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# REACTION OF ARYLTHALLIUM (III) COMPOUNDS WITH COPPER (II) AND (I) CYANIDES. SYNTHESIS OF ARYL CYANIDE

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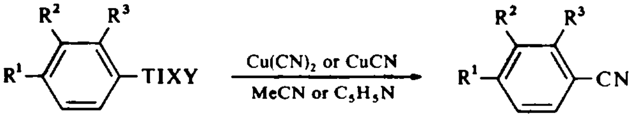
Abstract—Various kinds of arylthallium(III) salts react with copper(II) or (I) cyanide in acetonitrile or pyridine to give the corresponding aryl cyanides in good yield. In acrylonitrile the reaction using copper(I) cyanide was revealed to be of an ionic concerted intermolecular and not radical type.

As ONE of the many synthetic reactions utilizing arylthallium bis(trifluoroacetate),[1] Taylor and McKillop reported that the compound reacted with potassium cyanide under UV irradiation to form aryl cyanide.[2] Recently we have observed some reactions of arylthallium(III) compounds with copper(II) chloride[3] and bromide[4] which give the corresponding aryl halides by replacement of thallium by halide. Here we report that arylthallium(III) compounds react with copper(II) or (I) cyanide under mild conditions without UV irradiation to give the corresponding aryl cyanides in good yield.

## RESULTS AND DISCUSSIONS

When a mixture of arylthalium(III) salt (**1**) and copper(II) or (I) cyanide was stirred in organic solvents, such as acetonitrile or pyridine, under reflux for 5 to 10 hr, the corresponding aryl cyanide (**2**) was formed by replacement of thallium by a cyano group at the position where thallium was previously attached (eq. 1). In all systems studied pyridine is found to be the superior solvent for the purpose of preparing aryl cyanides.



**1** **2** (1)

Reaction of **1** with copper(II) cyanide was carried out in MeCN, dioxane, pyridine and AcOH and all of the mixtures (except the pyridine case where the mixture was a homogeneous black solution) were heterogeneous because of insolubility of copper(II) cyanide (Table 1). The following data is pertinent to the reaction using 10 mmol of $1(R^1 = R^2 = R^3 = H, X = OAc, Y = ClO_4 \cdot H_2O)$ and 20 mmol of copper(II) cyanide. In MeCN 28% yield of benzonitrile was observed at 81° for 10 hr, whilst no reaction occurred at 50°. By separate addition of pyridine, triphenylphosphine and KCN to the mixture [twice molar amounts of each to copper(II) cyanide], the yields of benzonitrile became 8, 2, and 17% respectively (5 hr at 81°). Although traces of phenyl acetate was observed in the AcOH reaction, separate reactions using copper(II) acetate and **1** gave no phenyl acetate in AcOH. The reason for low yield of *p*-anisonitrile is believed to be decomposition of **1** to anisole. The reaction of phenylmercury(II) acetate with copper(II) cyanide gave only a 5% yield of benzonitrile under conditions where 75% yield was obtained from **1**.

The formation of a copper salt containing an acetate group, probably copper(II) acetate cyanide, was confirmed as well as the formation of thallium(I) perchlorate in reactions of $1(R^1 = R^2 = R^3 = H, X = OAc, Y = ClO_4 \cdot H_2O)$ in MeCN. Although it might be plausible to consider that the reaction proceeds with equal amounts of **1** and copper(II) cyanide as eq. 2, the possibility that copper(II) cyanide decomposes to copper(I) cyanide and

$$ArTl(OAc)ClO_4 \cdot H_2O + Cu(CN)_2 \rightarrow ArCN + TlClO_4 + CuCNOAc \qquad (2)$$

cyanogen in such solvents as MeCN and pyridine (eq. 3) and then each or both react with **1** to give **2** is not excluded.

$$2\,Cu(CN)_2 \rightarrow 2\,CuCN + (CN)_2 \qquad (3)$$

The possibility that the reaction may occur with cyanogen only was excluded, because the reaction using equilmolar amounts of **1** and copper(II) cyanide gave a 53% yield of **2** in pyridine (Table 1).* We also observed neither evolution of cyanogen nor colour change of solution when 10 mmol of copper(II) cyanide was refluxed in 50 ml of MeCN for 5 hr. The catalytic effect of arylthallium(III) salts on this decomposition, however, is not obvious and the reaction with a slight amount of copper(I) cyanide might be conceivable in connection with the Sandmeyer aryl cyanide synthesis.[5] In this context further studies were carried out using copper(I) cyanide.

As in the case of the reaction using copper(II) cyanide, the mixture of **1** and copper(I) cyanide was heterogeneous in MeCN and homogeneous in pyridine. In most cases yields of **2** were better than when copper(II) cyanide was used (Table 2). Thallium(I) perchlorate and copper(I) acetate were formed as the inorganic compounds in the reaction using $1(R^1 = R^2 = R^3 = H, X = OAc, Y = ClO_4 \cdot H_2O)$. The stoichiometry of this reaction is described in eq. 3.

$$ArTl(OAc)ClO_4 \cdot H_2O + CuCN \rightarrow ArCN + TlClO_4 + CuOAc + H_2O \qquad (3)$$

Although pyridine was the best solvent for the preparation of **2** amongst those examined in both reactions using copper(II) and (I) cyanides, separate reactions revealed that coordination of pyridine to the copper salt and to the thallium of **1** did not improve the yield of **2**. For example, the reaction of $1(R^1 = R^2 = R^3 = H, X = OAc, Y = ClO_4 \cdot H_2O)$ with copper(I) cyanide-pyridine (1:1) complex in MeCN gave only 7·6% yield of benzonitrile under reflux for 5 hr (*c.f.* 23% in Table 2). The reaction of a 1:1 complex of $1(R^1 = R^2 = R^3 = H, X = Y = Cl)$ and pyridine with copper(I) cyanide gave 4·4% yield of benzonitrile in MeCN (reflux, 5 hr) compared

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* If cyanogen reacts with **1** like a halogen, the yield of **2** may not exceed 50% based on **1**.

TABLE 1. RESULTS OF THE REACTION OF 1 WITH $Cu(CN)_2$

| 1 | | | | | | $Cu(CN)_2$ | Solvent | React. Temp. | React. Time | 2 (yield, |
|---|---|---|---|---|---|---|---|---|---|---|
| $R^1$ | $R^2$ | $R^3$ | X | Y | (mmol) | (mmol) | (50 ml) | (°C) | (hr) | %)[a] |
| H | H | H | OAc | $ClO_4 \cdot H_2O$ | 10 | 20 | MeCN | 81 | 5 | 24[b] |
| H | H | H | OAc | $ClO_4 \cdot H_2O$ | 10 | 20 | $C_4H_8O_2$[c] | 100 | 5 | 15 |
| H | H | H | OAc | $ClO_4 \cdot H_2O$ | 5 | 10 | $C_5H_5N$[d] | 115 | 5 | 75 |
| H | H | H | OAc | $ClO_4 \cdot H_2O$ | 5 | 5 | $C_5H_5N$ | 115 | 5 | 53 |
| H | H | H | OAc | $ClO_4 \cdot H_2O$ | 10 | 20 | AcOH | 117 | 5 | 4[e] |
| H | H | H | OAc | OAc | 10 | 20 | MeCN | 81 | 5 | 19 |
| H | H | H | $OCOCF_3$ | $OCOCF_3$ | 5 | 10 | $C_5H_5N$ | 115 | 5 | 66 |
| H | H | H | Cl | Cl | 5 | 10 | MeCN | 81 | 5 | 9 |
| Me | H | H | OAc | $ClO_4 \cdot H_2O$ | 10 | 20 | MeCN | 81 | 5 | 35 |
| Me | H | H | OAc | $ClO_4 \cdot H_2O$ | 10 | 20 | $C_5H_5N$ | 115 | 5 | 51 |
| Me | Me | H | OAc | $ClO_4 \cdot H_2O$ | 10 | 20 | MeCN | 81 | 10 | 44 |
| Me | Me | H | OAc | $ClO_4 \cdot H_2O$ | 5 | 10 | $C_5H_5N$ | 115 | 5 | 63 |
| Me | H | Me | OAc | $ClO_4 \cdot H_2O$ | 10 | 20 | MeCN | 81 | 10 | 66 |
| Me | H | Me | OAc | $ClO_4 \cdot H_2O$ | 5 | 10 | $C_5H_5N$ | 115 | 5 | 90 |
| MeO | H | H | OAc | $ClO_4 \cdot H_2O$ | 10 | 20 | MeCN | 81 | 10 | 23[f] |

[a] Based on 1 (GLC determination). [b] Trace amounts of benzene and biphenyl detected. [c] Dioxane. [d] Pyridine. [e] Phenyl acetate (5%) obtained. [f] Anisole (9%) obtained. 2 was isolated by distillation; b.p. 107°/17 mm, m.p. 59·5–60·0° (lit.[19] m.p. 59·5–60·5°).

TABLE 2. RESULTS OF THE REACTION OF 1 WITH CuCN[a]

| 1 | | | | | CuCN | Solvent | React. Temp. | 2 (yield, |
|---|---|---|---|---|---|---|---|---|
| $R^1$ | $R^2$ | $R^3$ | X | Y | (mmol) | (50 ml) | (°C) | %)[b] |
| H | H | H | OAc | $ClO_4 \cdot H_2O$ | 10 | $C_5H_5N$[c] | 115 | 38 |
| H | H | H | OAc | $ClO_4 \cdot H_2O$ | 20 | $C_5H_5N$ | 115 | 58 |
| H | H | H | OAc | $ClO_4 \cdot H_2O$ | 20 | MeCN | 81 | 23[d] |
| H | H | H | Cl | Cl | 10 | MeCN | 81 | 3 |
| H | H | H | Cl | Cl | 20 | $C_5H_5N$ | 115 | 72 |
| Me | H | H | OAc | $ClO_4 \cdot H_2O$ | 20 | $C_5H_5N$ | 115 | 63 |
| Me | Me | H | OAc | $ClO_4 \cdot H_2O$ | 20 | $C_5H_5N$ | 115 | 77 |
| Me | H | Me | OAc | $ClO_4 \cdot H_2O$ | 20 | $C_5H_5N$ | 115 | 100 |
| Me | H | Me | OAc | $ClO_4 \cdot H_2O$ | 20 | MeCN | 81 | 62[e] |
| MeO | H | H | OAc | $ClO_4 \cdot H_2O$ | 20 | $C_5H_5N$ | 115 | 35 |

[a] Reaction time, 5 hr; 1, 5 mmol. [b] Based on 1 (GLC determination). [c] Pyridine. [d] A slight amount of benzene and biphenyl was observed. [e] This reaction was carried out under $N_2$ in the presence of 20 mmol of acrylonitrile.

TABLE 3. Tl-H COUPLING CONSTANTS IN PHENYLTHALLIUM(III)

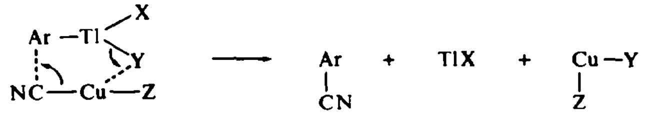
| | $PhTl^{2+}$[20] | $PhTlCl_2$[15] | | $PhTlOAcClO_4 \cdot H_2O$ | |
|---|---|---|---|---|---|
| | in $D_2O$ | in MeOH | in $C_5H_5N$ | in $D_2O$[12] | in $C_5H_5N$[a] |
| *ortho* | +948 | 850 | 812 | 912 | 869 |
| *meta* | +365 | 323 | 306 | 350 | 335 |
| *para* | +123 | 110 | 105·5 | 110 | 110 |

[a] This work.

with 3% yield in Table 2). The reason why addition of pyridine in reaction of **1** with copper(II) cyanide lowered the yield of benzonitrile can be ascribed to the coordination of pyridine with copper* and/or thallium. The interaction of pyridine with **1** was also observed from the determination of Tl–H spin–spin coupling constants in **1**($R^1 = R^2 = R^3 = H, X = OAc, Y = ClO_4 \cdot H_2O$) (Table 3; including the values of other papers). It was impossible, however, to correlate this phenomenon to the chemical reactivity of **1** with copper(II) and (I) cyanides in pyridine, because the factors determining the magnitudes of spin–spin coupling constants are so little understood.[7] One reason why pyridine is the best solvent for this reaction may be that it gives a homogeneous mixture and a rather high reaction temperature. The effect of triphenylphosphine could also be explained by the coordination with thallium and/or copper. In fact a phenylthallium dichloride-triphenylphosphine complex has been isolated.[8] Although the number of experiments was limited, the effects of X and Y upon the yields of **2** appeared to be small compared to that of solvent in both reactions using copper(II) and (I) cyanides.

It had been reported[9] that the reaction of phenylthallium(III) dichloride with KCN gave the complex $K[PhTl(CN)_3]$ which disproportionated to diphenylthallium(III) cyanide by heating in water. When **1**($R^1 = R^2 = R^3 = H$, $X = OAc$, $Y = ClO_4 \cdot H_2O$) and KCN or NaCN were stirred in MeCN for 1 hr under reflux, only the exchange of perchlorate group with cyano group occurred without disproportionation to diphenylthallium(III) compound. Separate reactions showed that **1**($R^1 = R^2 = R^3 = H$, $X = OAc$, $Y = CN$) thus formed gave no benzonitrile in various solvents under reflux. This result together with the fact that addition of KCN to the reaction of **1** with copper(II) cyanide resulted in no increase of the yield of **2** excludes the reaction scheme where **1** and copper(II) or (I) cyanide give an arylthallium(III) acetate cyanide followed by intramolecular formation of **2**. The thermal stability of the Tl–CN bond was also reported by Taylor *et al.*[2]

The reaction does not appear to involve radicals as reaction of **1**($R^1 = R^2 = R^3 = H, X = OAc, Y = ClO_4 \cdot H_2O$) with copper(I) cyanide in the presence of $CH_2{=}CHCN$ gave no significant amounts of benzene or biphenyl, none of arylated acrylonitrile, and no polymerisation of acrylonitrile even though an appreciable yield of benzonitrile (25%) was still obtained. The mechanism thus contrasts with that of the Sandmeyer reaction where a radical like one-electron-transfer scheme is proposed.[10] Although more work must be done for clarification of a detailed reaction mechanism, the experimental observations indicate an ionic concerted intermolecular scheme without free radical intermediates for this reaction,[11] similar to that proposed in the chlorination of **1** with copper(II) chloride (eq. 4).[3]



(4)

(Z = CuCN and maybe CN)

## EXPERIMENTAL

All organic materials were purified immediately before use by distillation, whilst commercially available copper(II) cyanide (purity, 95%), copper(I) cyanide, and other inorganic materials were used without further purification. Commercially available aryl cyanides were used as authentic samples for GLC.

* The 1:1 complexation of copper(II) cyanide with pyridine had been reported.[6]

Derivatives of 1 ($X = OAc$, $Y = ClO_4 \cdot H_2O$) were prepared by the reported method[12] with a slight modification in that a large amount of ether or *n*-hexane was added to the filtrate from the reaction without evaporation of solvent to crystallize 1.[13] 1 ($R^1 = R^2 = R^3 = H$, $X = Y = Cl$) was prepared from phenylboric acid and $TlCl_3 \cdot 4H_2O$ in boiling water according to the reported method,[14] m.p. 231–233° (lit.[14] m.p. 234°), and then converted to 1($R^1 = R^2 = R^3 = H$, $X = Y = OAc$) by addition of excess AgOAc in MeOH;[15] m.p. 195–198° (lit.[16] m.p. 193–195°). 1($R^1 = R^2 = R^3 = H$, $X = Y = OCOCF_3$) was prepared by a reaction of benzene with a TFA solution of thallium(III) trifluoroacetate at room temp for 1 hr. 1($R^1 = R^2 = R^3 = H$, $X = Y = C$)-pyridine (1:1) complex was obtained by the reported method;[15] m.p. 164° (dec) [lit.[9] m.p. 172° (dec)]. 1($R^1 = R^2 = R^3 = H$, $X = OAc$, $Y = CN$) was prepared as white amorphous crystals by addition of 20 mmol of NaCN to aqueous solution of 10 mmol of 1($R^1 = R^2 = R^3 = H$, $X = OAc$, $Y = ClO_4 \cdot H_2O$) at room temp; m.p. 268–272°, yield 73% (Found: C, 29·50; H, 2·18; N, 3·96. $C_9H_8NO_2Tl$ requires: C, 29·49; H, 2·20; N, 3·82%). Copper(I) cyanide–pyridine (1:1) complex[17] was prepared by heating 10 mmol of copper(I) cyanide in 50 ml of pyridine at reflux for 30 min, collecting white crystals after cooling, washing with anhydrous ether and drying over CaO; yield 93% (Found: C, 42·29; H, 3·06; N, 16·59. $C_6H_5N_2Cu$ requires: C, 42·72; H, 2·98; N, 16·60%).

*Reaction of* 1($R^1 = R^2 = R^3 = H$, $X = OAc$, $Y = ClO_4 \cdot H_2O$) *with* $Cu(CN)_2$ *in acetonitrile.* A mixture of 4·58 g (10 mmol) of 1 and 2·31 g (20 mmol) of $Cu(CN)_2$ in 50 ml of MeCN was maintained at reflux (81°) for 10 hr with stirring. Brown precipitates (4·55 g) were filtered off, and the filtrate concentrated to *ca.* 10 ml under reduced pressure to give more precipitates (1·05 g, 3·46 mmol of $TlClO_4$). After filtration, the filtrate was diluted with 100 ml sat. NaClaq and extracted with benzene. The benzene extract contained 2·8 mmol (28% yield) of benzonitrile and a trace of biphenyl (by GLC). Benzonitrile (0·21 g, 2 mmol) was isolated by distillation; b.p. 90°/40 mm. Brown precipitates were washed with hot water to leave 2·05 g of solid, shown to contain cyano and acetate groups by IR spectroscopy; probably a mixture of CuCN(OAc) and unreacted $Cu(CN)_2$. Addition of dil. HCl to the water-washings gave 1·24 g (5·17 mmole) of TlCl. Acidification of the filtrate before benzene extraction to prevent the complexation of the product 2 with thallium and/or copper resulted in no increase of the yield of 2.

*Reaction of* 1($R^1 = R^3 = Me$, $R^2 = H$, $X = OAc$, $Y = ClO_4 \cdot H_2O$) *with* $Cu(CN)_2$ *in pyridine.* A mixture of 2·43 g (5 mmol) of 1 and 1·16 g (10 mmole) of $Cu(CN)_2$ in 50 ml of pyridine was stirred for 5 hr at 115°. After filtration of brown precipitates [0·67 g; $Cu(CN)_2$ or CuCN–pyridine complex by IR spectroscopy], the filtrate was diluted with water and extracted with benzene to give more precipitates [1·04 g; a mixture of $Cu(CN)_2$ or CuCN–pyridine complex and $TlClO_4$ by IR]. Benzene extract which contained 4·50 mmol (90%) of 2,4-dimethyl-benzonitrile gave 0·46 g (3·5 mmol) of sample by distillation; b.p. 67·5°/12 mm. Addition of dil. HCl to the water layer gave 0·63 g (2·62 mmol) of TlCl.

*Reaction of* 1($R^1 = R^2 = Me$, $R^3 = H$, $X = OAc$, $Y = ClO_4 \cdot H_2O$) *with* CuCN *in pyridine.* A mixture of 2·45 g (5 mmol) of 1 and 1·79 g (20 mmol) of CuCN in 50 ml of pyridine was stirred for 5 hr under reflux. The same treatment as described above gave 3·85 mmol (77%) of 3,4-dimethylbenzonitrile, 0·54 g (2·25 mmol) of TlCl, and 2·69 g of a mixture of CuCN–pyridine (1:1) complex and $TlClO_4$. Distillation gave 0·39 g (3 mmol) of pure nitrile; b.p. 140°/20 mm, m.p. 66·5–67·5° (lit.[18] m.p. 66°).

*Reaction of* 1($R^1 = R^2 = R^3 = H$, $X = OAc$, $Y = ClO_4 \cdot H_2O$) *with CuCN–pyridine* (1:1) *complex in acetonitrile.* A yellowish green solution of a mixture of 2·29 g (5 mmol) of 1 and 3·38 g (20 mmol) of complex in 50 ml of MeCN was stirred for 5 hr under reflux. After filtration of 2·79 g of precipitates the filtrate was treated as described above and shown to contain 0·38 mmol (7·6% yield) of benzonitrile and 4 mmol of pyridine.

*Reaction of* 1($R^1 = R^2 = R^3 = H$, $X = Y = Cl$)*-pyridine* (1:1) *complex with* CuCN *in acetonitrile.* A mixture of 2·16 g (5 mmol) of complex and 1·79 g (20 mmol) of CuCN in 50 ml of MeCN was stirred for 5 hr under reflux, during which period the colur of the heterogeneous solution changed from white to yellowish green. Benzonitrile (0·22 mmol, 4·4% yield) and pyridine (0·30 mmol) were detected by GLC.

*Reaction of* 1($R^1 = R^3 = Me$, $R^2 = H$, $X = OAc$, $Y = ClO_4 \cdot H_2O$) *with* CuCN *in the presence of acrylonitrile.* A mixture of 2·43 g (5 mmol) of 1 and 1·79 g (20 mmol) of CuCN in 50 ml of MeCN containing 1·07 g (20 mmol) of acrylonitrile was refluxed for 5 hr under $N_2$. After filtration of pale brown precipitates (3·5 g), the filtrate was treated as described above. GLC analysis showed unreacted acrylonitrile, 3·12 mmol (62·4%) of 2,4-dimethylbenzonitrile and absence of aromatic coupling compound or arylated acrylonitrile. The pale brown precipitates were washed with hot water to remove $TlClO_4$ and 1 leaving a *ca.* 3:1 mixture of CuCN and CuOAc (elemental analysis and IR). No polyacrylonitrile was detected as no characteristic absorption of polyacrylonitrile at 1450 ($CH, CH_2$) and 1050 $cm^{-1}$ (C—C skeletal) in the IR spectrum[11] was observed.

*Spectral measurements.* IR spectra were obtained by means of Hitachi EPI-2 and EPS-3T. NMR spectra were determined by a Varian A-60 spectrometer in $CDCl_3$, $D_2O$ and pyridine. GLC analysis was carried out on a Shimadzu 5APTF apparatus, using PEG 6000 (25)%-Chromosorb-W 3m and Apz-L (30%)-Celite 3m columns with appropriate aromatic nitriles as internal standard (He as carrier gas).

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## REFERENCES

[1] E. C. Taylor and A. McKillop, *Accounts Chem. Res.* 3, 338 (1970)
[2] E. C. Taylor, H. W. Altland, R. H. Danforth, G. McGillivray and A. McKillop, *J. Am. Chem. Soc.* **92**, 3520 (1970)
[3] K. Ichikawa, Y. Ikeda and S. Uemura, *Chem. Comm.* 169 (1971)
[4] S. Uemura, K. Sohma, M. Okano and K. Ichikawa, *Bull. Chem. Soc. Japan* **44**, 2490 (1971)
[5] T. Sandmeyer, *Ber. Dtsh. Chem. Ges.* **17**, 2650 (1884); *Ibid.* **18**, 1492 (1885)
[6] F. W. Stauf and H. Hagenest, USP, 1, 880, 516; *Chem. Abstr.* **27**, 557 (1933)
[7] A. G. Lee, *The Chemistry of Thallium*, p. 250, Elsevier, Amsterdam (1971)
[8] J. M. Davidson and G. Dyer, *J. Chem. Soc.* (*A*) 1616 (1968)
[9] F. Challenger and O. V. Richards, *J. Chem. Soc.* 405 (1934)
[10] D. C. Nonhebel and W. A. Waters, *Proc. Royal Soc.* (*London*) **A242**, 16 (1957)
[11] F. M. Beringer and P. Bodlaender, *J. Org. Chem.* **34**, 1981 (1969)
[12] K. Ichikawa, S. Uemura, E. Uegaki and T. Nakano, *Bull. Chem. Soc. Japan* **44**, 545 (1971)
[13] S. Uemura, Y. Ikeda, O. Itoh and K. Ichikawa, *Ibid.* **44**, 2571 (1971)
[14] F. Challender and B. Parker, *J. Chem. Soc.* 1462 (1931)
[15] A. G. Lee, *J. Organometal. Chem.* **22**, 537 (1970)
[16] H. J. Kabbe, *Liebigs Ann.* **656**, 204 (1962)
[17] Laaketehdas Orion Oy. Brit. P. 896, 720; *Chem. Abstr.* **57**, 11113 (1962)
[18] R. Scholl and F. Kačer, *Ber. Dtsch. Chem. Ges.* **36**, 322 (1903)
[19] E. Bamberger and W. Pemsel, *Ibid.* **36**, 359 (1903)
[20] J. P. Maher and D. F. Evans, *J. Chem. Soc.* 637 (1965)