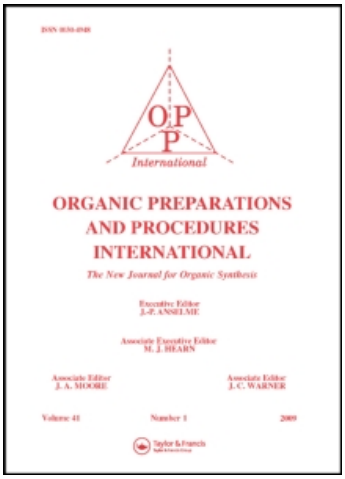

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CONVERSION OF 3-AROYLMETHYL-5-ARYLMETHYLENE-2,4-DIOXO-1,3-THIAZOLIDINES INTO 6-ARYL-4,5-DIHYDRO-1,2,4-TRIAZIN-3(2H)-ONES

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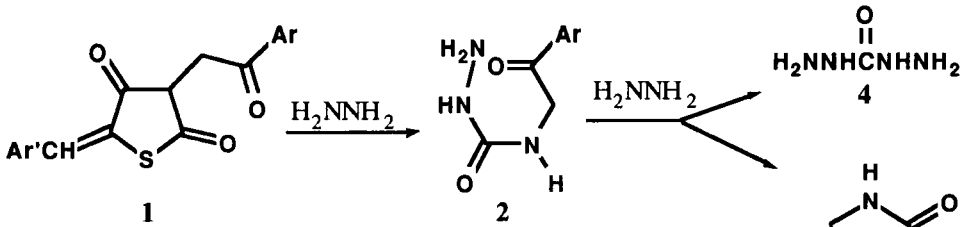
The chemistry of 4-thiazolidinones, especially their reaction with hydrazines, has been a subject of a series of publications from this laboratory.[1-3] The role of substituents at position-3 on the mode of cleavage of 3-substituted-2,4-dioxothiazolidines has been investigated.[3] In alcoholic solution, the 3-alkyl-4-thiazolidinones yielded mixtures of pyrazolinones[2,3] and N-alkylhydrazine carboxamides;[3] the route of interconversion into pyrazolinones has been discussed[2]. Our desire was to generate a properly N-substituted hydrazide *in situ* in order to use its latent ability to recyclize to a triazine ring system; it was anticipated that pyrazolinone formation would be suppressed in acetic acid since the hydrazine adducts, which are believed to be formed initially,[2] are unstable in this medium. Although several methods have been reported[4,5] for the synthesis of several mono- and polysubstituted-4,5-dihydro-1,2,4-triazin-3(2H)-ones from various starting materials of the 6-aryl derivatives, only the 6-phenyl analogue is known. We now report a facile conversion of the readily accessible (E,Z)-**1**[6] into a variety of 6-aryl-4,5-dihydro-1,2,4-triazin-3(2H)-ones **3**.

The thiazolidinones (**1**), obtained by treatment of the potassium salts of the respective 5-arylmethylene-2,4-dioxo-1,3-thiazolidines[7] with aroylmethyl bromides using a modification of the method of Lo et al.[8], were treated with hydrazine hydrate in acetic acid. Thus, hydrazine hydrate reacts with **1a-d** to give moderate yields of the respective triazines **3a-d**. Similar treatment of **1e** and **1f** afforded **3a** and **3b**, respectively. The structures of **3a-d** were deduced from analytical and spectral data. Their IR spectra showed stretching absorptions of OH, NH, C=O and C=N groups and their electronic spectra exhibited two peaks of medium intensity at 252-255 nm



1 2 3

a) Ar = Ar' = C_6H_5 b) Ar = 4-MeC_6H_4, Ar' = C_6H_5
c) Ar = 4-BrC_6H_4, Ar' = 4-ClC_6H_4 d) Ar = Ar' = 4-$MeOC_6H_4$
e) Ar = C_6H_5, Ar' = 4-ClC_6H_4 f) Ar = 4-MeC_6H_4, Ar' = 4-$MeOC_6H_4$

(ε 10,500-12,300) and 278-295 nm (ε 13,500-14,500) attributed to π–π* transitions. Furthermore, **3a**

is identical (mp and ir) with an authentic sample[4] and the ^{1}H NMR spectrum of **3b** shows the ring methylene and aromatic protons in the ratio of 2:4, respectively, and its MS spectrum exhibits a molecular ion peak consistent with the proposed structure. Trace amounts of carboxyhydrazide (**4**) were obtained from the mother liquor of **3a** by inoculation with a small crystal; this suggests that the intermediate hydrazine carboxamide **2** is partially degraded by further action of hydrazine. This may explain the relatively low yields of **3** obtained.

EXPERIMENTAL SECTION

All melting points are uncorrected. IR spectra were determined on a Unicam SP 1200 spectrophotometer using KBr disks. UV spectra of ethanol solutions were recorded on a Perkin-Elmer Lambda 3B spectrometer. ^{1}H NMR spectra were measured on a Varian EM 390-90 MHz instrument with tetramethylsilane as internal standard. Mass spectra were recorded on a double focussing model JEOL JMS-01SG-2 spectrometer operating at 75 ev.

TABLE 1. Analytical Data for Compounds **1** and **3**

Compd	Yield (%)	mp. (°C)	Elemental Analysis (Found) C	H	N	IR (cm^{-1})
1a	70	177-178	66.87 (67.00)	4.02 (4.20)	4.33 (4.25)	1730, 1670
1b	75	189-190	67.65 (67.55)	4.45 (4.40)	4.15 (4.20)	1730, 1670
1c	70	204-206	49.48 (49.60)	2.52 (2.50)	3.20 (3.00)	1735, 1670
1d	72	235-237	62.66 (62.40)	4.44 (4.60)	3.65 (3.50)	1735, 1670
1e	75	220-222	60.42 (60.25)	3.35 (3.50)	3.91 (4.10)	1730, 1665
1f	78	238-240	65.39 (65.20)	4.63 (4.60)	3.81 (3.65)	1730, 1670
3a	45 (50)[a]	228-230[b]	61.71 (61.50)	5.14 (5.20)	24.00 (23.80)	3000-3500, 1710, 1690, 1635
3b	50 (50)[b]	218-220	63.49 (63.50)	5.82 (5.85)	22.22 (22.00)	3000-3450, 1710, 1690, 1635
3c	50	198-200	42.52 (42.30)	3.14 (3.00)	16.53 (16.30)	3000-3500, 1700, 1680, 1640
3d	50	122-124	58.53 (58.30)	5.36 (5.35)	20.48 (20.50)	3000-3500, 1700 1675, 1640

a) Yield obtained upon treating **1e** with hydrazine hydrate. b) Yield obtained upon treating **1f** with hydrazine hydrate. c) lit.[4] mp. 225-227°.

TABLE 2. ^{1}H NMR and MS Spectral Data of Compounds **1a,c,e,f** and **3b**

Compd	^{1}H NMR (δ)[a]	$M^{+\cdot}$ (m/e)
1a	7.95 (s, 1H, olefinic H), 7.20-7.80 (m, 10H, ArH), 5.23 (s, 2H, CH_2COPh)	323
1c	7.50-8.20 (m, 9H, ArH + olefinic H), 5.35 (br s, 2H, CH_2COAr)	436
1e	8.15 (partially split d, 4H, ArH), 7.95 (s, 1H, olefinic H), 7.50-7.85 (m, 5H, ArH), 5.32 (s, 2H, CH_2COPh)	357
1f	7.82 (m, 3H, ArH + olefinic H), 7.20 (d, J = 7.0 Hz, 2H, ArH), 6.90 (d, J = 7.0 Hz, 2H, 2H, ArH), 5.15 (s, 2H, CH_2COAr), 3.80 (s, 3H, OCH_3), 2.41 (s, 3H, CH_3)	367
3b	8.20 (br s, 1H, 2-NH), 7.46 (d, J = 7.0 Hz, 2H, ArH), 7.12 (d, J = 7.0 Hz, 2H, ArH), 6.10 (br s, 1H, 4-NH), 4.35 (br s, 2H,5-CH_2)	189

a) All the spectra were measured on DMSO-d_6 solutions except for **3b** which was obtained in $CDCl_3$.

3-Aroylmethyl-5-arylmethylene-2,4-dioxo-1,3-thiazolidines (**1a-f**).- A solution of aroylmethyl bromide (50 mmol) in ethanol (50 ml) was added to a warm solution of each of the potassium salts of 5-arylmethylene-2,4-dioxo-1,3-thiazolidines[7] (50 mmol) in water (5 ml) and the mixture was boiled under reflux for 6 hrs. The reaction mixture was concentrated, poured onto ice-cold water and the precipitated solid was collected and recrystallized from ethanol-benzene to give the title compounds (Tables 1 and 2).

6-Aryl-4,5-dihydro-1,2,4-triazin-3(2H)ones (**3a-d**).- Hydrazine hydrate (99%, 10 mmol) was added to a solution of **1a-f** (3 mmol) in aqueous acetic acid (90% v/v, 30 ml) and the mixture was boiled under reflux for 6 hrs. during which time the odor of hydrogen sulfide gas became apparent. The reaction mixture was treated with charcoal, concentrated and poured onto iced water. The precipitated pale yellow solid was collected, washed thoroughly with water, dried and recrystallized from benzene or methanol to give the title compounds (Tables 1 and 2). Evaporation of the mother liquor left a sulfur-free nitrogenous viscous oil which failed to solidify. Seeding the mother liquor of **3a** with a small crystals of carboxyhydrazide and allowing the solution to stand for 2 days in the refrigerator afforded a few crystals of **4**, mp. 154-155°, undepressed on admixture with an authentic sample.[9]

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SYNTHESIS OF

NEW bis(*m*-PHENYLENE)-32-CROWN-10 DERIVATIVES

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High yields are generally not obtained in the synthesis of macrocycles because of the formation of linear and cyclic oligomeric by-products. Although optimized procedures for the synthesis of crown ethers, especially in the range up to 18-membered rings, have been developed,[1] we were interested in synthesizing significant quantities of functionalized semi-rigid 30-40 membered rings; the objective of the present study was to develop a simple method for the preparation of mono- and difunctionalized bis(*m*-phenylene)-32-crown-10.

The new macrocycle bis(5-methyl-1,3-phenylene)-32-crown-10 (**6**) was prepared (21%) *via* **1a** and the series of new compounds **2a-5a** according to a four-step route (Scheme) used by Bartsch et al.[2] for another crown ether. A one-step method has been used by Cram et al.[3] as well as in our laboratory[4] to synthesize bis(*p*-phenylene)-34-crown-10. Thus orcinol monohydrate (**1a**) was treated with tetra(ethylene glycol) ditosylate (**7**)[5] in dioxane/1-butanol at reflux for 24 hrs to produce macrocycle **6**