

## The Reaction of Potassium Hexacyanodinicelate(I) with Organic Halides

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Reaction of potassium hexacyanodinicelate(I) (1) with various organic halides in aqueous solutions were examined. Three types of reactions were observed to occur rather selectively depending on the halides used: hydrogenolysis in the case of *p*-cyanobenzyl bromide and phenacyl bromide; coupling in the case of benzyl, *p*-methylbenzyl, and *p*-methoxybenzyl bromide and *trans*- $\beta$ -bromostyrene; cyanation in the case of cinnamyl bromide. When the same reaction was carried out in the presence of carbon monoxide, carbonylation reaction occurred easily under mild conditions to give symmetrical ketone or ester. In the presence of acrylonitrile or ethyl acrylate, the reaction of 1 with benzyl bromide gave 4-phenylbutyronitrile and ethyl 4-phenylbutyrate, respectively. Unstable organonickel(II) complexes containing a carbon-nickel  $\sigma$  bond were postulated as intermediates in these reactions.

In recent years, a variety of anionic organometallic complexes have been shown to be excellent nucleophilic reagents in various synthetic reactions: *e.g.*, lithium acylmetal carbonylate in the synthesis of unsymmetrical ketones<sup>1</sup> or 1,4-dicarbonyl compounds,<sup>2</sup> reagents from nickel carbonyl and alkali metal alkoxides for alkoxy-carbonylation of alkenyl or alkyl halides,<sup>3</sup> potassium hexacyanodinicelate(I)<sup>3</sup> and sodium dicyanocuprate(I)<sup>4</sup> for cyanation of alkenyl halides, and lithium dialkylcuprate<sup>5</sup> in the reaction with organic halides or  $\alpha,\beta$ -unsaturated ketones.

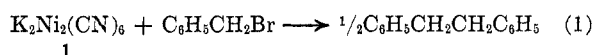
In a preliminary communication<sup>6</sup> the present authors have reported a reagent useful for the formation of new carbon-carbon bonds. Potassium hexacyanodinicelate(I) (1) in an aqueous solution reacted smoothly with benzyl bromide at room temperature to give bibenzyl (89.0%), and, in the presence of carbon monoxide (CO), the same reaction gave dibenzyl ketone in a high yield. In this report we wish to propose the formation of organonickel(II) complexes as precursors to the products resulted from the following reactions; *i.e.*, hydrogenolysis, coupling, cyanation, carbonylation (in the presence of CO), and benzylation (in the presence of olefins).

### Results

**Reaction of Potassium Hexacyanodinicelate(I) (1) with Organic Halides.**—To the blood-red aqueous acetone solutions of 1 were added dropwise organic halides (molar ratio, 1:R-X = 1:1 ~ 2) at 0° or at room temperature under a nitrogen atmosphere. The results of analyses of organic compounds formed are summarized in Table I.

When an aqueous acetone solution of 1 was treated with an equimolar amount of benzyl bromide at 0°, the color of the solution changed to pale yellow within 30 min. The pale yellow color remained unchanged even after the solution was stirred at 0° for 6 hr, but when the reaction temperature was raised up to 20°, a rapid decomposition took place to give a yellow-green suspension. Glpc analysis of the products showed the pres-

ence of the following compounds: bibenzyl (89.0%), benzaldehyde (0.6%), and benzyl alcohol (2.0%). When 2 mol of benzyl bromide was used per mol of 1, just 1 mol of halide was consumed to give bibenzyl (96.4% based on 1 used) and the excess of the halide was recovered (eq 1).



*p*-Methyl- and *p*-methoxybenzyl bromide gave exclusively the corresponding bibenzyl derivatives and in these reactions only a trace amount of hydrogenolysis product (*p*-xylene, *p*-methoxytoluene, respectively) was detected by glpc.<sup>7</sup> The reaction of 1 with *p*-cyanobenzyl bromide is interesting and, in this case, the yield of hydrogenolysis product, *p*-cyanotoluene, increased remarkably (50.0%) at the expense of coupling product, *p,p'*-dicyanobibenzyl.

It should be noted that the reactivity of 1 to organic halides and the product distribution depend greatly on the halides used. Although the cyanonickelate reagent 1 was quite inactive towards simple alkyl bromides and aryl halides, it showed a high reactivity towards alkenyl or allyl bromides; *i.e.*, *trans*- $\beta$ -bromostyrene and cinnamyl bromide reacted smoothly with 1 to give *trans,trans*-1,4-diphenyl-1,3-butadiene and cinnamyl cyanide, respectively, in high yields. When an equimolar amount of phenacyl bromide in *N,N*-dimethylformamide (DMF) was added dropwise to a solution of 1 in aqueous DMF at 0°, a rapid reaction occurred to give acetophenone (47.5%), 1,2-dibenzoyl ethane (9.4%), and a significant amount of black polymeric materials. The yield of coupling product, 1,2-dibenzoyl ethane, increased to 46.8% when the same reaction was carried out in anhydrous DMF.

**Reaction of Potassium Hexacyanodinicelate(I) (1) with Organic Halides in the Presence of CO.**—It was reported that 1 is coordinatively unsaturated and its aqueous solution easily absorbs two molecules of CO according to eq 2a to give the yellow carbonyl-cyanonickel(I) complex.<sup>8a,b</sup> But, very recently, the carbonylation of 1 has been found, actually, to form an equi-

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- (4) H. O. House and W. F. Fischer, *J. Org. Chem.*, **34**, 3626 (1969).
- (5) (a) G. M. Whitesides, W. F. Fischer, Jr., J. S. Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969); (b) J. Klein and R. M. Turkel, *ibid.*, **91**, 6186 (1969).
- (6) I. Hashimoto, M. Ryang, and S. Tsutsumi, *Tetrahedron Lett.*, 3291 (1969).

(7) The result in the case of *p*-methoxybenzyl bromide is not satisfactory in respect to the yield because the halide was easily hydrolyzed by water to the alcohol, but the ratio of coupling product to hydrogenated product would represent the reactivity of the halide toward 1 [A. Lapworth and J. B. Shoosmith, *J. Chem. Soc.*, **121**, 1391 (1922)].

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TABLE I  
REACTION OF POTASSIUM HEXACYANODINICKELATE(I) (1) WITH ORGANIC HALIDES

R-X	Solvent	Ratio, 1:RX	Temp, °C	Time, hr	Product, % <sup>a</sup>		
					R-H	R-R	R-CN
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	Water-acetone	1:1	0-20	8	<i>d</i>	89.0	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	Water-acetone	1:2	0-60	3	<i>d</i>	96.4	
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	Water-acetone	1:1	15	6	Trace	92.5	
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	Water-acetone	1:1.4	20	4	Trace	21.5	
<i>p</i> -NCC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	Water-acetone	1:1	20	10	50.0	11.5	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> Br	Water-acetone	1:1	20-50	12			
C <sub>6</sub> H <sub>5</sub> I	Water-acetone	1:1	15-45	12			
<i>trans</i> -C <sub>6</sub> H <sub>5</sub> CH=CHBr	Water-acetone	1:1	18-23	1		72.9	6.6
<i>trans</i> -C <sub>6</sub> H <sub>5</sub> CH=CHCH <sub>2</sub> Br	Water-acetone	1:2	5-20	10		6.7	83.0
C <sub>6</sub> H <sub>5</sub> C(=O)CH <sub>2</sub> Br	Water-DMF <sup>b</sup>	1:1	5	0.5	47.5	9.4	
C <sub>6</sub> H <sub>5</sub> C(=O)CH <sub>2</sub> Br	Methanol <sup>c</sup>	1:1	40-50	10	38.1	14.0	
C <sub>6</sub> H <sub>5</sub> C(=O)CH <sub>2</sub> Br	DMF <sup>b</sup>	1:1	0-10	10	12.0	46.8	
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> C(=O)CH <sub>2</sub> Br	Methanol <sup>c</sup>	1:1	30	15	13.7 <sup>e</sup>	32.6 <sup>f</sup>	

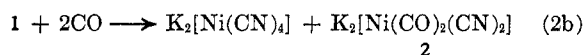
<sup>a</sup> Yields are based on 1 used. <sup>b</sup> *N,N*-Dimethylformamide. <sup>c</sup> Suspension. <sup>d</sup> No effort was made to detect it. <sup>e</sup> *p*-Bromoacetophenone. <sup>f</sup> *p,p'*-Dibromo-1,2-dibenzoylthane.

TABLE II  
REACTION OF POTASSIUM HEXACYANODINICKELATE(I) (1) WITH ORGANIC HALIDES IN THE PRESENCE OF CO

R-X	Solvent	Ratio, 1:RX	Temp, °C	Time, hr	Product, % <sup>a</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	Water-acetone	1:1.7	0-15	2	Dibenzyl ketone, 61.0
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	Water-acetone	1:1.1	10-45	21	<i>p,p'</i> -Dimethyldibenzyl ketone, 67.0
<i>n</i> -C <sub>4</sub> H <sub>9</sub> I	Water-methanol	1:2	0-30	4	Di- <i>n</i> -butyl ketone, 4
<i>trans</i> -C <sub>6</sub> H <sub>5</sub> CH=CHBr	Water-methanol	1:1.4	10-35	17	Methyl <i>trans</i> -cinnamate, 57.0 Cinnamaldehyde, 10.2

<sup>a</sup> Yields are based on 1 used.

molar amount of K<sub>2</sub>[Ni<sup>II</sup>(CN)<sub>4</sub>] and K<sub>2</sub>[Ni<sup>0</sup>(CO)<sub>2</sub>(CN)<sub>2</sub>] (2) as shown in eq 2b.<sup>8c</sup>



An excess of organic halides (molar ratio, 1:1.1 ~ 2) was introduced to an aqueous solution of 2 and gentle bubbling of CO was continued with vigorous stirring for several hours. The results are summarized in Table II.

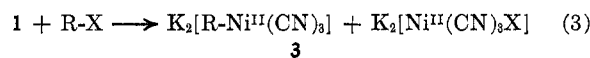
Benzyl and *p*-methylbenzyl bromide gave dibenzyl ketone and *p,p'*-dimethyldibenzyl ketone, respectively, in high yields in water-acetone solution. Formation of any methyl ester was not observed even if the same reaction was carried out in water-methanol solution. The carbonylating reagent 2 was also much less reactive towards alkyl halides, and *n*-butyl iodide gave di-*n*-butyl ketone only in a low yield. Contrary to the results from benzyl bromide, methyl *trans*-cinnamate (57.0%) and cinnamaldehyde (10.2%) were obtained from *trans*-β-bromostyrene in water-methanol.

**Reaction of Potassium Hexacyanodinickelate(I) (1) with Benzyl Bromide in the Presence of Olefin.**—When an excess of acrylonitrile was added to the aqueous solution of 1 at room temperature, a yellow color resulted instantly, presumably owing to the formation of a weak π complex between 1 and olefin. Benzyl bromide was then added dropwise at -7° with stirring. Upon work-up, a 23.0% yield of 4-phenylbutyronitrile and 57.4% bibenzyl was obtained. A similar reaction of 1 with benzyl bromide in the presence of ethyl acry-

late gave ethyl 4-phenylbutylate in a lower yield (8.0%) and bibenzyl (20.0%). A definite color change from red to yellow was observed when an excess of butadiene was added to an aqueous solution of 1, but an attempt at benzylation was unsuccessful and almost all of the benzyl bromide was recovered. It seems likely that a strong coordination of butadiene to 1 led to the prevention of the attack of benzyl bromide on 1.

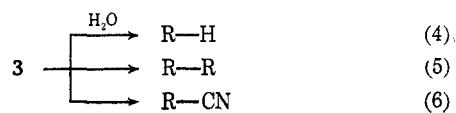
### Discussion

It is reasonable to consider the formation of unstable organonickel(II) σ complexes (3) as intermediates in the reaction of 1 with organic halides. In the reaction of 1



with benzyl bromide, the assumption of formation of tricyanobenzylnickelate(II) (3, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) was supported by the following chemical proofs, although our previous attempts to isolate it were unsuccessful and spectral study has not yet been done because of its thermal instability: (1) treatment of 1 with an equimolar amount of benzyl bromide in water-acetone at 0° gives a pale yellow solution which is stable at the temperature for several hours but decomposes near room temperature to afford bibenzyl almost quantitatively; (2) bubbling of CO into the yellow solution gives dibenzyl ketone (34%) as well as bibenzyl (50%); (3) treatment of the yellow solution with HgCl<sub>2</sub> gives benzylmercuric chloride (17%) and bibenzyl (60%); and (4) benzylation of olefins occurs when an appropriate olefin is present in the reaction system.

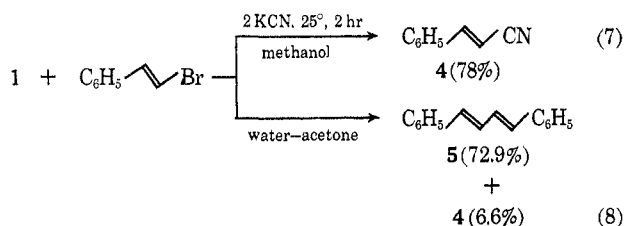
Decomposition of **3** in aqueous solutions gave the three types of products by hydrogenolysis (eq 4), coupling (eq 5), or cyanation (eq 6).



In some cases, competition between the former two or the latter two types occurred. Phenacyl bromide in aqueous solution underwent hydrogenolysis to yield acetophenone as a main product but, when anhydrous DMF was used as a solvent, the coupling product, 1,2-dibenzoylthane, was mainly formed. *trans*- $\beta$ -Bromostyrene gave the coupling product in a high yield, whereas the nitrile was produced from cinnamyl bromide. It should be noted that the course of decomposition depends largely on the structural type of the organic moiety. Especially in a series of *para*-substituted benzyl bromides, a definite substitution effect on the product distribution was observed; benzyl, *p*-methylbenzyl, and *p*-methoxybenzyl bromide gave the corresponding coupling products almost exclusively, but *p*-cyanobenzyl bromide gave *p*-cyanotoluene as a main product.

Tricyanobenzylnickelate(II) (**3**, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>), as well as pentacyanobenzylcobaltate(III),<sup>9</sup> is classified as hydrolytically inert in contrast to benzylchromium(III) species<sup>10</sup> which is easily hydrolyzed by water to give mainly toluene.

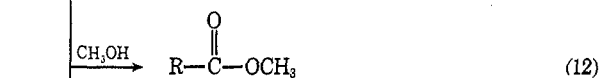
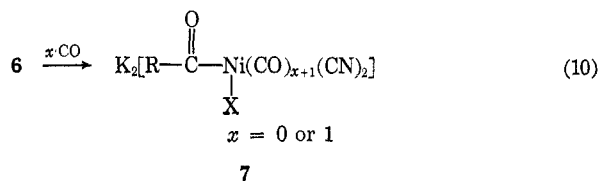
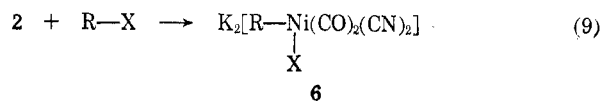
Reaction of **1** with *trans*- $\beta$ -bromostyrene is interesting. Recently, Corey and Hegedus<sup>3</sup> reported that 78% of *trans*- $\beta$ -cyanostyrene **4** was obtained from this reaction in methanol in the presence of 2 mol equiv of KCN (eq 7). However, when the same reaction was



carried out in the absence of KCN in water-acetone, the coupling product was obtained in a good yield and the yield of the nitrile **4** drastically decreased. Contrary to the formation of cinnamyl cyanide from **1** and cinnamyl bromide in a high yield, the presence of free cyano ion is necessary for the cyanation of *trans*- $\beta$ -bromostyrene.

Carbon monoxide insertion reactions into the carbon-metal  $\sigma$  bond of alkyl (or aryl) transition metal complexes are well known and their mechanistic considerations have been done by several workers.<sup>11</sup> Carbonylation reaction of organic halides by the carbonyl cyanonickelate(I) reagent **2** seems to proceed *via* the

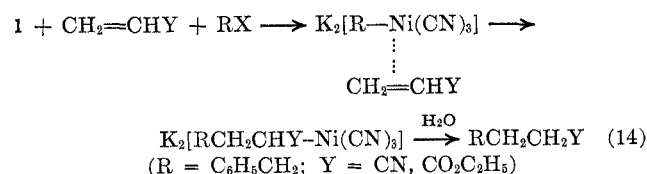
formation of organonickel(II)  $\sigma$  complexes (**6**) as intermediates, according to eq 9-13.



Comparison of the reactivity of **2** and nickel carbonyl (**8**) toward various organic halides is of particular interest. In the present reaction using **2**, symmetrical ketones were obtained in a high yield from benzyl or *p*-methylbenzyl bromide and, in a much lower yield, from *n*-butyl iodide, but any ester or carboxylic acid was not obtained from these halides when water-methanol or water-acetone was used as a solvent. It has, however, been reported that the reaction of **8** with benzyl bromide gave dibenzyl ketone in DMF solution and ethyl phenylacetate in ethanol in high yields.<sup>12</sup> On the other hand, alkyl or alkenyl halides are known to be inert to **8** and can be converted to esters only by a more powerful carbonylating reagent (alkali metal alkoxide-**8**-alcohol system),<sup>3</sup> and therefore the high reactivity of **2** (and **1**) toward *trans*- $\beta$ -bromostyrene is attractive.

The formation of cinnamaldehyde (10.2%) as a by-product in the reaction of **2** and *trans*- $\beta$ -bromostyrene is intriguing because, in general, acyl transition metal complexes are known to afford carboxylic acids instead of aldehydes by hydrolysis,<sup>11a</sup> but the mechanism leading to the aldehyde (eq 13) is still open to question.

The fact that an aqueous solution of **1** easily absorbs CO makes it possible to expect the coordination of other unsaturated compounds, which has, indeed, been postulated in the reaction of cyclization of a certain acetylenic compound<sup>13</sup> or of hydrogenation of olefins.<sup>14</sup> Olefin insertion reactions into alkyl transition metal  $\sigma$  bonds are also reported.<sup>15</sup> From the analogy of previously observed reactions, the benzylation reaction of olefins using **1** is explicable by eq 14.



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(15) (a) I. Rhee, M. Ryang, and S. Tsutsumi, *J. Organometal. Chem.*, **9**, 361 (1967); (b) R. F. Heck, *J. Amer. Chem. Soc.*, **91**, 6707 (1969).

A similar benzylation reaction using chromium(II) was reported by Koichi and Davis.<sup>16</sup>

### Experimental Section

**General.**—Benzyl bromide,  $\beta$ -bromostyrene (trans 92.5%, cis 7.5%), *n*-butyl iodide, phenacyl bromide, *p*-bromophenacyl bromide, acrylonitrile, and ethyl acrylate were of reagent grade and purified by distillation or recrystallization from ethanol. *p*-Methylbenzyl bromide, mp 40° (lit.<sup>17</sup> mp 39°), *p*-methoxybenzyl bromide, bp 128–130° (15 mm) [lit.<sup>18</sup> bp 124–126° (12 mm)], and cinnamyl bromide, bp 90–91° (2 mm) [lit.<sup>19</sup> bp 84–85° (0.8 mm)], were prepared from the corresponding alcohols by the action of phosphorous tribromide in carbon tetrachloride in the presence of pyridine. *p*-Cyanobenzyl bromide was prepared by the reported method<sup>20</sup> and purified by sublimation *in vacuo*, mp 115–115.5°. Commercially available  $K_2Ni(CN)_4 \cdot H_2O$  was dried *in vacuo* at 100°. *N,N*-Dimethylformamide (DMF) was fractionated and dried over molecular sieves. All solvents were saturated with nitrogen before use and all the reactions were carried out under a nitrogen atmosphere. Gas-liquid partition chromatographic analyses were performed on a Yanagimoto GCG-5DH instrument using 2.5 m  $\times$  3 mm columns packed with 20% SE-30 or 20% PEG-20M. Yields were based on potassium hexacyanodinickele(I) used.

**Preparation of Potassium Hexacyanodinickele(I) (1).**—The cyanonickelate(I) reagent 1 was prepared by the reported method<sup>21</sup> with a slight modification. To a solution containing 24.1 g (0.100 mol) of anhydrous potassium tetracyanonickelate(II),  $K_2Ni(CN)_4$ , in ca. 300 ml of liquid ammonia was added 2.80 g (0.070 g-atom) of potassium in the form of small pieces. Ammonia was then evaporated slowly with stirring at atmospheric pressure and later *in vacuo*. Residual red powder was washed with five successive 60-ml portions of methanol in order to remove the remaining ammonia and resulting KCN and dried *in vacuo*.<sup>22</sup>

**Reaction of Potassium Hexacyanodinickele(I) (1). A. With *p*-Methylbenzyl Bromide in Water-Acetone.**—Potassium hexacyanodinickele(I) (1) (0.0267 mol) in 160 ml of water was charged into a 400-ml five-necked flask equipped with a dropping funnel, gas-inlet and -outlet tubes, a thermometer, and a mechanical stirrer, and 100 ml of acetone was added. *p*-Methylbenzyl bromide (4.95 g, 0.0267 mol) in 30 ml of acetone was added *via* the dropping funnel, slowly with efficient stirring, over a period of 90 min at room temperature. The initially blood-red solution turned to dark red during the addition, and a dark green suspension was finally obtained. The reaction mixture was stirred at room temperature for 2 hr. After filtration of inorganic materials, the yellow filtrate was concentrated to ca. 100 ml at reduced pressure, followed by extraction with 200 ml of ether. The colorless ether extract was washed with aqueous NaCl and was dried over anhydrous  $MgSO_4$ . After removal of the ether, the residual oil was distilled under reduced pressure to give the following fractions: (1) bp 58–60° (15 mm), 0.79 g of diacetone alcohol containing a trace amount of *p*-xylene (detected by glpc); (2) bp 90–120° (1.1 mm), 0.16 g of colorless oil; (3) bp 121–126° (1.1 mm), 2.49 g of colorless oil. Fraction 3 crystallized on standing to give colorless needles which were found to be *p,p'*-dimethylbibenzyl, mp 82° (lit.<sup>23</sup> 82–83°). Glpc analysis (column, 20% PEG-20M; 120–240°, 4°/min program; carrier gas, He, 10 ml/min) indicated that fraction 2 contained 0.03 g (0.9%) of *p*-methylbenzyl alcohol and 0.10 g (total yield 2.59 g, 92.5%) of *p,p'*-dimethylbibenzyl.

**B. With *p*-Cyanobenzyl Bromide in Water-Acetone.**—To a solution containing 0.030 mol of 1 in 90 ml of water and 100 ml of

acetone was added dropwise 5.9 g (0.030 mol) of *p*-cyanobenzyl bromide in 40 ml of acetone with vigorous stirring at room temperature over a period of 30 min. The color of the solution changed from red to yellow, and near the end of addition, to light green. After the same treatment as above, the organic layer was distilled under reduced pressure to give the following fractions: (1) bp 92–98° (14 mm), 1.95 g of *p*-cyanotoluene (50.0%); (2) bp 100–110° (0.3 mm), 1.25 g of recovered *p*-cyanobenzyl bromide. The residue (ca. 1 g) was chromatographed on silica gel. From the ether eluate, colorless needles of *p,p'*-dicyanobibenzyl were obtained: mp 200–201° (recrystallized from ethanol) (lit.<sup>24</sup> mp 198°); yield 0.40 g (11.5%); ir (KBr) 2220  $cm^{-1}$  ( $C\equiv N$ ).

**C. With *trans*- $\beta$ -Bromostyrene in Water-Acetone.**—To a solution containing 0.035 mol of 1 in 120 ml of water and 70 ml of acetone was added dropwise 6.4 g (0.035 mol) of *trans*- $\beta$ -bromostyrene in 30 ml of acetone with stirring at room temperature over period of 30 min. The reaction proceeded exothermically and the temperature of the reaction mixture rose from 18 to 23°. The color of the solution changed from blood-red to transient black, and at the end of addition, to dark green. Stirring was continued for a further 30 min. After the same treatment, the filtrate was extracted with 100 ml of ether and 150 ml of benzene. Removal of solvent gave a pale yellow oil which crystallized on cooling to 0°. Filtration of the resulting crystals and washing with 30 ml of cold methanol gave 1.74 g of colorless leaflets, mp 151–152.5°. A sample of *trans,trans*-1,4-diphenyl-1,3-butadiene (5), prepared by another method,<sup>25</sup> showed the same behavior and the melting point was undepressed when mixed with the above sample. Their ir spectra were also identical in all respects. Distillation of the mother liquor under reduced pressure gave 0.30 g (6.6%) of *trans*- $\beta$ -cyanostyrene (4) and another 0.89 g of 5 (total yield 2.63 g, 72.9%).

**D. With Cinnamyl Bromide in Water-Acetone.**—To a solution containing 0.035 mol of 1 in 120 ml of water and 110 ml of acetone was added 13.8 g (0.070 mol) of cinnamyl bromide in 50 ml of acetone with stirring at 5° during 1 hr. Stirring was continued for a further 9 hr at room temperature until the reaction mixture gave a yellowish green suspension. After similar treatment, the organic layer was distilled under reduced pressure. A fraction of bp 93–96° (0.8 mm) gave 4.19 g (83.0%) of cinnamyl cyanide: mp 61–61.5° (recrystallized from ethanol) (lit.<sup>26</sup> 59–60°); ir 2270 ( $C\equiv N$ ) and 1655  $cm^{-1}$  ( $C=C$ ). The residue was chromatographed on a 2.5  $\times$  15 cm silica gel column. From the petroleum ether-benzene (4:1) eluate, 0.55 g of colorless leaflets was obtained, mp 80.5–81.5°, which was found to be *trans,trans*-1,6-diphenyl-1,5-hexadiene (lit.<sup>27</sup> mp 80.5–81°) (yield 6.7%).

*Anal.* Calcd for  $C_{15}H_{18}$ : C, 92.26; H, 7.74. Found: C, 92.19; H, 7.85.

**E. With Phenacyl Bromide in DMF.**—A mixture of 0.035 mol of 1 and 7.0 g (0.035 mol) of phenacyl bromide in 200 ml of DMF was stirred at 0–10° for 10 hr. The color of the solution changed from red to dark reddish brown. The reaction mixture was poured into 700 ml of water and was extracted with ether. After similar treatment, 0.51 g (20.0%) of acetophenone (identified by ir and glpc) and 1.87 g (46.8%) of 1,2-dibenzoyl ethane (melting point and mixture melting point with authentic sample,<sup>28</sup> 145–146°) were obtained.

**F. With *p*-Bromophenacyl Bromide in Methanol.**—When *p*-bromophenacyl bromide instead of phenacyl bromide was reacted with an equimolar amount of 1 in absolute methanol in the usual manner, the following two compounds were isolated: *p*-bromoacetophenone (13.7%) and *p,p'*-dibromo-1,2-dibenzoyl ethane (32.6%), mp 180–181° (purified by sublimation *in vacuo*). Melting point of the latter compound was not depressed by admixture with authentic sample.<sup>28</sup>

**Reaction of Potassium Hexacyanodinickele(I) (1) in the Presence of CO. A. With *p*-Methylbenzyl Bromide in Water-Acetone.**—Into a red solution containing 0.035 mol of 1 in 120 ml of water and 100 ml of acetone, CO was bubbled at 10° with vigorous stirring. The color of the solution changed to yellow within 10 min. *p*-Methylbenzyl bromide (7.0 g, 0.038 mol) in 30 ml of acetone was added at 10°. Stirring and gentle bubbling of CO were continued for 21 hr at 10–45°. A small amount of

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greenish-white solid precipitated in the course of the reaction. After similar treatment, the organic part was distilled under reduced pressure to give the following fractions: (1) bp 78–85° (1.0 mm), 0.93 g of *p*-methylbenzyl alcohol; (2) bp 135–160° (1.0 mm), 2.70 g of colorless needles. Fraction 2 was recrystallized from ethanol to give colorless crystals, mp 54–55°, which were identified as *p,p'*-dimethyldibenzyl ketone: ir (KBr) 1703  $\text{cm}^{-1}$  (C=O); nmr ( $\text{CCl}_4$ )  $\tau$  7.70 (s, 6,  $\text{CH}_3$ ), 6.55 (s, 4,  $\text{CH}_2$ ), and 3.10 (s, 8,  $\text{C}_6\text{H}_4$ ).

*Anal.* Calcd for  $\text{C}_{17}\text{H}_{18}\text{O}$ : C, 85.67; H, 7.61. Found: C, 85.55; H, 7.39.

Glpc analysis (column, 20% SE-30; 200–280°, 4°/min program; carrier gas, He, 10 ml/min) of fraction 2 showed the presence of a trace amount of *p,p'*-dimethylbibenzyl as a sole impurity.

**B. With *trans*- $\beta$ -Bromostyrene in Water–Methanol.**—Carbon monoxide was bubbled into a solution containing 0.035 ml of 1 in 120 ml of water and 100 ml of methanol. *trans*- $\beta$ -Bromostyrene (9.2 g, 0.050 mol) in 20 ml of methanol was added, and stirring and gentle bubbling of CO were continued for 17 hr at 10–35°. After similar treatment, the organic part was distilled under reduced pressure. A fraction of bp 80–87° (2 mm) was collected to give 4.50 g of pale yellow liquid. The ir spectrum and quantitative glpc analysis (column 20% PEG-20M; 120–280°, 4°/min program; carrier gas, He, 10 ml/min) of the fraction showed the presence of the following compounds: 3.23 g (57.0%) of methyl *trans*-cinnamate, 0.47 g (10.2%) of cinnamaldehyde, 0.10 g (2.2%) of *trans*- $\beta$ -cyanostyrene, and 0.59 g of recovered *trans*- $\beta$ -bromostyrene.

**Reaction of Potassium Hexacyanodinicelate(I) (1) with Benzyl Bromide in the Presence of Acrylonitrile or Ethyl Acrylate.**—To a solution containing 0.035 mol of 1 in 120 ml of water and 40 ml of acetone was added 5.3 g (0.10 mol) of acrylonitrile with stirring. The color of the solution changed immediately to transparent yellow. Benzyl bromide (6.0 g, 0.035 mol) in 20 ml of acetone was added dropwise with stirring at –7° in a

period of 1 hr. The reaction mixture was gradually warmed to room temperature during 12 hr with efficient stirring. After similar treatment described above, the organic layer was distilled to give 3.00 g of distillate, bp 89–91° (0.7 mm), which was subjected to quantitative glpc analysis (column, 20% PEG-20M; 130–240°, 4°/min program; carrier gas, He, 12 ml/min) and was found to consist of the following two compounds: 1.17 g (23.0%) of 4-phenylbutyronitrile and 1.83 g (57.4%) of bibenzyl.

When a reaction similar to the preceding example was carried out using ethyl acrylate instead of acrylonitrile, ethyl 4-phenylbutyrate and bibenzyl were obtained in 8.0 and 20.0% yield, respectively (analyzed by ir spectra and glpc). Authentic samples of 4-phenylbutyronitrile and ethyl 4-phenylbutyrate were prepared by the reported methods.<sup>15a</sup>

**Isolation of Benzylmercuric Chloride.**—To a solution containing 0.035 mol of 1 in 140 ml of water and 40 ml of acetone was added 6.0 g (0.035 mol) of benzyl bromide in 30 ml of acetone at 0° with stirring. The red color of the solution turned pale yellow within 30 min. Mercuric chloride (9.50 g, 0.035 mol) in 30 ml of acetone was added dropwise at 0° over a period of 1 hr. After usual treatment, 1.88 g (17.0%) of benzylmercuric chloride, mp 104–106° (recrystallized from ethanol) (lit.<sup>29</sup> 104°), and 1.91 g (60.0%) of bibenzyl were isolated.

**Registry No.**—1, 123-87-132; benzyl bromide, 100-39-0; *p*-methylbenzyl bromide, 104-81-4; *p*-methoxybenzyl bromide, 2746-25-0; *p*-cyanobenzyl bromide, 17201-43-3; *trans*- $\beta$ -bromostyrene, 588-72-7; *trans*-cinnamyl bromide, 26146-77-0; phenacyl bromide, 70-11-1; *p*-bromophenacyl bromide, 99-73-0; *n*-butyl iodide, 542-69-8; *p,p'*-dimethyldibenzyl ketone, 26146-78-1.

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## Synthesis, Spectra, and Reactions of *N*-Triphenylmethylpyridinium Salts. Reaction of Triphenylmethyl Chloride with Pyridine under High Pressure

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*N*-Triphenylmethyl- (trityl-) pyridinium chloride (I) was synthesized from trityl chloride and pyridine by means of high pressure (4000–5000 atm) in dioxane or pyridine solution at 60–70°. Compound I was found to react rapidly with methanol and water to produce trityl methyl ether and triphenylcarbinol, respectively. With moisture, it was converted into the molecular complex (II) of triphenylcarbinol and pyridinium chloride in the solid state. The ir, uv, visible, and nmr spectra of I were compared to those of *N*-tritylpyridinium perchlorate and fluoroborate. The deshielding of pyridine ring protons of these *N*-tritylpyridinium compounds is much smaller than that of other *N*-alkylpyridinium compounds. Explanation of this phenomenon is suggested. *N*-tritylpyridinium bromide (III) was synthesized from trityl bromide and pyridine without applying high pressure. The differences between trityl chloride and bromide in the formation of *N*-tritylpyridinium compounds are also discussed.

It has long been known that the yellow color of the trityl ion in nitromethane solutions of trityl chloride discharged immediately upon addition of pyridine. This phenomenon was attributed to the formation of tritylpyridinium chloride (I).<sup>1</sup> The solids "tritylpyridinium chloride" reported in the literature<sup>2</sup> were

shown to be a complex (II) of triphenylcarbinol and pyridinium chloride associated through a weak hydrogen bond in the solid state.<sup>3</sup>

Generally, in nucleophilic reactions the stronger nucleophilic reagent, pyridine, would be expected to react faster with alkyl halides than methanol.<sup>4</sup> However, the synthesis of *N*-tritylpyridinium chloride from trityl chloride and pyridine by conventional procedures was unsuccessful, although under similar conditions methanol reacted readily with trityl chloride to form trityl methyl ether.<sup>3</sup> Failure to synthesize *N*-tritylpyridinium chloride may be attributed to its unfavorable

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