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Preparation of Aryl Hydrazonates and 1,2-Diacylhydrazines by Phase Transfer Catalysis

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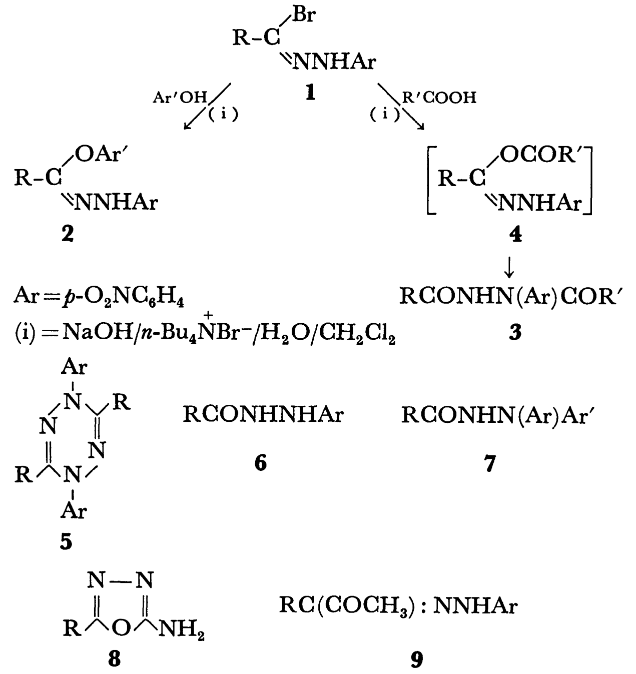
(Received October 21, 1980)

Synopsis. A series of aryl hydrazonates has been prepared in excellent yield (>90%) by phase-transfer-catalysis technique from the corresponding phenol and hydrazonoyl bromides in dichloromethane in the presence of tetrabutylammonium iodide. 1,2-Diacyl derivatives of arylhydrazines were also prepared by the same technique using carboxylic acids in place of phenols.

Recently the phase-transfer-catalysis as a synthetic tool has attracted the attention of several investigators.[1,2] We have extended the application of this technique to the preparation of aryl hydrazonates (**2**) and 1,2-diacylhydrazines (**3**) by the reaction of hydrazonoyl bromides (**1**) with phenols and carboxylic acids, respectively. In both cases tetrabutylammonium iodide was used as the phase transfer catalyst (Scheme 1). Both esters **2** and hydrazides **3** with ortho halogen atom in the *N*-aryl moiety proved useful in synthesis of 4*H*-1,3,4-benzoxadiazine derivatives.[3] The results are given herewith.

Results and Discussion

Treatment of **1** and phenol or naphthol with tetrabutylammonium iodide and sodium hydroxide in dichloromethane at room temperature affords the corresponding aryl hydrazonates (**2**) in 91—96% yields. Previously reported aryl hydrazonates were prepared by treating hydrazonoyl halides (**1**) with sodium phenolates in ethanol[4] or in benzene.[5,6] Alternatively, a mixture of hydrazonoyl halide (**1**) and phenol is treated with triethylamine in benzene[6,7] to give **2**. Reaction of **1** with phenol in the presence of sodium acetate was reported to give **3** ($R'=CH_3$) instead of **2**.[8] The yield of **2** prepared by either of the foregoing procedures did not exceed 65%. The phase transfer catalysis method described here seems to be more convenient and leads to excellent yields of **2**, eliminating the formation of tetrazines (**5**) or hydrazides (**6**) as competing reaction products. The structures of the esters prepared (Table 1) were confirmed by elemental analysis and spectral data. For example,



Scheme 1.

TABLE 1. ARYL HYDRAZONATES, **2**

Compound No.	R	Ar	Mp °C	Yield %	Molecular formula (Lit, Mp/°C)	N (%) Found	N (%) Calcd
2a	C_6H_5	C_6H_5	172	93	(172)[4]		
2b	C_6H_5	$1\text{-}C_{10}H_7$	201	91	$C_{23}H_{17}N_3O_3$	11.01	10.96
2c	C_6H_5	$2\text{-}C_{10}H_7$	179	93	$C_{23}H_{17}N_3O_3$	10.89	10.96
2d	$4\text{-}CH_3C_6H_4$	$1\text{-}C_{10}H_7$	201	90	$C_{24}H_{19}N_3O_3$	10.51	10.57
2e	$4\text{-}CH_3C_6H_4$	$2\text{-}C_{10}H_7$	186	95	$C_{24}H_{19}N_3O_3$	10.49	10.57
2f	$4\text{-}ClC_6H_4$	$1\text{-}C_{10}H_7$	218	94	$C_{23}H_{16}ClN_3O_3$	10.00	10.05
2g	$4\text{-}ClC_6H_4$	$2\text{-}C_{10}H_7$	215	93	$C_{23}H_{16}ClN_3O_3$	9.98	10.05
2h	$4\text{-}NO_2C_6H_4$	$1\text{-}C_{10}H_7$	205	96	$C_{23}H_{16}N_4O_5$	12.98	13.08
2i	$4\text{-}NO_2C_6H_4$	$2\text{-}C_{10}H_7$	218	92	$C_{23}H_{16}N_4O_5$	12.93	13.08
2j	CH_3	$1\text{-}C_{10}H_7$	167	90	$C_{18}H_{15}N_3O_3$	13.00	13.07
2k	CH_3	$2\text{-}C_{10}H_7$	162	94	$C_{18}H_{15}N_3O_3$	12.93	13.07
2l	$(CH_3)_2CH$	$1\text{-}C_{10}H_7$	123	94	$C_{20}H_{19}N_3O_3$	11.87	12.02
2m	$(CH_3)_2CH$	$2\text{-}C_{10}H_7$	130	91	$C_{20}H_{19}N_3O_3$	12.00	12.02

Table 2. 1,2-Diacyl-1-*p*-nitrophenylhydrazines, **3**

Compound No.	R	R′	Mp °C	Yield %	Molecular formula (Lit, Mp/°C)	N (%) Found	N (%) Calcd
3a	C_6H_5	C_6H_5	169	95	$C_{20}H_{15}N_3O_4$	11.57	11.63
3b	C_6H_5	1-$C_{10}H_7$	210	97	$C_{24}H_{17}N_3O_4$	10.10	10.21
3c	C_6H_5	4-ClC_6H_4	233	93	$C_{20}H_{14}ClN_3O_4$	10.58	10.61
3d	4-$CH_3C_6H_4$	1-$C_{10}H_7$	200	94	$C_{25}H_{19}N_3O_4$	9.90	9.87
3e	4-$CH_3C_6H_4$	4-ClC_6H_4	231	96	$C_{21}H_{16}ClN_3O_4$	10.15	10.25
3f	$(CH_3)_2CH$	C_6H_5	148	97	(148)[16]		
3g	$(CH_3)_2CH$	1-$C_{10}H_7$	163	94	$C_{21}H_{19}N_3O_4$	11.06	11.13
3h	$(CH_3)_2CH$	4-ClC_6H_4	222	95	$C_{17}H_{16}ClN_3O_4$	11.49	11.61
3i	CH_3	C_6H_5	165	97	$C_{15}H_{13}N_3O_4$	14.00	14.04

the infrared spectra of **2** reveal, in each case, two characteristic bands near 1255 and 1070 cm^{-1} assignable to an aryl ether linkage. Their electronic absorption spectra in ethanol are of typical hydrazones. The structures of **2** were also substantiated by the identification of 1,1-diaryl-2-acylhydrazines (**7**) obtained by thermolysis of **2** in xylene.[4,7]

1,2-Diacylhydrazines (**3**) ($R'=CH_3$) are usually prepared by treatment of hydrazonoyl halides (**1**) with sodium acetate in acetic acid or in water.[9–11] However, this method leads in some cases to hydrolysis product **6** or intramolecular nucleophilic substitution products, for example **8**.[12,13] Ciusa and Mega[14] claimed the formation of **9** by treatment of **1** ($R=C_6H_5$, Ar=2-Br, 4-$NO_2C_6H_4$) with sodium acetate. We have found that treatment of a mixture of **1** and carboxylic acid with tetrabutylammonium iodide and sodium hydroxide in dichloromethane at room temperature eliminates all such side reactions, giving **3** in yields higher than 93%. In this reaction, the initially formed hydrazonoyl carboxylate **4** undergoes a rapid 1,3-acyl migration to give **3**.[15] All compounds in series **3** exhibit in their infrared spectra two CO bands near 1675 and 1685 cm^{-1} and an NH band near 3250 cm^{-1}. The new 1,2-diacyl-1-aryl hydrazines (**3**) prepared by phase transfer catalysis method are given in Table 2.

Experimental

All melting points are uncorrected. Microanalyses were performed at Galbraith Laboratories, Inc., Knoxville, Tennessee, U. S. A. The IR and UV spectra were recorded on Pye-Unicam spectrophotometers, models SP1000 and SP8000, respectively.

Aldehyde *p*-nitrophenylhydrazones were converted into the corresponding hydrazonoyl bromides (**1**) by reaction with bromine in glacial acetic acid.[4]

Aryl Hydrazonates. As a general procedure a solution of hydrazonoyl bromide (1.6 mmol) in dichloromethane (15 ml) is added to a rapidly stirred solution of the appropriate phenol (2.1 mmol), sodium hydroxide (0.082 g, 2.1 mmol) and tetrabutylammonium iodide (0.022 g, 0.06 mmol) in water (15 ml). The mixture was stirred at room temperature for 1 h and then diluted with chloroform (25 ml). The organic layer was separated and washed successively with 5% sodium hydroxide solution and water, dried with anhydrous sodium sulfate. The solvent was removed and the residue was triturated with methanol. The crude solid formed was collected and crystallized from acetic acid or ethanol to give the corresponding aryl hydrazonates (Table 1).

*1,2-Diacyl-1-(*p*-nitrophenyl)hydrazines (**3**). General Method:* To a rapidly stirred solution of carboxylic acid (1.4 mmol), sodium hydroxide (0.055 g, 1.4 mmol), and tetrabutylammonium iodide (0.011 g, 0.03 mmol) in water (15 ml) was added the appropriate hydrazonoyl bromide (1.3 mmol) in dichloromethane (15 ml) and the mixture was stirred at room temperature for 1 h. The mixture was diluted with chloroform (30 ml) and the organic layer separated, dried with anhydrous sodium sulfate, and evaporated. The crude product was collected, washed with water and crystallized from acetic acid, to give hydrazides **3** in 93—97% yields (Table 2).

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