Anal. Calcd for $C_{15}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.60; H, 7.51.

Registry No.—ω-(Methylsulfinyl)acetophenone, 2813-22-1; **2**, 20708-04-7; **3**, 20708-05-8; **4**, 20708-06-9; **5**, 20708-07-0; **6**, 20708-08-1; **7**, 20708-09-2; ethyl 4-benzoyl-3-butenate, 20708-10-5.

Reaction of Sodium Dicyanocuprate with Vinyl and Aryl Halides[1a]

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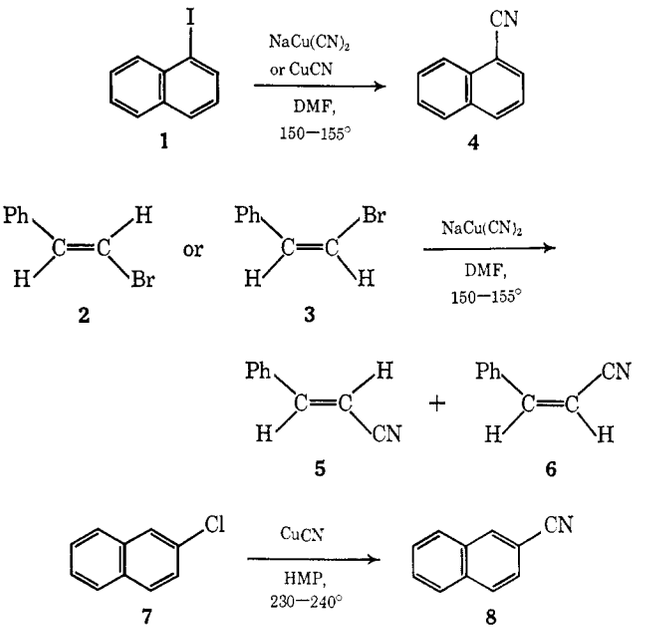
The advantageous use of lithium dialkyl- or diarylcuprates [*e.g.*, $LiCu(CH_3)_2$] as reagents for conjugate addition to unsaturated carbonyl compounds[2] and for coupling reactions with alkyl and aryl halides[3] raised the question whether analogous di- or polycyanocuprate species might offer advantages in the conversion of aryl and vinyl halides to the corresponding cyano compounds. The conversion of aryl or vinyl halides into the corresponding cyanides has usually been effected by heating the halide with copper(I) cyanide[4] to 150–220° in solvents (or diluents) such as pyridine, quinoline, dimethylformamide, N-methylpyrrolidone, or dimethyl sulfoxide.

The reactions of alkali metal cyanides, MCN, with copper(I) cyanide to form a series of cyano cuprate species, $M_nCu(CN)_{n+1}$ where n = 1, 2, or 3, have been described.[5] From formation of the complexes $M^+Cu(CN)_2^-$ where M = Li, Na, or K by reaction of CuCN with M^+CN^- in dimethylformamide (DMF) solution, we conclude that the sodium derivative was most satisfactory for preparative use; at 80°, a 1 *M* solution of $NaCu(CN)_2$ in dimethylformamide (DMF) was readily obtained whereas the K and Li salts were less soluble. Reaction of this solution with the aryl iodide **1** or the vinyl bromides **2** or **3** at 150–155° for periods of 4 to 10 hr yielded the corresponding nitriles **4**–**6** (Scheme I). For comparison the reaction **1** → **4** was complete in 2–4 hr with CuCN in DMF and the reaction **2** → **5** was complete in 2 hr with CuCN in refluxing N-methylpyrrolidone.[4e] The aryl chloride **7** failed to react under these circumstances but was converted into the nitrile **8** in good yield by heating to 230–240° for 3 hr with CuCN in hexamethylphosphoramide (HMP). Although the conversion **1** → **4** proceeded approximately four times as fast when the cyanide reagent was CuCN rather than $NaCu(CN)_2$, the reaction in dimethylformamide solution was more convenient with the complex $NaCu(CN)_2$ because a homogeneous reaction mixture was maintained throughout the reaction period.

SCHEME I



From the data obtained (Table I) in conversions of the vinyl bromides **2** and **3** into the unsaturated nitriles, we are led to suggest that the initial conversion of bromide to the cyanide proceeds with retention of configuration (*e.g.*, **3** → **6**). However, the products are not configurationally stable to the reaction conditions so that mixtures of the isomeric nitriles **5** and **6** are formed from either vinyl bromide.

TABLE I

REACTION OF SODIUM DICYANOCUPRATE WITH *cis*- AND *trans*-β-BROMOSTYRENES

		Yield, %			
Starting halide	Reaction time, hr	*cis*-β-Bromostyrene 3	*trans*-β-Bromostyrene 2	*cis*-Cinnamonitrile 6	*trans*-Cinnamonitrile 5
trans isomer **2**	6		13	9	78
	10		3	14	74
	24			14	58
cis isomer **3**	2	30	1.5	56	9
	4	3.5	0.5	50	43
	6			35	51
	11			19	57

From these studies, we conclude that the cyanocuprate species, $M_nCu(CN)_{n+1}$, are somewhat less reactive than CuCN in reactions with aryl and vinyl halides.

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(2) (a) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966); (b) H. O. House and W. F. Fischer, Jr., *ibid.*, **33**, 949 (1968).

(3) (a) E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967); **90**, 5615 (1968); (b) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *ibid.*, **91**, 4871 (1969).

(4) (a) R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.*, **19**, 121 (1965); (b) D. T. Mowry, *Chem. Rev.*, **42**, 189 (1948); (c) R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1097 (1964); (d) M. S. Newman and D. K. Phillips, *J. Amer. Chem. Soc.*, **81**, 3667 (1959); (e) M. S. Newman and H. Boden, *J. Org. Chem.*, **26**, 2525 (1961); (f) L. Friedman and H. Shechter, *ibid.*, **26**, 2522 (1961); (g) E. J. Corey and L. S. Hegedus [*J. Amer. Chem. Soc.*, **91**, 1233 (1969)] have recently described the conversion of the vinyl bromide **2** to the nitrile **5** with $K_4Ni_2(CN)_6$.

(5) (a) M. H. Ford-Smite, "The Chemistry of Complex Cyanides," Her Majesty's Stationery Office, London, 1964, p 34; (b) M. Sneed, J. Maynard, and R. Bronsted, "Comprehensive Inorganic Chemistry," Vol. 2, D. Van Nostrand Co., Inc., New York, N. Y., 1954, pp 81, 91; (c) W. P. Griffith, *Quart. Rev.*, **16**, 188 (1962); (d) R. M. Izatt, H. D. Johnson, G. D. Watt, and J. J. Christensen, *Inorg. Chem.*, **6**, 132 (1967); (e) R. E. Dodd and R. P. H. Gasser, *Proc. Chem. Soc.*, 415 (1964); (f) G. Guiseppetti and C. Tadim, *Periodica Mineral.*, **35**, 431 (1966); (g) D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1957); (h) S. K. Tobia and M. F. El-Shahat, *J. Chem. Soc., A*, 2444 (1968).

However, sodium dicyanocuprate does offer a solubility advantage in DMF solution. The reactivity of either copper(I) cyanide or the dicyanocuprate toward aryl and vinyl halides is distinctly less than the corresponding reactions with diaryl- or dialkylcuprates.[3] A similar low order of reactivity was noted[3b] for the acetylide $(PhC{\equiv}C)_3CuLi_2$ in which the carbon ligands are electronically similar to cyano functions. Finally, our studies with the delocalized enolate anions derived from malonic esters and from acetophenone have provided no indication that the presence of soluble copper(I) species will accelerate the reactions of these anions with either alkyl or aryl halides. Because of these observations, we are inclined to the belief that the coupling reaction of organocopper(I) compounds with alkyl, vinyl, and aryl halides does not involve preliminary ionization of the carbon–copper(I) bond ($R_2Cu^- \rightleftharpoons RCu + R^-$) since the groups, R, most likely to provide appreciable concentrations of carbanions are those which are least reactive toward halides.

Experimental Section[6]

Starting Materials.—Commercial samples of 1-Iodonaphthalene (**1**), 2-chloronaphthalene (**7**), CuCN, and NaCN were used without further purification. Anhydrous LiCN was obtained by reaction of anhydrous HCN with a suspension of LiH; the resulting suspension of LiCN was collected and dried under reduced pressure. Samples of pure *cis*- and *trans*-β-bromostyrene (**3** and **4**) were obtained as described elsewhere.[3b]

Reaction with 1-Iodonaphthalene (1).—To a heated (150–155°) solution of 104 mg (2.10 mmol) of NaCN and 179 mg (2.00 mmol) of CuCN in 10 ml of DMF was added 5.0 ml of a DMF solution containing 1.11 mmol of 1-iodonaphthalene and a known amount of hexamethylbenzene (an internal standard). Aliquots were removed periodically and partitioned between saturated aqueous NaCN and Et_2O. The organic layers were dried, concentrated, and analyzed by glpc. With the column employed,[7] the components were eluted with the following retention times: hexamethylbenzene, 8.0 min; 1-cyanonaphthalene (**4**), 10.3 min; 1-iodonaphthalene (**1**), 15.9 min. The half-life for the reaction was approximately 50 min and after a reaction time of 4 hr, the calculated yield of 1-cyanonaphthalene was 98.5%. A collected[7] sample of the cyanide **4** was identified with an authentic sample by comparison of ir spectra and glpc retention times.

For comparison, a solution containing 179 mg (2.00 mmol) of CuCN, 282 mg (1.11 mmol) of 1-iodonaphthalene, and hexamethylbenzene in 15 ml of DMF was heated to 150–155° for 4 hr. As the reaction progressed a brown precipitate (presumably CuI) separated. The final reaction mixture was worked-up and analyzed[7] as previously described; the calculated yield of 1-cyanonaphthalene (**1**) was 97%. When the same reaction was repeated with a total reaction time of 30 min at 150–155°, the calculated yields were 88% 1-cyanonaphthalene and 12% unchanged 1-iodonaphthalene.

Reaction with *trans*-β-Bromostyrene (2).—A solution of 483 mg (9.85 mmol) of NaCN, 895 mg (9.98 mmol) of CuCN, 891 mg (4.86 mmol) of *trans*-β-bromostyrene, and a known amount of biphenyl (an internal standard) in 10 ml of warm (90°) DMF was heated to reflux. Periodically, aliquots of the reaction solution were removed and partitioned between saturated aqueous NaCN and PhH. The organic layers were dried, concentrated, and analyzed (Table I). With the glpc column employed,[8] the relative retention times of components were as follows: *cis*-β-bromostyrene (**3**), 10.7 min; *trans*-β-bromostyrene (**2**), 11.7 min; biphenyl, 19.1 min; *cis*-cinnamonitrile (**6**), 24.0 min; *trans*-cinnamonitrile (**5**), 34.0 min. A collected[8] sample of the *trans*-nitrile **5**, $n^{27}D$ 1.5995 [lit.[9] bp 150° (30 mm), $n^{20}D$ 1.6031], ir (liquid film), 2220 (conjugated C≡N), 1625 (conjugated C=C), and 970 cm^{-1} (*trans* CH=CH), was identified with an authentic sample by comparison of ir spectra and glpc retention times. A collected[8] sample of the *cis*-nitrile **6**, $n^{27}D$ 1.5818 [lit.[9] bp 132° (30 mm), $n^{20}D$ 1.5843], had ir absorption (liquid film) at 2220 (conjugated C≡N), 1615 (conjugated C=C), and 775 cm^{-1} (*cis* CH=CH).

Reaction with *cis*-β-Bromostyrene (3).—A solution prepared from 897 mg (10.0 mmol) of CuCN, 486 mg (9.94 mmol) of NaCN, 912 mg (4.98 mmol) of *cis*-β-bromostyrene, and biphenyl in 10 ml of DMF was heated to 150°. Aliquots were removed periodically and subjected to the previously described work-up and analysis procedures to give the results summarized in Table I.

Reaction with 2-Chloronaphthalene (7).—After a solution prepared from 498 mg (10.1 mmol) of NaCN, 894 mg (9.99 mmol) of CuCN, 812 mg (5.00 mmol) of 2-chloronaphthalene, and hexamethylbenzene (an internal standard) in 10 ml of DMF had been refluxed for 24 hr, the reaction product contained only the unchanged starting material. On the glpc column employed[7] the retention times of relevant compounds were as follows: 2-chloronaphthalene (**7**), 7.5 min; hexamethylbenzene, 9.5 min; 1-cyanonaphthalene (**4**), 12.0 min; and 2-cyanonaphthalene (**8**), 13.5 min.

After a solution of 6.63 g (74.0 mmol) of CuCN and 1.28 g (7.40 mol) of 2-chloronaphthalene in 10.0 ml of HMP had been heated to 230–240° with stirring for 3.0 hr, the crude product amounted to 1.10 g (96%) of crude 2-cyanonaphthalene (**8**), mp 61–64°; no 1-cyanonaphthalene (**4**) was detected in the reaction product.[7] Recrystallization from hexane separated 1.02 g (85%) of 2-cyanonaphthalene as white prisms: mp 65–66° (lit.[10] mp 66°); ir (CCl_4), 2225 cm^{-1} (C≡N); mass spectrum, molecular ion *m/e* 153, abundant fragments, *m/e* 126, 75, 74, 63, 51, and 50; nmr (CCl_4), δ 8.05 (1 H d, J = 0.8 Hz, aryl CH at C-1), 7.3–7.9 (7 H, m, aryl CH).

For comparison, a solution of 1.33 g (14.8 mmol) of CuCN, 738 mg (14.8 mmol) of NaCN, and 661 mg (4.07 mmol) of 2-chloronaphthalene in 10 ml of HMP was heated to 225° for 4 hr during which the reaction mixture turned a very dark color. After the usual isolation and analysis[7] procedures, the calculated yields were 7% 2-cyanonaphthalene (**8**) and 93% starting chloride **7**.

Registry No.—Sodium dicyanocuprate, 21445-44-3; **1**, 90-14-2; **2**, 588-72-7; **3**, 588-73-8; **7**, 91-58-7.

(6) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer, Model 237, grating spectrophotometer. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The nmr spectra were determined at 60 Mc with a Varian Model A-60 nmr spectrometer. The chemical shift values are expressed either in hertz or δ values (parts per million) relative to a tetramethylsilane internal standard. The mass spectra were obtained with a CEC Model 21-130 or a Hitachi (Perkin-Elmer) mass spectrometer. All reactions involving organometallic reagents were conducted under a nitrogen atmosphere. In each case where yields are calculated from gas chromatographic data, the chromatographic apparatus has been calibrated with known mixtures of authentic samples.

(7) A glpc column packed with silicone gum, no. SE-52, suspended on Chromosorb P was employed for this analysis.

(8) A glpc column packed with nitrile silicone gum, no. XE-60, suspended on Chromosorb P was employed for this analysis.

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A Thermal Isomerization Equilibrium between Conjugated and Unconjugated Unsaturated Keto Esters

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Instances in which compounds isomerize out of conjugation are quite unusual. In 1958 King[1] observed that, in the absence of oxygen, 12-oxo-*trans*-10-oct-

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