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# The structure of the products of coupling aryldiazonium salts with phenacylthiocyanates. Correction of literature reports

MOHAMED H. ELNAGDI,*‡ AHMED HAFEZ H. ELGHANDOUR* and KAMAL U. SADEK†‡
*Chemistry Department, Faculty of Science, Cairo University, Giza, A.R. Egypt and † Chemistry Department, Faculty of Science, Minia University, Minia, A. R. Egypt

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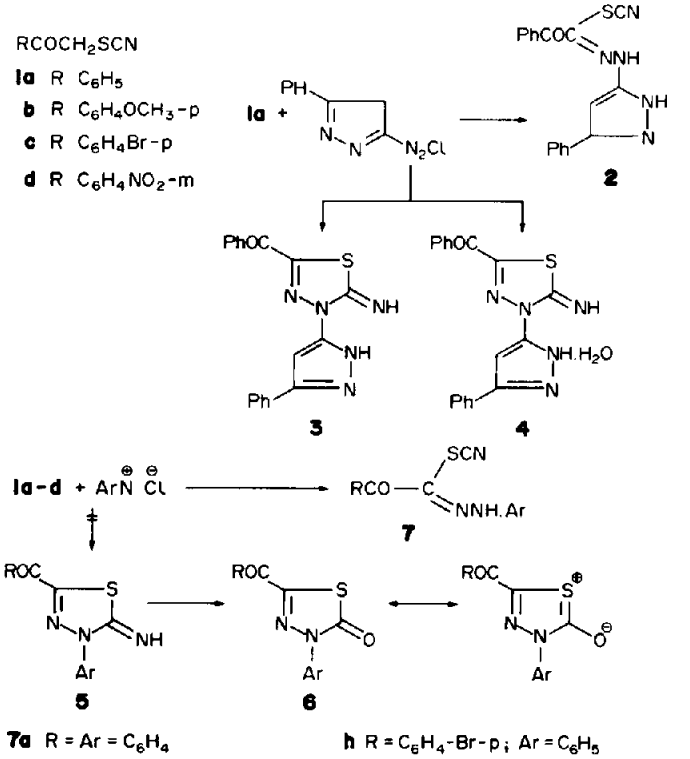
**Abstract**—A variety of coupling products of phenacylthiocyanates **1a–d** with aryldiazonium chlorides is reported. The i.r., u.v., $^{13}C$ NMR as well as the chemical behaviour of the coupling products clearly reveal that they are hydrazones (**7**) and not thiadiazol-2-imines (**5**) as previously reported.

## INTRODUCTION

Some time ago we reported that 3-phenylpyrazol-5-yldiazonium chloride couples with phenacylthiocyanate (**1a**) to yield the hydrazone **2** [1]. Recently, two articles dealing with the structure of this product have been published [2, 3]. Although both articles reported exactly the same experimental procedures, they reported totally different data for the products and came to different conclusions. In one paper the product earlier reported to be **2** was assigned as an isomeric cyclic thiadiazol-2-imine (**3**) while in the other the product was considered to be the hydrate of **3**, namely **4**. This and other discrepancies [4] make it difficult to rely on the conclusions made in both papers. The authors of both papers have relied heavily on the absence of a signal for SCN in the i.r. spectrum of the coupling products and similarity to the previous reported formation of 3-aryl-5-benzoyl-1,3,4-thiadiazol-2-imines (**5**) on coupling **1a** with aryldiazonium salts [5]. However, 1,3,4-thiadiazol-2-imines are expected

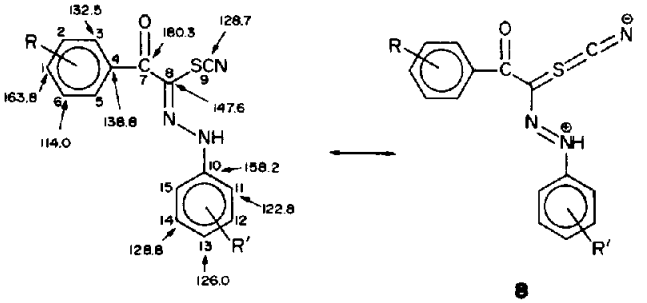
‡Authors to whom correspondence should be addressed.

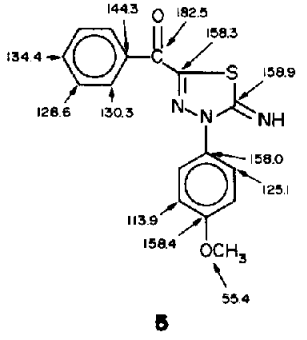


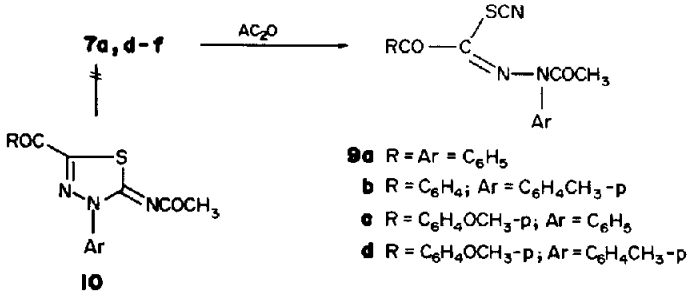
to hydrolyse readily into the more aromatic 1,3,4-thiadiazol-2-ones (**6**) under mild conditions, in contrast to the observed stability of **2** and **7** under the reaction conditions. It seemed thus of value to reinvestigate the structure proposed for **5**. In the present article we report the results of our investigation on the structure and chemistry of coupling of **1a–d** with aryldiazonium chlorides which clearly reveals that the hydrazones **7** are the readily formed products of coupling.

## RESULTS AND DISCUSSION

**1a–d** were reacted with aryldiazonium chlorides to yield the corresponding coupling products. The i.r. spectra of these coupling products revealed—in each case—bands for aroyl CO and NH groups. In the i.r. spectra of products of the coupling of *m*-nitrophenacylthiocyanate with aryldiazonium salts a band associated with the SCN functional group was observed. Thus, these products should be formulated as **7k–n**. However, i.r. spectra of several of the coupling products revealed an absence of any SCN absorption. For these products the cyclic structure **5** also seems possible. But this finding cannot be utilized alone to establish this structure for these coupling products as the cyano group sometimes does not reveal any characteristic absorption in the i.r. spectra [6]. Consequently, we have compared the u.v. spectra of these products with those of the acyclic hydrazones **7k–n**. The u.v. spectra of all the compounds prepared revealed a maximium at 390–370 nm depending on the nature of the substituent. Such a band was earlier considered as associated with an arylhydrazone linkage [7]. The similarity of these u.v. spectra made us believe that products **7a–n** are really hydrazones in spite of the absence of a SCN signal. This belief was further supported by the $^{13}C$ NMR spectra. For example, the $^{13}C$ NMR spectra of **7e** showed six non-coupled carbons at $\delta = 180.3$, 163.8, 158.2, 147.6, 138.8, 128.7 ppm. The signal at 180.3 was assigned to the CO function at C-7. The signal at 163.8 was assigned to C-1; it is in good agreement with the value of 159.9 reported for C-1 in anisole. Further deshielding by the CO function is expected. The signal at 158.2 was assigned to C-10 and is again in agreement with the reported value for C-1 in phenylhydrazine (152.3). The



signal at 147.6 was assigned to C-8 and finds a parallel with values for carbons with similar functional groups [8,9]. The signals at $\delta = 138.8$ and 128.7 ppm remained. The former was assigned to C-4 and the latter to C-9 (SCN) [10]. The coupled carbons were similarly assigned as aryl carbons using data in the tables of BREITMAIER and VOELTER [8].

The $^{13}$C NMR data of the other products of coupling aryldiazonium salts with phenacylthiocyanates could similarly only be interpreted in terms of the arylhydrazone structure rather than the thiadiazol-2-imine structure.

Only one thiadiazol-2-imine derivative (**5**; R = $C_6H_5$; Ar = $C_6H_4OCH_3$-*p*) could be isolated in the pure state via coupling **1a** with diazotized *p*-anisidine and warming the resulting product in a weakly basic medium for a short period. Attempts to cyclize other products similarly did not afford pure cyclic products; mixtures of products were obtained which could not be separated. The $^{13}$C NMR of this derivative revealed a pattern completely different from that of the acyclic products. Thus, the resonance for the SCN group that appeared normally at $\delta$128 ppm disappeared and a new signal at $\delta$158.9 appeared for C=NH. Also the signal for the hydrazone carbon, normally at $\delta$147.0 ppm, appeared at 158.3 ppm (*cf.* formula).

The absence of a SCN signal in the i.r. spectra of **7a–j** may be attributed to the hydrazones being mainly in the charge separated canonical form **8**. In agreement with this is the appearance of the phenyl carbons of the arylhydrazone moiety at a higher field than expected for such carbons. When a strong electron withdrawing substituent is present on the aryl moiety, the direction of polarization in the molecule changes and **7** is then the predominating resonance form and a SCN signal appears.

When refluxed in acetic anhydride, compounds **7a, d–f** afforded the corresponding acetyl derivatives. These may be formulated as **9** or isomeric **10**. Structure **9** was considered the more likely based on the

Table 1

| Compd. | M.p. (°C) | Yield % | Crys. Solv. | Mol. Form. | % Analysis calcd./found C | H | N | S |
|---|---|---|---|---|---|---|---|---|
| **5** | 120–122 | 72 | a | $C_{16}H_{13}N_3O_2S$ | 61.7 | 4.2 | 13.5 | 10.3 |
| | | | | | 62.0 | 4.4 | 13.6 | 10.5 |
| **7a** | 81–82 | 78 | a | $C_{15}H_{11}N_3OS$ | 64.0 | 3.9 | 14.9 | 11.4 |
| | | | | | 64.3 | 4.0 | 15.0 | 11.3 |
| **7b** | 92–94 | 80 | a | $C_{15}H_{10}ClN_3OS$ | 57.1 | 3.2 | 13.3 | 10.2 |
| | | | | | 57.3 | 3.2 | 13.5 | 10.3 |
| **7c** | 125–126 | 75 | a | $C_{15}H_{10}ClN_3OS$ | 57.1 | 3.2 | 13.3 | 10.2 |
| | | | | | 56.8 | 3.3 | 13.2 | 10.3 |
| **7d** | 104–105 | 80 | a | $C_{16}H_{13}N_3OS$ | 65.1 | 4.4 | 14.2 | 10.9 |
| | | | | | 65.2 | 4.8 | 14.0 | 11.0 |
| **7e** | 130–133 | 65 | a | $C_{16}H_{13}N_3O_2S$ | 61.7 | 4.2 | 13.5 | 10.3 |
| | | | | | 61.5 | 4.4 | 13.2 | 10.6 |
| **7f** | 144–145 | 77 | a | $C_{17}H_{15}N_3O_2S$ | 62.8 | 4.6 | 12.9 | 9.8 |
| | | | | | 62.6 | 5.0 | 13.2 | 9.6 |
| **7g** | 137–138 | 70 | a | $C_{17}H_{15}N_3O_3S$ | 59.8 | 4.4 | 12.3 | 9.5 |
| | | | | | 59.5 | 4.7 | 12.5 | 9.6 |
| **7h** | 100–102 | 66 | a | $C_{15}H_{10}BrN_3OS$ | 50.0 | 2.8 | 11.7 | 8.9 |
| | | | | | 50.0 | 3.0 | 11.9 | 9.0 |
| **7i** | 163–165 | 60 | a | $C_{15}H_9BrClN_3OS$ | 45.7 | 2.3 | 10.7 | 8.1 |
| | | | | | 45.5 | 2.3 | 10.8 | 8.2 |
| **7j** | 140–142 | 65 | b | $C_{16}H_{12}BrN_3OS$ | 51.3 | 3.2 | 11.2 | 8.6 |
| | | | | | 51.5 | 3.2 | 11.5 | 8.7 |
| **7k** | 87–88 | 66 | b | $C_{15}H_{10}N_4O_3S$ | 55.2 | 3.1 | 17.2 | 9.8 |
| | | | | | 55.5 | 3.0 | 17.3 | 9.9 |
| **7l** | 212–214 | 70 | b | $C_{15}H_9BrN_4O_3S$ | 44.5 | 2.2 | 13.8 | 7.9 |
| | | | | | 44.5 | 2.2 | 13.7 | 7.8 |
| **7m** | 106–108 | 70 | b | $C_{15}H_9ClN_4O_3S$ | 50.0 | 2.5 | 15.5 | 8.9 |
| | | | | | 50.2 | 2.6 | 15.5 | 8.8 |
| **7n** | 124–125 | 70 | b | $C_{16}H_{12}N_4O_3S$ | 56.5 | 3.6 | 16.5 | 9.4 |
| | | | | | 56.5 | 3.8 | 16.7 | 9.5 |
| **9a** | 151–153 | 72 | a | $C_{17}H_{13}N_3O_2S$ | 63.2 | 4.1 | 13.0 | 9.9 |
| | | | | | 63.4 | 4.4 | 12.9 | 10.0 |
| **9b** | 126–128 | 76 | a | $C_{18}H_{15}N_3O_2S$ | 64.1 | 4.5 | 12.5 | 9.5 |
| | | | | | 64.1 | 4.0 | 12.7 | 9.3 |
| **9c** | 185–187 | 75 | a | $C_{18}H_{15}N_3O_3S$ | 61.2 | 4.3 | 11.9 | 9.1 |
| | | | | | 61.4 | 4.1 | 11.8 | 9.0 |
| **9d** | 149–150 | 72 | a | $C_{19}H_{17}N_3O_3S$ | 62.1 | 4.7 | 11.4 | 8.7 |
| | | | | | 62.4 | 4.4 | 11.6 | 8.8 |

a: Ethanol; b: ethanol–dioxan.

Table 2. Infrared and u.v. spectra of compounds listed in Table 1

| Compd. | i.r. ($cm^{-1}$) (NH) | (SCN) | (C=O) | (C=N) | u.v. $\lambda_{max}$ (acetone) |
|---|---|---|---|---|---|
| **5** | 3300 | | 1640 | 1610 | |
| **7a** | 3350 | | 1660 | 1620 | |
| **7b** | 3350 | | 1650 | | 368 |
| **7c** | 3320 | | 1650 | 1610 | 374 |
| **7d** | 3250 | | 1660 | 1620 | 378 |
| **7e** | 3350 | | 1640 | | 374 |
| **7g** | 3350 | | 1650 | 1620 | 381 |
| **7h** | 3200 | | 1660 | 1630 | 375 |
| **7i** | 3200 | | 1650 | | 376 |
| **7j** | 3250 | | 1650 | 1620 | |
| **7k** | 3100 | 2180 | 1680 | 1620 | 378 |
| **7l** | 3200 | 2200 | 1650 | 1620 | |
| **7m** | 3150 | 2150 | 1680 | 1620 | 374 |
| **7n** | 3200 | 2200 | 1670 | | 387 |
| **9a** | | | 1660, 1640 | 1620 | |
| **9b** | | | 1650, 1640 | | |
| **9c** | | | 1650, 1640 | | |
| **9d** | | | 1645, 1640 | | |

Table 3. $^{13}C$ NMR spectra of selected compounds

| Compd. | $^{13}C$ NMR $\delta$ ppm C-7 | C-8 | C-9 | C-10 | C-aromatics |
|---|---|---|---|---|---|
| **5** | | | | | *cf.* formula |
| **7b** | 182.9 | 134.2 | 128.3 | 158.3 | 128.6, 129.9, 130.6, 131.6, 131.8, 133.8, 135.2 |
| **7e** | 180.3 | 147.6 | 128.7 | 158.2 | 114.0, 122.8, 128.8, 132.5, 138.8, 163.8 55.6 ($OCH_3$) |
| **7k** | 182.9 | 134.2 | 128.3 | 158.3 | 125.0, 128.6, 129.2, 130.3, 130.6, 131.6, 135.4, 135.9, 136.6 |
| **7n** | 216.2 | 147.5 | 127.8 | 158.0 | 122.2, 124.8, 124.9, 127.7, 129.4, 130.3, 135.4, 135.9, 136.6, 20.5($CH_3$) |
| **9c** | 181.5 | 164.6 | 128.9 | 155.9 | 113.9, 124.6, 127.1, 128.6, 133.1, 138.6, 165.1, 27.1, 181 (acetyl group) |

$^{13}C$ NMR which revealed a pattern very similar to that of the hydrazones **7** and different from that expected for a thiadiazol-2-imine derivative.

It can be concluded that products of coupling **1a–d** with aryldiazonium chlorides are really the hydrazones (**7**) and not the thiadiazol-2-imines (**5**).

## EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were recorded (KBr) on a Shimadzu 408 spectrophotometer. The u.v. spectra were measured on a Perkin–Elmer Lambda 15 u.v.–vis spectrophotometer. $^{13}C$ NMR were obtained in DMSO-$d_6$ on a Nicolet spectrometer (75 MHz) with $Me_4Si$ as internal standard, and chemical shifts are expressed in $\delta$ ppm. Analytical data were obtained from the analytical data unit at Cairo University.

*Coupling aryldiazonium chlorides with phenacylthiocyanates*

*General procedure.* A solution of aryldiazonium chloride (0.01 mol) was added to the cold solution of phenacylthiocyanate **1a–d** (0.01 mol) in DMF–ethanol mixture (100 ml 50:50) containing sodium acetate (5 g). The solid product, so formed, was collected by filtration and crystallized from the proper solvent (*cf.* Table 1).

For the synthesis of **5** (R = $C_6H_5$; Ar = $C_6H_4OCH_3$-*p*) a suspension of the product of coupling **1a** with diazotized *p*-anisidine (2 g) was heated under reflux in ethanol (50 ml) containing sodium acetate (3 g) for 15 min. The reaction mixture was poured onto cold water and the solid product, formed on standing, was collected by filtration and crystallized from ethanol.

*Reaction of* **7a, d–f** *with acetic anhydride*

Compounds **7a, d f** (3 g) in acetic anhydride (50 ml) were heated under reflux for 15 min. The reaction mixture was evaporated under reduced pressure and the remaining product was triturated with water. The solid product, so formed, was collected by filtration and crystallized from the proper solvent (*cf.* Table 1).

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