which gave 304 mg (3.3%) of blue crystals, mp 56–58°, after crystallization from ethanol.

Rechromatography followed by recrystallization of material similar to the foregoing yielded blue crystals of II: mp 60–61°; $\lambda_{max}$, mμ (log ε), 249 (4.45), 292 (4.66), 557 (2.65), 597 (2.59), 654 (2.17).

*Anal.* Calcd for $C_{16}H_{18}$: C, 91.43; H, 8.57. Found: C, 91.22; H, 8.65.

The 1,3,5-trinitrobenzene adduct of II prepared in and recrystallized from ethanol consisted of brown crystals, mp 126–27°.

*Anal.* Calcd for $C_{22}H_{21}N_3O_6$: C, 62.41; H, 4.96; O, 22.69. Found: C, 62.24; H, 5.09; N, 9.86; O, 22.50.

**1-(2′,4′-Dinitrophenyl)quinolinium Fluoride.**—Quinoline (6.5 g, 0.05 mole) was dissolved in 30 ml of benzene and 11.0 g (0.06 mole) of 2,4-dinitrofluorobenzene was added. The mixture was heated under reflux for 1 hr during which time the mixture turned dark orange. As the mixture was cooled overnight at ice temperature a precipitate formed. The product after four recrystallizations from hexane consisted of very pale yellow crystals, mp 78–79° (lit.[13] mp 78–79°).

*Anal.* Calcd for $C_9H_7N \cdot C_6H_3FN_2O_4$: C, 57.15; H, 3.20; N, 13.33. Found: C, 56.98; H, 3.26; N, 13.43.

**Reaction of 1-(2′,4′-Dinitrophenyl)quinolinium Fluoride with N-Methylaniline.**—As N-methylaniline (3.3 g, 0.035 mole) was added to a solution of 1-(2′,4′-dinitrophenyl)quinolinium fluoride (5.0 g, 0.016 mole) in 30 ml of methanol, a deep red coloration developed. The mixture was heated under reflux for 4 hr and allowed to stand overnight. Orange-red crystals formed in the reaction mixture; these were collected and recrystallized from acetone. A mixture melting point with N-methyl-N-phenyl-2,4-dinitroaniline gave no depression.

**4-(γ-Hydroxypropyl)-6,8-dimethylazulene** (IV).—To a solution of 17.3 g (0.10 mole) of 4,6,8-trimethylazulene in 800 ml of anhydrous ether, cooled to −20° and under a nitrogen atmosphere, was added dropwise 150 ml of a 15.17% solution of *n*-butyllithium in hexane. During the addition, the reaction mixture turned from violet to clear gold, indicating formation of the lithium salt of 4,6,8-trimethylazulene.[14] After stirring 0.5 hr a solution of 20 ml (0.42 mole) of ethylene oxide in 20 ml of anhydrous ether was added dropwise. The reaction mixture turned purple and formed a fine brown precipitate. After 45 min of stirring 5 ml (0.11 mole) of ethylene oxide was added. The reaction mixture was stirred for 6 hr, warmed to room temperature, washed with 2 *N* hydrochloric acid, washed with water until neutral, dried, and concentrated. Chromatography of the residue on alumina with ether as the eluent led to a purple oil. The oil was rechromatographed. Elution with hexane caused separation of two bands. The first band, eluted with hexane, yielded 4,6,8-trimethylazulene. The second band was eluted with ether and yielded a blue oil. Vacuum distillation of the oil gave 3.81 g (19%) of viscous blue oil: bp 193–97° (0–1 mm); $\lambda_{max}$ in cyclohexane 550 and 590 mμ; ν 3400 $cm^{-1}$.

The adduct of IV and 1,3,5-trinitrobenzene was prepared in ethanol and recrystallized successively from ethanol–water, cyclohexanol, and hexane. The adduct was brown and melted at 85.5–87°.

*Anal.* Calcd for $C_{21}H_{21}N_3O_7$: C, 59.01; H, 4.97; N, 9.83; O, 26.20. Found: C, 59.23; H, 5.09; N, 9.73; O, 26.02.

**4-(γ-Bromopropyl)-6,8-dimethylazulene.**—A mixture of 4.0 g (0.018 mole) of 4-(γ-hydroxypropyl)-6,8-dimethylazulene (IV), 9 ml (0.053 mole) of 48% hydrobromic acid, 1.2 ml of concentrated sulfuric acid, and 5 ml of hexane was refluxed for 1 hr. After 16 hr at room temperature, the reaction mixture was diluted with water, neutralized with sodium carbonate, and extracted with ether. The ether layer was washed with water, dried, concentrated, and chromatographed on alumina. Three fractions were obtained utilizing 25, 50, and 75% mixtures of acetone to hexane or acetone to ether as eluents. Repeated chromatography was necessary to bring about good separation of the fractions. The first fraction was 0.38 g (15%) of a blue oil identified as starting material IV. The second fraction yielded 0.32 g (7%) of crude 4-(γ-bromopropyl)-6,8-dimethylazulene as a blue oil, $\lambda_{max}$ in cyclohexane 552 and 572 mμ.

A brown crystalline adduct of 6-(γ-bromopropyl)azulene and 1,3,5-trinitrobenzene was prepared in and recrystallized from ethanol.

*Anal.* Calcd for $C_{21}H_{20}N_3O_6Br$: C, 51.44; H, 4.11; N, 8.57; Br, 16.30; O, 19.58. Found: C, 51.61; H, 4.19; N, 8.34; Br, 16.44; O, 19.66.

A third fraction, a blue solid (mp 110–111°), was not identified.

**Acknowledgment.**—We express our gratitude to Messrs. John Engel and Herbert Petty, who as National Science Foundation Undergraduate Research Participants during the summer of 1963 and during 1963–1964, respectively, contributed to the synthetic and spectral studies.

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[13] F. Kröhnke, private communication; mp 174–175° reported in *Chem. Ber.*, **91**, 1300 (1958), has been found to be in error.

[14] K. Hafner, K. Pelster, and H. Palzelt, *Ann.*, **650**, 80 (1961).

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# The Effect of Nucleophiles on the Stoichiometric Hydroformylation Reaction[1]

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The yield of aldehydes obtained from the stoichiometric hydroformylation of 1-pentene with $HCo(CO)_4$ is greatly enhanced by adding nucleophiles such as benzonitrile in appropriate concentrations. The ratio of straight-chain to branched-chain aldehyde is thereby increased and the extent of olefin isomerization is greatly reduced. Stabilization of the acylcobalt complex at the tricarbonyl level and avoidance of tetracarbonyl formation appear to account for the remarkable effects.

The rate of the high-pressure catalytic hydroformylation of olefins is increased by the addition of organic bases such as pyridine, quinoline, and triethylamine[3-6] or of oxygenated compounds such as ketones and alcohols.[7] No detailed mechanism has been suggested to explain the observed results, although it is thought that these compounds somehow enhance the cleavage of dicobalt octacarbonyl by hydrogen to form cobalt hydrocarbonyl.[4,5]

A similar effect was observed when catalytic amounts of benzonitrile were added to the stoichiometric hydroformylation reaction of 1-pentene.[8]

$$\begin{aligned} xs\ CH_3CH_2CH_2CH{=}CH_2 + 2HCo(CO)_4 + CO \longrightarrow \\ CH_3(CH_2)_4CHO + CH_3(CH_2)_2CH(CH_3)CHO + \\ Co_2(CO)_8 + CH_3{-}CH_2{-}CH{=}CH{-}CH_3 \end{aligned}$$

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[2] Public Health Service Predoctoral Fellow, 1962–1965.

[3] T. Yoshida, R. Iwanaga, and H. Mori, U. S. Patent 2,848,304 (1958).

[4] R. Iwanaga, *Bull. Chem. Soc. Japan*, **35**, 865 (1962).

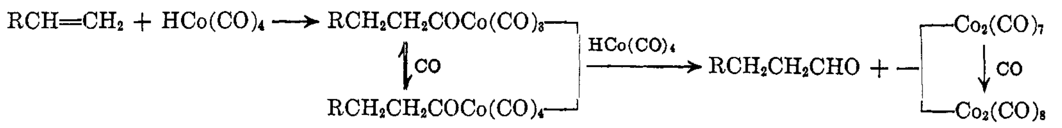
[5] R. Iwanaga, *ibid.*, **35**, 869 (1962).

[6] H. Uchida and A. Matsuda, *ibid.*, **36**, 1351 (1963).

[7] Y. Takegami, C. Yokokawa, and Y. Watanabe, *ibid.*, **37**, 935 (1964).

[8] G. L. Karapinka, Ph.D. Dissertation, University of Cincinnati, 1962.

CHART I



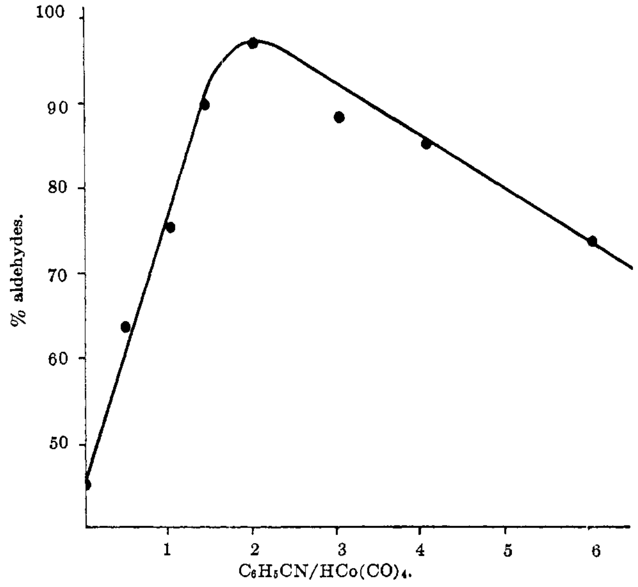


Figure 1.—Effect of benzonitrile concentration on yield of aldehydes (under nitrogen, 25°).

This observation has now been further explored and the results are reported herein.

## Results

Although the temperature of reaction and the presence or absence of an atmosphere of carbon monoxide have an enormous effect on the rate and yield of aldehyde from 1-pentene,[9,10] it has now been found that the presence of benzonitrile has an equally dramatic effect. Pertinent reaction data are shown in Table I.

TABLE I

HYDROFORMYLATION OF 1-PENTENE. EFFECT OF ATMOSPHERE AND NUCLEOPHILE[a]

| Atm | 1-P/Co[b] | $C_6H_5CN$/ Co[c] | % aldehydes[d] | B/S | % 2-P[e] | Time, min |
|---|---|---|---|---|---|---|
| $N_2$ | 10 | 2 | 99 | .5 | 1 | 10 |
| $N_2$[f] | 25 | ... | 39 | 2.6 | 52 | 32 |
| CO | 10 | 2 | 90 | .7 | 4 | 10 |
| CO | 10 | ... | 44 | 2.0 | 65 | 15 |

[a] Total volume in all cases was 20 ml; temp 25 ± 2°. [b] 1-pentene/cobalt hydrocarbonyl ratio. [c] Benzonitrile/cobalt hydrocarbonyl ratio. [d] Based upon the consumption of 2 moles of $HCo(CO)_4$ for each mole of aldehyde. [e] Per cent of 2-pentene in recovered olefin. [f] Reference 9.

Not only is the yield of aldehyde greatly enhanced, but the extensive isomerization of the excess 1-pentene is greatly reduced and the proportion of straight-chain aldehyde is increased. As can be seen from Figure I, the effect of the concentration of benzonitrile is maximal at a molar ratio of about $2C_6H_5CN/1HCo(CO)_4$ in the concentration range employed. The amount of isomerization of 1-pentene to 2-pentene was minimal at this ratio.

The word "nucleophile" has been used loosely and there is no single criterion for quantifying nucleophilicity. The compounds listed in Table II certainly differ in their nucleophilicity. Measured by their effect on the H-O stretching frequency of phenol,[11] the nucleophilicity of the nitriles is EtCN > $CH_3CN$ > $C_6H_5CH_2CN$ > $C_6H_5CN$. As Table II shows, the yield of aldehydes decreases in approximately the reverse order: $C_6H_5CN$ > $CH_3CN$ > EtCN > $C_6H_5CH_2CN$. Triphenylphosphine reacts instantaneously with $HCo(CO)_4$ to form $HCo(CO)_3(C_6H_5)_3P$ which is not a hydroformylation catalyst under these conditions and hence addition of $PPh_3$ kills the reaction. Pyridine is such a strong base that it reacts instantly to give the salt $PyH^+[Co(CO)_4]^-$,[12,13] and accordingly the yield of aldehyde is zero.

TABLE II

EFFECT OF NUCLEOPHILE ON HYDROFORMYLATION OF 1-PENTENE[a]

| Nucleophile | Aldehydes, % | B/S[b] | 2-Pentene, %[c] | Time, min[d] |
|---|---|---|---|---|
| Benzonitrile | 91 | 0.7 | 4 | 2–3 |
| Acetonitrile | 82 | 0.7 | 1 | 2–3 |
| Thioanisole | 58 | 1.2 | 14 | 2–3 |
| Propionitrile | 55 | 1.0 | ... | 2–3 |
| Thiophenol | 52 | 1.7 | 13 | 2–3 |
| Anisole | 47 | 0.5 | 1 | 6 |
| Phenylacetonitrile | 42 | 0.7 | ... | 6 |
| None | 44 | 2.0 | 65 | 10 |
| Triphenylphosphine | 0 | ... | ... | Instantaneous |
| Pyridine | 0 | ... | ... | Two layers |

[a] 1 atm of CO; 25°; molar ratio of nucleophile/$HCo(CO)_4$ of 2. [b] Ratio of branched to straight-chain aldehyde. [c] Percentage of 2-pentene in recovered pentene. [d] For disappearance of $HCo(CO)_4$.

## Discussion

Part of the reaction pathways for the stoichiometric hydroformylation may be written as shown in Chart I. Unequivocal evidence for the intermediate acylcobalt tetracarbonyl has been reported[10,14] and it has been shown[15] that this tetracarbonyl reacts with triphenylphosphine in a fast reaction whose rate is independent of the phosphine concentration.

We have studied the rate of the cleavage of the acylcobalt tetracarbonyl with $HCo(CO)_4$ with and without nucleophile (benzonitrile) present and find that the two rates are essentially equal and both substantially slower than the over-all rate of the hydroformylation reaction. In these studies the rate of disappearance of $HCo(CO)_4$ was measured and reasonably good first-order plots were obtained in all cases. It was also shown that the rate of the reaction between $HCo(CO)_4$ and $C_6H_5CN$ as measured by CO evolution is

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(9) G. L. Karapinka and M. Orchin, *J. Org. Chem.*, **26**, 4187 (1961).

(10) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

(11) P. von R. Schleyer and A. Allerhand, *ibid.*, **85**, 866 (1963); see also J. Weinstein and E. McIninch, *ibid.*, **82**, 6064 (1960).

(12) I. Wender, H. W. Sternberg, and M. Orchin, *ibid.*, **74**, 1216 (1952).

(13) W. Hieber and R. Wiesboeck, *Chem. Ber.*, **91**, 1146, 1157 (1958).

(14) D. J. Breslow and R. F. Heck, *Chem. Ind.*, 467 (1960).

(15) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 651 (1963).

quite slow compared with the hydroformylation reaction.

In order to obtain high yields of aldehyde from the hydroformylation in the presence of excess olefin, it is essential that the rate of acylcobalt formation be very much slower than the rate of its cleavage otherwise the $HCo(CO)_4$ is not available for the cleavage to aldehyde. Since the nucleophile does not enhance the rate of acylcobalt tetracarbonyl cleavage by $HCo(CO)_4$, its effectiveness must be important in one or more of the earlier steps of the reaction.

The results seem to indicate that the key intermediate is the acylcobalt tricarbonyl. Nucleophiles of optimum strength in appropriate concentration complex weakly with the tricarbonyl in competition with carbon monoxide, and under these conditions cleavage of the tricarbonyl with $HCo(CO)_4$ is rapid. Strong nucleophiles (excess carbon monoxide, triphenylphosphine) fix the cobalt in the five coordinated state and retard cleavage with $HCo(CO)_4$. Further work is in progress.

## Experimental Section

**Reaction of 1-Pentene with $HCo(CO)_4$ in the Presence of Nucleophiles.**—A 0.36 *M* solution of cobalt hydrocarbonyl was prepared in the usual manner[16] and carefully dried by immersion in a Dry Ice–acetone bath. A 14-ml aliquot was removed (5.0 mmoles), and transferred to a serum-stoppered side-arm flask, equipped with a Teflon-coated stirring bar. The entire system had previously been purged with either CO or $N_2$, depending on the atmosphere required for the experiment. The nucleophile (9 mmoles) was mixed with 5 ml of 1-pentene (45 mmoles) and added to the cobalt hydrocarbonyl solution. The total volume of solution was 20 ml. Under a CO atmosphere, 20 to 30 ml of gas were absorbed in about 2 min, after which gas evolution began to take place. The amount evolved depended on the length of time allowed for each reaction. The CO absorption never approached the theoretical quantity expected for the amount of aldehydes produced. After about 10 min, 3 ml of N,N-dimethylformamide was added, and, after the evolution of about 98 ml of gas (approximately 5 mmoles), 10 ml of water was added. The organic layer was removed, dried, and then analyzed by vapor phase chromatography (vpc). Isomeric pentenes were separated at room temperature at a pressure of 35 psi of He on a 8-ft column packed with 20% by weight with 550 silicone oil. Percentages of 1- and 2-pentene (*cis* plus *trans*) were calculated from the area under the curves. At 135°, on the same column, the aldehydes and $C_6H_5CN$ were separated. Using pure aldehydes as standards, it was possible to calculate the molar volume of the aldehydes obtained in each experiment. The yield of aldehyde was calculated on the basis of 2 moles $HCo(CO)_4$ per mole aldehyde. No benzylamine was found. Duplicate runs always were made with the same batch of cobalt hydrocarbonyl in order to eliminate variations introduced by the aging of the various dicobalt octacarbonyl solutions. The approximate duration of the reactions was ascertained by titration of the reaction solution for $HCo(CO)_4$. The reactions under $N_2$ were over in about 1 min, while those under CO were complete in about 2 min.

**Reaction of Benzonitrile with $HCo(CO)_4$.**—A 20-ml solution containing 5 mmoles of $HCo(CO)_4$ and 18 mmoles of benzonitrile, was stirred under a CO atmosphere. Gas evolution began almost immediately and stopped after 60 min, at which time nearly 169 cc of gas had been evolved (approximately 4.7 mmoles). The gas was analyzed by means of mass spectrometry and found to contain only CO. A small amount of the dark solution was transferred to another flask, and 2 ml of 1-pentene was added; vpc analysis showed no aldehydes. The remainder of the solution was reacted with excess triphenylphosphine, and a brown precipitate formed with gas evolution. Infrared analysis of the precipitate showed the absence of benzonitrile (confirmed by a sodium fusion test). The spectrum and properties of this brown precipitate indicated it to be $[Co(CO)_3(C_6H_5)_3P]_2$.

**Reaction of $C_6H_5SH$ and $HCo(CO)_4$.**—When 8 mmoles of cobalt hydrocarbonyl was treated with 16 mmoles of thiophenol, rapid gas evolution occurred and a total of 692 ml was evolved (approximately 14 mmoles). A stable black compound was isolated but not characterized.

**Preparation of Hexanoylcobalt Tetracarbonyl.**—To a previously prepared solution of sodium cobalt tetracarbonyl (23.8 mmoles)[17] was added 3.65 ml (25 mmoles) of freshly distilled hexanoyl chloride, at 0° and under a CO atmosphere. The solution was stirred for 30 min at which time the color had turned a deep yellow. Upon completion of the reaction, a 2-ml aliquot was removed and then treated in a gasometric apparatus with a 0.2 *M* solution of $I_2$ and the volume of evolved CO measured. The concentration of the acyl complex was found to be 0.2*M*.

**Reaction of Cobalt Hydrocarbonyl and Hexanoylcobalt Tetracarbonyl in the Presence of Benzonitrile.**—A 100-ml side-arm flask, attached to the gasometric apparatus and flushed with CO, was equipped with septum and magnetic stirring bar and injected with a 21-ml solution of hexanoylcobalt tetracarbonyl in hexane (4.5 mmoles) at room temperature. A previously mixed 11.5-ml solution, containing 4.5 mmoles of cobalt hydrocarbonyl and 9.0 mmoles of benzonitrile, was then also injected into the flask. At appropriate intervals, 0.5-ml aliquots were removed and titrated with 0.01 *N* NaOH to a phenolphthalein end point, to determine the concentration of cobalt hydrocarbonyl remaining in solution. The data fit a standard first-order plot and gave a value of $k = 0.3 \text{ min}^{-1}$. At the end of the reaction (55 min), 5 ml of N,N-dimethylformamide was added. Part of the hydrocarbon layer was removed and vpc analysis showed 98% *n*-hexaldehyde and 2% branched aldehyde.

When the identical reaction was repeated omitting benzonitrile, essentially the same results were obtained.

**Reaction of Hexanoylcobalt Tetracarbonyl with Benzonitrile.**—An ether solution containing 7.6 mmoles of hexanoylcobalt tetracarbonyl in hexane was reacted with 15.2 mmoles of benzonitrile, under a nitrogen atmosphere. After 4 hr no gas evolution or color change had taken place. Addition of excess triphenylphosphine liberated 7.4 mmoles of CO, showing that the acyl complex had not been destroyed during the reaction.

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[16] L. Roos and M. Orchin, *J. Am. Chem. Soc.*, **87**, 5502 (1965).

[17] S. V. Dighé, Ph.D. Dissertation, University of Cincinnati, 1965.