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The Reaction of 2,4,6-Triphenyl-1,3-thiazinylium Perchlorate with Active Methylenes

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Synopsis. The reaction of 2,4,6-triphenyl-1,3-thiazinylium perchlorate (**4**) with several active methylenes was studied. Methyl cyanoacetate or benzoylacetonitrile reacted with **4** to give 3-cyano-2,4,6-triphenylpyridine, while malononitrile led to 1-mercapto-1,3-diphenyl-4,4-dicyanobutadiene and cyanoacetamide led to 2-hydroxy-3-cyano-4,6-diphenylpyridine. The reaction of diethyl malonate, nitromethane, or nitroethane with **4** gave 2-[bis(ethoxycarbonyl)methyl]-, 2-nitromethyl-, or 2-(1-nitroethyl)-2,4,6-triphenyl-2*H*-1,3-thiazine respectively. These results showed that the reaction manner of **4** to these active methylenes is significantly different from that of 2,4,6-triphenyl-1,3-oxazinylium salt.

Concerning the reaction of 2,4,6-triphenylpyrylium salt (**1**) and its S-analog, 2,4,6-triphenylthiopyrylium salt (**2**), with active methylenes, **1** and **2** usually lead to the same products, 1-substituted 2,4,6-triphenylbenzenes; however, with malononitrile and nitromethane **1** and **2** lead to different products.[1,2] This fact suggested that the reactivities of **1** and **2** are slightly different from each other. The reaction of 2,4,6-triphenyl-1,3-oxazinylium perchlorate (**3**) with active methylenes gives various pyridine derivatives *via* butadienes as intermediates;[3,4] however, the reactivity of the S-analog of **3**, 2,4,6-triphenyl-1,3-thiazinylium perchlorate (**4**) has not yet been investigated. In this study, the reaction of **4** with several active methylenes was examined, and the reactivity of **4** was compared with those of **1**, **2**, or **3**.

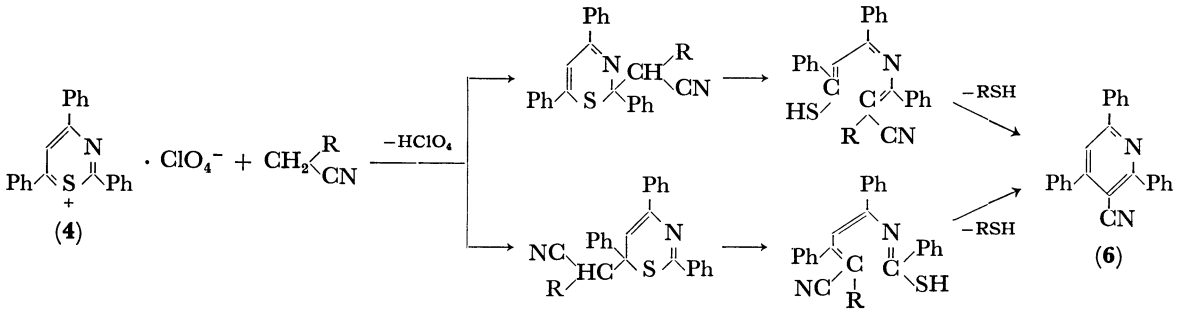
Results and Discussion

On treatment with methyl cyanoacetate, **1** or **2** leads to 2,4,6-triphenylbenzonitrile (**5**),[1,2] while **3** gives 2-benzoylamino-3-methoxycarbonyl-4,6-diphenylpyridine.[3] When **4** was refluxed with this reagent in MeOH–MeONa, 3-cyano-2,4,6-triphenylpyridine (**6**) was given in a good yield. **6** is the N-analog of **5**; consequently, the behavior of **4** in response to this reagent is different from that of **3**, but similar to that of **1** or **2**. Two courses may be supposed for this reaction, as is shown in Scheme 1 (R=$COOCH_3$).

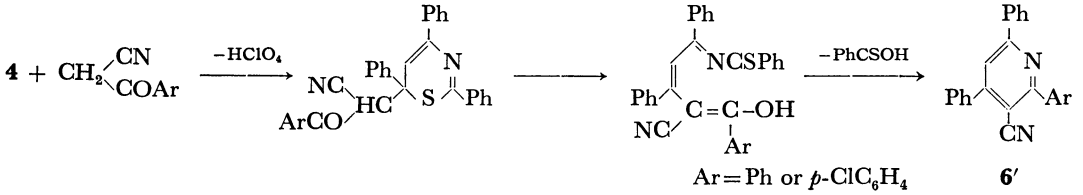
On treatment with benzoylacetonitrile, **1** and **2** also give **5**. On the other hand, it has been shown that **3** with this reagent undergoes the reaction of Scheme 2 and leads to **6'** (Ar=Ph).[4] The reaction of **4** with this reagent also gave **6**. This indicates at least three courses in Scheme 1 (R=Ph) and Scheme 2 (Ar=Ph). In order to check the course, **4** was treated with *p*-chlorobenzoylacetonitrile, and the resulting product was identified as **6**. The reaction course in Scheme 2 was, thus, obviated, and one of the two ways of Scheme 1 was suggested to be the reaction course. Therefore, **4** is different from **3** in its behavior in reaction to this reagent.

Cyanoacetamide leads to **5** on treatment with **1** or **2**. The reaction of **3** with this reagent gives 2-hydroxy-3-cyano-4,6-diphenylpyridine (**7**).[4] On the other hand, treatment with **4** resulted in **7**; for this reaction, the two courses may also be supposed. It is, however, difficult to study their reaction courses more closely because the reactions of these three reagents with **4** proceed very readily without the isolation of their intermediates.

Malononitrile behaves quite differently in response to **1**, **2**, or **3** to give different products.[1-3] The reaction of **4** with this reagent gave **8**, with a small amount of **6**. The reaction course for **6** was supposed to be as is shown

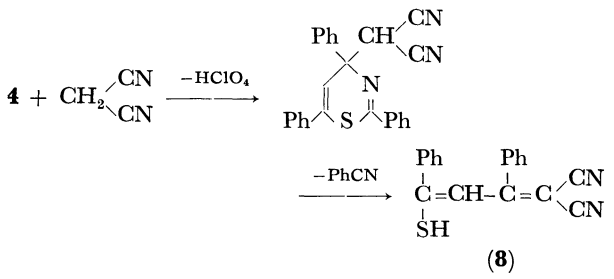


Scheme 1.



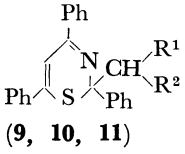
Scheme 2.

in Scheme 1 (R=CN), while **8** was identified as 1-mercapto-1,3-diphenyl-4,4-dicyanobutadiene, which is given on the treatment of 3,5-diphenyl-1,2-dithiolylium salt with this reagent;[5] it was found that this reaction mode was unique, as is shown in Scheme 3.



Scheme 3.

Diethyl malonate, nitromethane, and nitroethane reacted with **4** in dioxane-triethylamine to afford **9**, **10**, and **11** respectively. Their analytical data and the molecular weights by MS spectrometry showed that they were adducts of the 1,3-thiazinylium cation and the carbanion of active methylenes. Since their IR spectra had no absorption assigned to N–H and S–H stretching, it was suggested that these products were not chain compounds. The UV spectra were closely similar to each other (λ_{max}=244 nm, ε=25800—27600); consequently, they were thought to have the same skeletal structure. According to their CMR spectra, which was checked by means of the ^{1}H-off-resonance method, **9**, **10**, and **11** were confirmed to be 2-[bis-(ethoxycarbonyl)methyl]-, 2-nitromethyl-, and 2-(1-nitroethyl)-2,4,6-triphenyl-2*H*-1,3-thiazine respectively.



(**9**, **10**, **11**)

9: R^1=$COOC_2H_5$, R^2=$COOC_2H_5$
10: R^1=H, R^2=NO_2
11: R^1=CH_3, R^2=NO_2

The reaction of **4** with other active methylenes, such as dibenzoylmethane, ethyl benzoylacetate, benzoylacetamide, and ethyl carbamoylacetate, gave no product.

Hence, it is proved that **4** is less active than **3** against several active methylenes, and that the reaction manners of **3** and **4** are significantly different from each other.

Experimental

3-Cyano-2,4,6-triphenylpyridine (6). Into a solution of 3 mmol of methyl cyanoacetate, benzoylacetonitrile, or *p*-chlorobenzoylacetonitrile in 4 ml of 1.0 mol dm^{-3} MeOH–MeONa, 0.86 g (2 mmol) of **4** was stirred at room temperature for 10 min, and then the mixture was refluxed for 1 h. The reaction mixture was poured into dilute hydrochloric acid. The resulting precipitate was collected by filtration and recrystallized from acetic acid to give 0.54 g (81%), 0.58 g (87%), or 0.39 g (59%) of **6** (mp=225.3 °C) respectively. The IR spectrum of **6** was completely superimposed on that of an authentic sample.[4]

2-Hydroxy-3-cyano-4,6-diphenylpyridine (7). Cyanoacetamide was treated with **4** by the procedure described above. The resulting precipitate was purified by reprecipitation from aqueous sodium hydroxide–hydrochloric acid to give 0.39 g (72%) of **7** (mp>300 °C). The IR spectrum of **7** agreed with that of an authentic sample.[3]

1-Mercapto-1,3-diphenyl-4,4-dicyanobutadiene (8). Into a solution of 0.20 g (3 mmol) of malononitrile in 4 ml of 1.0 mol dm^{-3} MeOH–MeONa, 0.86 g (2 mmol) of **4** was stirred at room temperature for 10 min, and then the mixture was refluxed for 1 h. The reaction mixture was allowed to stand overnight and then filtered to separate the resulting crystalline (0.12 g, 18%) of **6**. The filtrate was poured into dilute hydrochloric acid, and the resulting precipitate was recrystallized from acetonitrile to give 0.34 g (59%) of **8** (mp=225.5 °C).[5] Found: S, 11.09%. Calcd for $C_{18}H_{12}N_2S$: S, 11.12%.

2-[Bis(ethoxycarbonyl)methyl]-, 2-Nitromethyl-, or 2-(1-Nitroethyl)-2,4,6-triphenyl-2H-1,3-thiazine (9, 10, 11). Into a solution of 3 mmol of diethyl malonate, nitromethane, or nitroethane and 0.4 ml of triethylamine in 4 ml of dioxane, 0.86 g (2 mmol) of **4** was stirred at room temperature, after which the solution was allowed to stand for 5 d. The reaction mixture was poured into dilute hydrochloric acid, and the resulting precipitate was recrystallized from methanol (**9**) or acetic acid (**10**, **11**) to yield 0.71 g (73%), 0.48 g (62%), or 0.44 g (55%) respectively. Their data are shown as follows.

9: Mp, 118.0 °C; MS, 485 (M^+), 412 ([$M-COOC_2H_5$]$^+$). 326 ($C_{22}H_{16}NS^+$), 237 ($C_{15}H_{11}NS^+$), and 121 *m/e* ($C_6H_5CS^+$); IR (KBr), 1750, 1625, 1490, 1445, 1360, 1325, and 1300 cm^{-1}; UV (EtOH), λ_{max} 244 nm (25800); CMR ($CDCl_3$), 167.19 (-COOR), 142.27, 137.46, 137.34, 132.71—126.13 (arom.), 120.13 (=CH–), 69.04 (–$\overset{|}{C}$–), 64.00 (–$\overset{|}{C}$H–), 61.18 (–CH_2–), 14.05 (–CH_3), and 13.75 ppm (–CH_3). Found: C, 71.74; H, 5.69; N, 2.82; S, 6.56%. Calcd for $C_{29}H_{27}NSO_4$: C, 71.73; H, 5.61; N, 2.89; S, 6.60%.

10: Mp, 165.3 °C; MS, 386 (M^+), 339 ([$M-HNO_2$]$^+$), 326, 237, and 121 *m/e*; IR (KBr), 1630, 1530, 1490, 1445, and 1375 cm^{-1}; UV (EtOH), λ_{max} 244 nm (27600); CMR ($CDCl_3$), 140.85, 136.90, 135.12, 131.58—126.46 (arom.), 117.99 (=CH–), 84.88 (–CH_2–), and 67.25 ppm (–$\overset{|}{C}$–). Found: C, 71.41; H, 4.69; N, 7.05; S, 8.55%. Calcd for $C_{23}H_{18}N_2SO_2$: C, 71.48; H, 4.69; N, 7.25; S, 8.30%.

11: Mp, 156.2 °C; MS, 400 (M^+), 353 ([$M-HNO_2$]$^+$), 326, 237, and 121 *m/e*; IR (KBr), 1630, 1530, 1490, 1445, 1380, and 1355 cm^{-1}; UV (EtOH), λ_{max} 244 nm (26000), CMR ($CDCl_3$), 140.86, 137.14, 135.19, 131.57—126.47 (arom.), 117.17 (=CH–), 91.85 (–$\overset{|}{C}$$HNO_2$), 69.69 (–$\overset{|}{C}$–), and 15.37 ppm (–$CH_3$). Found: C, 71.78; H, 4.98; N, 6.95; S, 8.00%. Calcd for $C_{24}H_{20}N_2SO_2$: C, 71.98; H, 5.03; N, 6.99; S, 8.01%.

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