazine-2-carbonitrile (XV). Yield 70%, mp 118–119°C. IR spectrum, ν, cm^{-1}: 3008, 2971, 2915, 2869, 2248, 1581, 1569, 1502, 1475, 1448, 1384, 1357, 1309, 1282, 1265, 1234, 1114, 1070, 1006, 865, 806, 538. ^1H NMR spectrum, δ, ppm: 3.73 m (4H, CH_2NCH_2), 3.87 m (4H, CH_2OCH_2), 4.00 s (3H, OCH_3). Found, %: C 48.73; H 5.11; N 31.72. $C_9H_{11}N_5O_2$. Calculated, %: C 48.86; H 5.01; N 31.66.

4-Dimethylamino-6-(3-nitrophenoxy)-1,3,5-triazine-2-carbonitrile (XVI). Yield 70%, mp 160–162°C. IR spectrum, ν, sm^{-1}: 3103, 2927, 2854, 2255, 1606, 1577, 1533, 1504, 1471, 1417, 1388, 1349, 1265, 1205, 1064, 1014, 966, 892, 869, 819, 804, 754, 719, 663. ^1H NMR spectrum, δ, ppm: 3.09 s and 3.24 s (6H, NCH_3, $\Delta\nu = 45$ Hz), 7.50–7.65 m and 8.05–8.20 m (4H, *m*-C_6H_4). Found, %: C 50.43; H 3.60; N 29.48. $C_{12}H_{10}N_6O_3$. Calculated, %: C 50.35; H 3.52; N 29.36.

4-Dimethylamino-6-(4-methylphenoxy)-1,3,5-triazine-2-carbonitrile (XVII). Yield 72%, mp 121–123°C. IR spectrum, ν, cm^{-1}: 3037, 2931, 2881, 2250, 1604, 1573, 1498, 1425, 1392, 1355, 1245, 1213, 1197, 1166, 1064, 1012, 817, 802. ^1H NMR spectrum, δ, ppm: 2.37 s (3H, CH_3), 3.06 s and 3.20 s (3H each, NCH_3, $\Delta\nu = 42$ Hz), 7.04 d and 7.18 d (4H, H_{arom}, $J = 3.2$ Hz). Found, %: C 61.10; H 5.02; N 27.51. $C_{13}H_{13}N_5O$. Calculated, %: C 61.16; H 5.13; N 27.43.

4-Phenoxy-6-(pyrrolidin-1-yl)-1,3,5-triazine-2-carbonitrile (XVIII). Yield 64%, mp 102–104°C. IR spectrum, ν, cm^{-1}: 3066, 2975, 2929, 2881, 2252, 1602, 1567, 1523, 1484, 1382, 1338, 1249, 1199, 1000, 962, 908, 806, 773, 694. ^1H NMR spectrum, δ, ppm: 1.92 m (4H, CH_2CH_2), 3.45 t and 3.59 t (4H, CH_2N-CH_2, $J = 4.7$ Hz), 7.13–7.54 m (5H, C_6H_5). Found, %: C 63.00; H 4.82; N 26.13. $C_{14}H_{13}N_5O$. Calculated, %: C 62.91; H 4.91; N 26.20.

4-Morpholino-6-(pyrrolidin-1-yl)-1,3,5-triazine-2-carbonitrile (XIX). Yield 75%, mp 129–132°C. IR spectrum, ν, cm^{-1}: 3004, 2973, 2921, 2879, 2850, 2252, 1560, 1508, 1492, 1479, 1440, 1342, 1307, 1251, 1220, 1110, 1068, 1020, 997, 977, 858, 798, 628, 539. ^1H NMR spectrum, δ, ppm: 1.94 m (4H, CH_2CH_2), 3.50 t and 3.57 t (4H, CH_2NCH_2, $J = 4.5$ Hz), 3.73 t and 3.88 t (8H, NCH_2CH_2O, $J = 5.2$ Hz). Found, %: C 55.34; H 6.32; N 32.20. $C_{12}H_{16}N_6O$. Calculated, %: C 55.37; H 6.20; N 32.29.

4,6-Bis(dimethylamino)-1,3,5-triazine-2-carbonitrile (XX). Yield 59%, mp 136–138°C. IR spectrum, ν, cm^{-1}: 2925, 2873, 2796, 2250, 1592, 1564, 1488, 1405, 1396, 1355, 1311, 1195, 1047, 1018, 958, 848, 798. ^1H NMR spectrum, δ, ppm: 3.00 s and 3.09 s (3H each, NCH_3, $\Delta\nu = 32$ Hz). Found, %: C 50.12; H 6.36; N 43.75. $C_8H_{12}N_6$. Calculated, %: C 49.99; H 6.29; N 43.72.

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