

**SYNTHESIS AND ATTEMPTED [4+2] CYCLOADDITION REACTION OF
2,4,6-TRIS(PHENYLSELENO AND ARYLTELLURO)-1,3,5-TRIAZINES
WITH DIETHYL ACETYLENEDICARBOXYLATE**

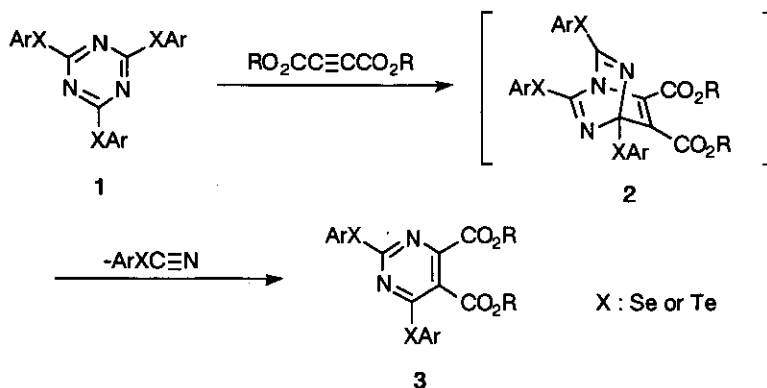
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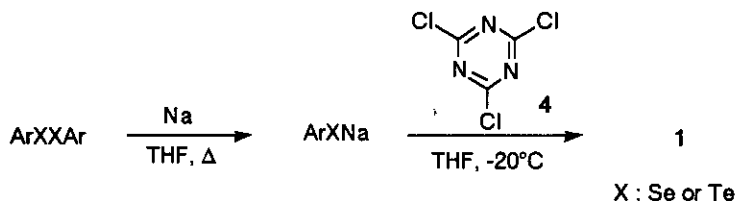
Abstract -- 2,4,6-Tris(phenylseleno and aryltelluro)-1,3,5-triazines were synthesized by the reaction of 2,4,6-trichloro-1,3,5-triazine with corresponding arylchalcogenide anions. These 2,4,6-tris(arylchalcogeno)-1,3,5-triazines failed to undergo the Diels-Alder reaction with diethyl acetylenedicarboxylate.

In connection with our ongoing program, we needed some previously unknown 2,6-diarylseleno- and 2,6-diaryltelluropyrimidine-4,5-dicarboxylic acid derivatives (**3**). Since these compounds appeared to us not easily accessible from commercial materials, we decided to obtain them by replacing the C=N fragment of 1,3,5-triazine ring by the C=C moiety from acetylenedicarboxylate according to the well established sequence¹ of ring transformation as shown in Scheme 1. Compound (**1**) would undergo the hetero-Diels-Alder reaction with acetylenedicarboxylate to form the 1,4-adduct (**2**), which would subsequently extrude a nitrile molecule to form the expected pyrimidine derivative (**3**). Such strategy has so far been extensively used for the generation of various nitrogen heterocyclic compounds.¹ 1,3,5-Triazines are known to react with electron-rich dienophiles as well as electron-deficient dienophiles by a [4+2] cycloaddition reaction.²



Scheme 1

2,4,6-Tris(phenylseleno)-1,3,5-triazine (**1a**) and 2,4,6-tris(aryltelluro)-1,3,5-triazines (**1b-1d**) were prepared by the reaction of 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride; **4**) with sodium benzeneselenolate and arenetellurolates respectively, the latter reagents being generated *in situ* from the reaction of the corresponding diaryl dichalcogenides with sodium metal in tetrahydrofuran (THF). Although arylchalcogenide anions are strong nucleophiles, the reaction required prolonged heating for completion. The compounds (**1a-1d**) obtained are yellow, well crystallized solids with a faint disagreeable odor (Table 1). Since 2,4,6-tris(aryloxy)- and 2,4,6-tris(arythio)-1,3,5-triazines are already known,^{3,4} our synthesis completes the whole set of 2,4,6-tris(arylchalcogeno)-1,3,5-triazine series.



According to the literature procedure,² triazines (**1**) were heated with diethyl acetylenedicarboxylate in 1,4-dioxane under reflux, but to our disappointment they failed to react any further. Even after a week long heating, starting materials (**1**) were recovered almost unchanged. Although many types of ring transformation reactions have been successfully

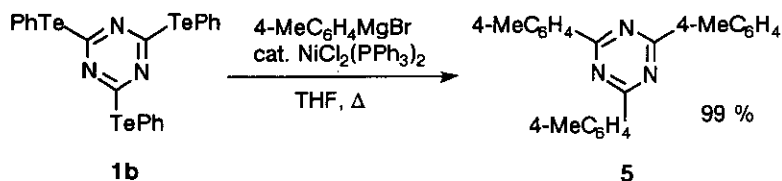
accomplished for azaarenes using the Diels-Alder/retro Diels-Alder strategy,² the method failed for triazines (1).

Table 1. 2,4,6-Tris(phenylseleno and aryltelluro)-1,3,5-triazines obtained

Compound	Ar	X	m.p./°C	Yield/% ^a
1a	Ph	Se	106-107	70
1b	Ph	Te	96-100	68
1c	4-MeC ₆ H ₄	Te	142-143	70
1d	4-ClC ₆ H ₄	Te	132-134	78

^a Yields refer to isolated compounds and are not optimized.

Reaction of trichlorotriazine (4) with alkyl- or arylmagnesium halides is reported to give *C*-substituted derivatives. However, complete displacement of three chlorine atoms is not easily feasible even in the presence of a large excess of the Grignard reagent.^{5,6} A rough generalization was made to the effect that one of the chlorine atoms of 4 reacts with alkyl Grignard reagents, while in the case of aryl Grignard reagents, one or two chlorine atoms undergo replacement.⁷ In the presence of a nickel(II) complex catalyst, aryltelluro moieties on the triazine ring could be readily replaced by aryl groups.⁸ Thus, when 2,4,6-tris(phenyltelluro)-1,3,5-triazine (**1b**) was heated with three equiv. of 4-methylphenylmagnesium bromide in THF in the presence of a catalytic amount of bis(triphenyl-phosphine)dichloronickel(II), all three phenyltelluro groups were smoothly substituted for tolyl groups to give 2,4,6-tris(4-methylphenyl)-1,3,5-triazine (**5**) in almost quantitative yield.



Since a variety of triazine-based herbicides and crop-protection chemicals are in use,⁹ compounds (1a-1d and 5) were screened for herbicidal activity. Triazine (1d) showed a weak activity toward wild mustard (*Brassica kaber*) and pig weed (*Amaranthus retroflexus*), but others were inactive.

EXPERIMENTAL

Mps were determined with a Yanagimoto hot plate apparatus and are uncorrected. Ir spectra were recorded as KBr pellets on a Hitachi 260-10 spectrophotometer, while ¹H, ¹³C, ⁷⁷Se and ¹²⁵Te nmr spectra were measured for solution in CDCl₃ using a JEOL GSX270 spectrometer. Mass spectra were obtained on a Hitachi M-80B instrument operating at 20 eV. Trichlorotriazine (4) was purchased from Wako Chemical, Ltd. Diaryldichalcogenides¹⁰ and bis(triphenylphosphine)-dichloronickel(II)¹¹ were prepared according to the reported procedures.

Preparation of 2,4,6-Tris(phenylseleno and aryltelluro)-1,3,5-triazines (1a-1d).

Typical Procedure: To a solution of diphenyl diselenides (20.5 g, 50 mmol) in THF (15 ml) was added sodium (3.5 g, 150 mmol) and the resulting mixture was heated at reflux for 36 h under an argon atmosphere. The black solution obtained was cooled to -20 °C and a solution of 2,4,6-trichloro-1,3,5-triazine (5.55 g, 30 mmol) in THF (20 ml) was added. The color immediately turned red and the mixture was allowed to leave to room temperature with stirring, and then poured into a saturated ammonium chloride solution at 0 °C. The organic phase was extracted with ether and the extract was washed with water, dried over magnesium sulfate, and evaporated under reduced pressure. The solid residue was purified by silica gel chromatography using hexane as an eluent to give 2,4,5-tris(phenylseleno)-1,3,5-triazine (1a, 11.5 g, 70 %) as yellow crystals, mp 106-107 °C. **2,4,6-Tris(phenylseleno)-1,3,5-triazine (1a).** ¹H Nmr(CDCl₃) δ 7.1-7.3(9H, m), 7.4-7.5(6H, m); ¹³C nmr(CDCl₃) δ 125.60, 128.87, 129.07, 135.55, 180.29; ⁷⁷Se nmr(CDCl₃) δ 518.62; ir(KBr) 1440, 1245, 1220, 780 cm⁻¹; ms(20 eV) m/z(rel intensity) 549([C₂₁H₁₅N₃⁸⁰Se₃]⁺; 3), 547([C₂₁H₁₅N₃⁷⁸Se⁸⁰Se]⁺; 4), 545([C₂₁H₁₅N₃⁷⁸Se₂⁸⁰Se]⁺; 3), 543([C₂₁H₁₅N₃⁷⁸Se₃]⁺; 2), 392(3), 314(69), 234(20), 157(100). Anal. Calcd for C₂₁H₁₅N₃Se₃: C, 46.18; H, 2.77; N, 7.69. Found: C, 46.42; H, 2.73; N, 7.75.

2,4,6-Tris(phenyltelluro)-1,3,5-triazine (1b). ¹H Nmr(CDCl₃) δ 7.1-7.4(9H, m), 7.6-7.7(6H, m); ¹³C nmr(CDCl₃) δ 114.30, 128.77, 129.38, 139.27, 172.32; ¹²⁵Te nmr(CDCl₃) δ 764.20; ir(NaCl) 1575, 1465, 1430, 1210, 1020, 1000, 780, 760, 730, 685 cm⁻¹; ms(20 eV) m/z(rel intensity) 699

($[\text{C}_{21}\text{H}_{15}\text{N}_3^{130}\text{Te}_3]^+$; 0.6), 697($[\text{C}_{21}\text{H}_{15}\text{N}_3^{128}\text{Te}^{130}\text{Te}_2]^+$; 1.7), 695($[\text{C}_{21}\text{H}_{15}\text{N}_3^{128}\text{Te}_2^{130}\text{Te}]^+$; 2.5), 693 ($[\text{C}_{21}\text{H}_{15}\text{N}_3^{128}\text{Te}_3]^+$; 2.8), 523(2), 410(22), 284(13). Anal. Calcd for $\text{C}_{21}\text{H}_{15}\text{N}_3\text{Te}_3$: C, 36.44; H, 2.18, N, 6.07. Found: C, 36.77; H, 2.26; N, 6.01.

2,4,6-Tris(4-methylphenyltelluro)-1,3,5-triazine (1c). ^1H Nmr(CDCl_3) δ 2.36(9H, s), 6.97(6H, d, $J=7.6$ Hz), 7.56(6H, d, $J=7.6$ Hz); ^{13}C nmr(CDCl_3) δ 21.44, 110.56, 130.22, 138.57, 139.30, 172.34; ir(KBr) 1420, 1215, 1200, 790, 750 cm^{-1} ; ms(20 eV) m/z (rel intensity) 739($[\text{C}_{24}\text{H}_{21}\text{N}_3^{130}\text{Te}_3]^+$; 7), 737($[\text{C}_{24}\text{H}_{21}\text{N}_3^{128}\text{Te}^{130}\text{Te}_2]^+$; 10), 735($[\text{C}_{24}\text{H}_{21}\text{N}_3^{128}\text{Te}_2^{130}\text{Te}]^+$; 11), 733($[\text{C}_{24}\text{H}_{21}\text{N}_3^{128}\text{Te}_3]^+$; 9), 438(32), 312(18), 221(61). Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{Te}_3$: C, 39.26; H, 2.88, N, 5.72. Found: C, 39.17; H, 2.83; N, 5.54.

2,4,6-Tris(4-chlorophenyltelluro)-1,3,5-triazine (1d). ^1H Nmr(CDCl_3) δ 7.14(6H, d, $J=8.5$ Hz), 7.56(6H, d, $J=8.5$ Hz); ^{13}C nmr(CDCl_3) δ 111.68, 129.65, 135.59, 140.81, 172.50; ir(KBr) 1420, 1220, 1200, 1085, 1005, 810, 760, 750 cm^{-1} ; ms(20 eV) m/z (rel intensity) 803($[\text{C}_{21}\text{H}_{12}^{35}\text{Cl}_2^{37}\text{ClN}_3^{130}\text{Te}_3]^+$; 0.4), 801($[\text{C}_{21}\text{H}_{12}^{35}\text{Cl}_2^{37}\text{ClN}_3^{128}\text{Te}^{130}\text{Te}_2]^+$; 1.0), 799($[\text{C}_{21}\text{H}_{12}^{35}\text{Cl}_2^{37}\text{ClN}_3^{128}\text{Te}_2^{130}\text{Te}]^+$; 1.5), 797($[\text{C}_{21}\text{H}_{12}^{35}\text{Cl}_2^{37}\text{Cl}^{128}\text{Te}_3]^+$; 1.5), 480(41), 352(39), 241(100). Anal. Calcd for $\text{C}_{21}\text{H}_{12}\text{Cl}_3\text{N}_3\text{Te}_3$: C, 31.71; H, 1.52; N, 5.28. Found: C, 31.95; H, 1.54; N, 5.37.

Reaction of 2,4,6-tris(phenyltelluro)-1,3,5-triazine with aryl Grignard reagent in the presence of nickel(II) catalyst.

To a solution of 2,4,6-tris(phenyltelluro)-1,3,5-triazine (0.23 g, 0.33 mmol) and bis(triphenylphosphine)dichloronickel(II) (0.032 g, 0.05 mmol) in THF (20 ml) was added dropwise a solution of 4-methylphenylmagnesium bromide (1 mmol) in THF (1 ml) at room temperature and the resulting mixture was heated under reflux for 8 h. The reaction mixture was quenched by the addition of dilute hydrochloric acid and the black solution was filtered on a pad of Celite 545. The filtrate was extracted with ether, and the combined extracts were dried over magnesium sulfate and evaporated. A solid residue was passed over silica gel using hexane as a solvent to give 2,4,6-tris(4-methylphenyl)-1,3,5-triazine (5) in almost quantitative yield. (mp $>250^\circ\text{C}$, lit.,¹² 278-280 $^\circ\text{C}$)

2,4,6-Tris(4-methylphenyl)-1,3,5-triazine (5). ^1H Nmr(CDCl_3) δ 2.38(9H, s), 7.29(6H, d, $J=8.4$ Hz), 8.58(6H, d, $J=8.4$ Hz); ^{13}C nmr(CDCl_3) δ 21.73, 128.89, 129.30, 133.72, 142.83, 171.34; ir(KBr) 1605, 1580, 1505, 1400, 1360, 1175, 795 cm^{-1} ; ms(20 eV) m/z (rel intensity) 351(M^+ ; 47), 117(100).

Attempted Diels-Alder reaction of 2,4,6-tris(arylchalcogeno)-1,3,5-triazines with ethyl acetylenedicarboxylate.

To a solution of 2,4,6-tris(phenyltelluro)-1,3,5-triazine (0.35 g, 0.5 mmol) in 1,4-dioxane (20 ml) was added ethyl acetylenedicarboxylate (0.095 g, 0.55 mmol) and the resulting mixture was heated at reflux for 7 d under an argon atmosphere. The reaction mixture was evaporated under reduced pressure to afford starting materials almost unchanged.

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REFERENCES

1. R. A. Carboni and R. V. Lindsay, Jr., J. Am. Chem. Soc., 1959, **81**, 4342; J. Sauer and G. Heinrichs, Tetrahedron Lett., 1966, 4979; P. Roffey and J. P. Verge, J. Heterocycl. Chem., 1969, **6**, 497; A. E. A. Porter and P. G. Sammes, J. Chem. Soc., Chem. Commun., 1970, 1130; H. Neunhoeffer and G. Werner, Tetrahedron Lett., 1970, 3355; A. Steigel and J. Sauer, Tetrahedron Lett., 1970, 3357; H. Neunhoeffer and H. -W. Frühauf, Liebigs Ann. Chem., 1972, **758**, 125; H. Neunhoeffer and G. Werner, Liebigs Ann. Chem., 1972, **761**, 39; H. Neunhoeffer and G. Werner, Tetrahedron Lett., 1972, 1517; H. Neunhoeffer and G. Werner, Liebigs Ann. Chem., 1973, 437; P. J. Machin, A. E. A. Porter, and P. G. Sammes, J. Chem. Soc., Perkin Trans. 1, 1973, 404; H. Neunhoeffer and G. Werner, Liebigs Ann. Chem., 1974, 1190; D. L. Boger and J. S. Panek, Tetrahedron Lett., 1983, **24**, 4511; V. N. Charushin and H. C. van der Plas, J. Org. Chem., 1983, **48**, 2667; V. N. Charushin and H. C. van der Plas, Recl. Trav. Chim. Pays-Bas, 1983, **102**, 73.
2. H. Neunhoeffer and M. Bachmann, Chem. Ber., 1975, **108**, 3877.
3. A. W. van Muijwijk, A. P. G. Kieboom, H. van Bekkum, Recl. Trav. Chim. Pays-Bas, 1974, **93**, 204.
4. K. Wakabayashi and M. Okuzu, Nippon Dojo-Hiryogaku Zasshi, 1970, **41**, 237.
5. R. H. Hirt, H. Nidecker, and R. Berchtold, Helv. Chim. Acta, 1950, **33**, 1365.
6. H. Bader, E. R. Ruckel, F. X. Markey, C. G. Santangelo, and P. Schickedantz, J. Org. Chem., 1965, **30**, 702.

7. E. M. Smolin and L. Rapoport, 's-Triazine and Derivatives,' Interscience Publishers, Inc., New York, 1959, p. 58.
8. S. Uemura, S. Fukuzawa, and S. R. Patil, J. Organometl. Chem., 1983, **243**, 9.
9. 'Herbicide Handbook,' 4th ed., Weed Science Society of America, Champaign, 1979; 'Kirk-Othmer Encyclopedia of Chemical Technology,' 3rd ed., Vol. 12, John-Wiley & Sons, New York, 1980, pp. 315-319.
10. M. R. Detty, B. J. Murray, D. L. Smith, and N. Zumbulyadis, J. Am. Chem. Soc., 1983, **105**, 875.
11. L. Venanzi, J. Chem. Soc., 1958, 719.
12. S. Yanagida, M. Yokoe, I. Katagiri, M. Ohoka, and S. Komori, Bull. Chem. Soc. Jpn., 1973, **46**, 306.

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