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The Carboxyalkylation of Ketones with α-Halo Acids to Yield γ-Keto Acids by Means of Lithium Amide. Influence of Metallic Cation[1]

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RECEIVED DECEMBER 28, 1959

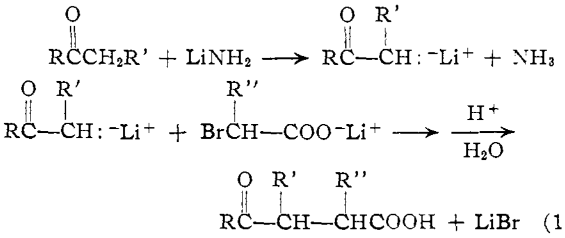
A new method for the synthesis of γ-keto acids by utilizing a displacement reaction between lithium salts of ketones and lithium salts of α-halo acids has been developed. The method appears to be fairly general and gave good yields with a variety of ketones and α-halo acids. The method, however, fails or gives poor yields with ketones that are readily self-condensed, with ketones containing aromatic nitro groups, and with α-halo acids containing two alkyl substituents on the α-carbon. The nature of the metallic cation accompanying either ketone anion or halo acid anion has a pronounced effect on product yield. Yields are highest when lithium is the cation in both moieties, are much poorer when sodium is substituted for lithium with either component, and fails completely when potassium is used with either anion. Solubilities of the various alkali salts involved were measured, and the results indicated that solubility factors could not account for the differences in cation effect observed.

The attachment of an acetic acid or substituted acetic acid residue to the α-carbon of a ketone has usually involved a multi-step problem in synthesis. For example, the reported synthesis of 1,2,3,4-tetrahydronaphthalene-1-oxo-2-acetic acid requires four steps from α-tetralone, involving condensation with ethyl oxalate, decarbonylation to β-keto ester, alkylation of the sodium salt of the ester with methyl bromoacetate, and hydrolysis and decarboxylation.[2] A similar series of reactions has been used with cyclohexanone to prepare 2-keto-1-cyclohexylacetic acid.[3] Recent newer approaches developed include the alkylation of the pyrrolidine enamine of cyclohexanone with ethyl bromoacetate,[4] and the aldol-type condensations of ketones with glyoxylic acid and its esters.[5]

Syntheses of γ-keto acids or esters by direct displacement between a ketone anion and an α-halo acid or ester apparently have not been reported. In initial attempts to achieve this reaction, we treated the lithium salt of acetophenone in ether with an equivalent of *t*-butyl bromoacetate. The hindered ester was used in order to inhibit a potential Claisen-type condensation leading to β-diketone. We obtained less than a 10% yield of desired γ-keto ester, little recovery of starting materials and much tarry residue. Similar results were obtained using a 100% excess of lithium acetophenone. Since a displacement reaction *can* be achieved between a β-keto ester anion and an α-halo ester,[2,3] the failure to realize displacement with the more strongly basic ketone anion may be due to participation of the latter in acid-base exchange with the α-hydrogen of the α-halo ester to yield ketone and α-halo ester anion which then react to give the tarry, polymeric materials which were observed.

It had been hoped that by using the lithium rather than the sodium or potassium salts of the ketone, the displacement reaction might have been realized before acid-base exchange occurred, since certain condensations in which an acid-base exchange was a likely side-reaction have been realized when the cation was lithium, but not at all or in much diminished yield when it was sodium or potassium.[6] Apparently, the rate of displacement reaction in this instance was slower than that of acid-base exchange even when the cation was lithium.

However, if a salt of an α-halo acid were used instead of an α-halo ester, the negative charge on the acid anion might render the α-hydrogen much less acidic and less prone to enter into acid-base exchange. This expectation has been realized. Treatment of lithium acetophenone with an equivalent of the lithium salt of bromoacetic acid for 10 hours in refluxing ether gave a 38% yield of β-benzoylpropionic acid (I). Further, by using a 100% excess of lithium acetophenone, the yield of displacement product was increased to 61%. This method now has been found to be applicable to a wide variety of ketones and α-halo acids so as to constitute a rather general method of synthesis of γ-keto acids, as illustrated by eq. 1.



$$\mathrm{R\overset{O}{\overset{\|}{C}}CH_2R' + LiNH_2 \longrightarrow R\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{C}}H{:}^-Li^+ + NH_3}$$

$$\mathrm{R\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{C}}H{:}^-Li^+ + Br\overset{R''}{\overset{|}{C}}H-COO^-Li^+ \longrightarrow \xrightarrow[H_2O]{H^+}}$$

$$\mathrm{R\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{C}}H-\overset{R''}{\overset{|}{C}}HCOOH + LiBr} \quad (1)$$

The generality of the method has been illustrated by the preparation of γ-keto acids I–X. The yields for these syntheses from various combinations of ketones and acids are summarized in Table I.

In the procedure employed, the lithium salt of the α-bromo acid was conveniently generated *in situ* by adding one equivalent of an ether solution of the acid to an ether mixture of two equivalents of lithium ketone plus one equivalent of lithium amide. Attempts to substitute dioxane or tetrahydrofuran as solvents in place of ether gave lower yields. Several experiments showed that the refluxing period could be shortened from 10 hours to 4 hours with only a small (2–6%) decrease in yield, although all the reactions reported in Table I were run for the full 10-hour period.

It can be seen from Table I that the method gave good yields with a variety of alkyl aryl ketones, in-

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[1] Preliminary results on this work were reported by the authors in *Chemistry & Industry*, 255 (1959).

[2] W. E. Bachmann and G. D. Johnson, THIS JOURNAL, **71**, 3463 (1949).

[3] N. Chatterjee, *J. Indian Chem. Soc.*, **12**, 591 (1935).

[4] G. Stork, R. Terrell and J. Szmuszkovicz, THIS JOURNAL, **76**, 2029 (1954).

[5] M. S. Newman, W. Sagar and C. C. Cochrane, *J. Org. Chem.*, **23**, 1832 (1958).

[6] C. R. Hauser and W. H. Puterbaugh, THIS JOURNAL, **75**, 1068 (1953); D. Nightingale and F. T. Wadsworth, *ibid.*, **69**, 1181 (1947).

TABLE I

YIELDS OF γ-KETO ACIDS FROM CARBOXYALKYLATION OF KETONES BY LITHIUM AMIDE

Ketone	Acid, α-bromo-	Acid product	Crude yield, %	Purity,[a] %	Corrected yield,[b] %
Acetophenone	Acetic	β-Benzoylpropionic (I)	61.3	99.3	61
Propiophenone	Acetic	β-Benzoylbutyric (II)	48.6	98.8	48
Butyrophenone	Acetic	β-Benzoylvaleric (III)[c]	59.6	97.4	55
p-Methoxyacetophenone	Acetic	β-(*p*-Methoxybenzoyl)-propionic (IV)	42.3	96.1	41
m-Nitroacetophenone	Acetic	....[d]	..	..	..
p-Chloropropiophenone	Acetic	β-(*p*-Chlorobenzoyl)-butyric (V)[c]	67.3	95.0	64
α-Tetralone	Acetic	1,2,3,4-Tetrahydronaphthalene-1-oxo-2-acetic (VI)	76.0	95.0	72
Cyclohexanone	Acetic	2-Oxo-1-cyclohexylacetic (VII)	48.6	96.4	47
Cyclopentanone	Acetic	...	..	..	..
Acetophenone	Propionic	α-Methyl-β-benzoylpropionic (VIII)	53.6	93.1	50
α-Tetralone	Propionic	α-(1,2,3,4-Tetrahydronaphthalene-1-oxo-2)-propionic (IX)[c]	70.0	88.0	62
p-Chloropropiophenone	Propionic	α-Methyl-β-(*p*-chlorobenzoyl)-butyric (X)[c]	77.6	80.0	61
Acetophenone	Isobutyric	....[f]	..	..	..

[a] As determined by neutral equivalent of the crude product. [b] Obtained by multiplying crude yield times the purity. [c] These represent new compounds; see Experimental. Recrystallization of all the other acid products gave m.p.'s in agreement with the previously reported literature values and neutralization equivalents in accord with theory. [d] Only a small yield of tarry product. [e] Mixture of high boiling, acidic products. [f] Less than a 5% yield of crude material.

cluding those with halogen and methoxy groups in the ring. The good yield with α-tetralone is noteworthy, as it suggests possible application to syntheses in the steroid series. Of further interest is the fact that salts of acids higher than acetic can be used, since the reaction of lithium α-bromopropionate with several ketones gave yields only slightly lower than those obtained with lithium bromoacetate. However, the method did fail when two alkyl groups were substituted on the α-carbon of the acid, as with α-bromoisobutyric acid. Further limitations can be noted in that poor yields were obtained with cyclopentanone and *m*-nitroacetophenone. In the former case, the ketone is known to be quite prone to base-catalyzed self-condensation.[7] Probably any ketone which is especially prone to undergo self-condensation will give low yields under the present reaction conditions. With the nitro ketone, mainly tars were obtained under the usual reaction conditions.

Since a 100% excess of ketone anion was used, the yields reported in Table I are based on the α-halo acid. Recovery of the excess ketone varied. With acetophenone, only 62% of the excess was recovered along with resinous product presumably resulting from ketone self-condensation. Fortunately, with the less available α-tetralone, all of the 100% excess was recovered along with 10% of the stoichiometrically required ketone, so that in this case the yield based on ketone consumed would be 81%. No attempts were made to recover unreacted bromo acids.

Certain of the keto acids prepared in this study, while not previously obtainable by direct displacement from the ketone, can be prepared by Friedel–Crafts reaction between succinic anhydride and some substituted benzenes. However, this method is limited by the orientation requirements of the reaction, and by the availability of substituted succinic anhydride derivatives. Recently, the reaction of Grignard reagents with succinyl chloride has been shown to yield γ-keto acids,[8] but this method suffers from the same limitations regarding availability of substituted succinyl chlorides.

Influence of the Metallic Cation.—Early experiments showed that yields of γ-keto acids were much poorer when sodium amide was substituted for lithium amide in the reaction. It thus seemed desirable to study the effect of the cation upon yields. Since a cation accompanies both the attacking ketone anion and the α-halo acid salt, nine different experimental combinations using the three common alkali cations are possible. Seven of these combinations were run employing acetophenone and iodoacetic acid as the reactants. When mixtures of cation components were employed, it was necessary to vary the procedure in that the alkali salts of iodoacetic acid had to be prepared separately and one equivalent of the proper salt added to an ether solution or mixture of two equivalents of the alkali ketone. The reaction was then completed as usual. Two of the possible combinations were omitted when it seemed apparent that they would not add to the conclusions which could be drawn. The results are given in Table II.

TABLE II

EFFECT OF ALKALI CATION UPON YIELDS OF β-BENZOYLPROPIONIC ACID FROM ALKALI ACETOPHENONES AND ALKALI IODOACETATES

Alkali salt of acetophenone	Alkali salt of iodoacetic acid	β-Benzoylpropionic acid Yield, %
Lithium	Lithium	63
Lithium	Sodium	37
Lithium	Potassium	0
Sodium	Lithium	25
Sodium	Sodium	17
Potassium	Lithium	0
Potassium	Potassium	0

It can be seen from Table II that the yield of γ-keto acid was highest when lithium was the cation accompanying both moieties, and that the yield fell sharply when sodium was used as cation in either the ketone anion or acid salt. The reaction failed completely when potassium was the cation in either component.

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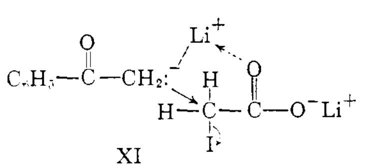
[7] C. R. Hauser and B. O. Linn, THIS JOURNAL, **79**, 731 (1957).

[8] J. Cason and E. J. Reist, *J. Org. Chem.*, **23**, 1668 (1958).

To determine whether these results were due primarily to solubility phenomena, the solubilities of the various salts were measured in ether. The lithium and sodium salts of acetophenone were completely soluble in the concentrations used in our experiments (approximately 0.8 *M*). In fact, measurements in higher concentrations showed that the solubility of lithium acetophenone in ether is at least 1.5 *M*, and that of sodium acetophenone at least 1.1 *M*. The solubility limit may not have been reached in either case. Potassium acetophenone, however, is essentially insoluble in ether, the solubility being no greater than 0.01 *M*. On the other hand, the alkali salts of iodoacetic acid were *all* found to be essentially insoluble in ether. The solubilities of these salts were no greater than 0.005 *M* with no significant differences between the three cations. Thus, solubility differences alone would account only for the failure of the reactions involving the potassium salt of acetophenone

Possibly the greater effectiveness of lithium when it is the cation in the iodoacetic acid salt may be due to relatively greater coördination of the lithium cation with the acid anion. This would yield a more neutral molecule which would be less repulsive to the approach of the ketone anion required for displacement. A similar explanation may account for the observation that hydrolysis of the half *sec*-butyl ester of phthalic acid is fifteen times as fast with sodium hydroxide as with a tetraalkylammonium hydroxide.[9] Greater coördination of the lithium cation may likewise account for the greater stability of lithium salts of β-hydroxy esters[10] and of certain hindered tertiary carbinols[11] over the corresponding sodium and potassium salts.

The greater effectiveness of lithium when it is the cation accompanying the ketone anion is in line with a previous observation that lithium reagents generally give higher yields of displacement products than the corresponding sodium reagents in certain reactions,[12] although the wide differences observed in yields in the present study are greater than might have been anticipated. Possibly the displacement is facilitated by a ring mechanism in which coördination of the cation plays a major role, as in XI



XI

Finally, the nature of the halogen atom was found to have some effect on reaction yields. Reaction of lithium acetophenone with the lithium salts of chloro-, bromo- and iodoacetic acids gave yields of β-benzoylpropionic acid of 20, 61 and 63%, respectively. Since there was no significant difference between the two latter halides, the less expensive bromo acids were used in the experiments reported in this paper.

Experimental[13]

γ-Keto Acids from Carboxyalkylation of Ketones by Lithium Amide. General Procedure.—To a stirred suspension of lithium amide[6] prepared from 1.65 g. (0.235 g. at.) of lithium wire in 200 ml. of liquid ammonia in a flame-dried, nitrogen-purged flask, was added over 5–7 minutes a solution of 0.15 mole of the appropriate ketone in 50 ml. of ether. As soon as addition was complete, a hot water-bath was applied and the ammonia rapidly driven off and replaced by 100 ml. of ether. After the bulk of the ammonia had evaporated (5–9 minutes), as evidenced by refluxing of the ether, the solution was refluxed 3 minutes. The heating bath was removed, and a solution of 0.075 mole of the α-bromo acid[14] in 50 ml. of ether was added over 10 minutes.[15] The reaction then was completed by refluxing for 10 hours. The heating mantle was removed, and the mixture decomposed by the addition, cautious at first, of 60 ml. of water. The layers were separated and the ether layer extracted with two 20-ml. portions of water. The combined aqueous layers were extracted with 25 ml. of ether, heated to boiling to expel dissolved ether, filtered from charcoal, cooled, and made strongly acid with concentrated hydrochloric acid. The cooled solid product (in certain cases scratching and seeding was necessary to induce crystallization) was filtered with suction, washed, and dried overnight *in vacuo*. Yield and purity were determined by weight and neutralization equivalent of the dried product. The combined ether layers from the extractions were washed with saturated sodium chloride solution containing a little HCl, dried over sodium sulfate, the solvent removed, and the residue distilled to yield recovered ketone. **New γ-Keto Acids Prepared by the General Procedure. β-Benzoylvaleric Acid** (III).—Two recrystallizations from benzene-petroleum ether (30–60°) gave large prisms, m.p. 68.5–70.0°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; neut. equiv., 206.2. Found: C, 69.99; H, 7.02; neut. equiv., 205.3.

The semi-carbazone was prepared and, after recrystallizing from ethanol, gave m.p. 176.0–176.5°.

Anal. Calcd. for $C_{13}H_{17}N_3O_3$: C, 59.30; H, 6.51. Found: C, 59.41; H, 6.64.

β-(*p*-Chlorobenzoyl)-butyric Acid (V).—Recrystallization from ethanol-water yielded an oil which crystallized on scratching to give a white solid, m.p. 82–83°, whose neutralization equivalent (262) suggested a di-hydrate. This material was recrystallized from ligroin (66–75°), using a large volume of the latter solvent and evaporating part of it so as to remove the water of hydration. This procedure yielded white needles, m.p. 81–82.5°.

Anal. Calcd. for $C_{11}H_{11}ClO_3$: C, 58.29; H, 4.89; neut. equiv., 226.7. Found: C, 58.19; H, 4.89; neut. equiv., 225.5.

The semi-carbazone was prepared and after recrystallizing from ethanol gave m.p. 170.0–170.5°.

Anal. Calcd. for $C_{12}H_{14}ClN_3O_3$: C, 50.80; H, 4.97. Found: C, 51.06; H, 4.96.

α-(1,2,3,4-Tetrahydronaphthalene-1-oxo-2)-propionic Acid (IX).—The product as obtained was apparently a mixture of diastereoisomers. Originally a thick, light brown oil, it was very resistant to crystallization, and would invariably have

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[9] O. L. Brady and J. Jakobovits, *J. Chem. Soc.*, 767 (1950).

[10] C. R. Hauser and W. H. Puterbaugh, THIS JOURNAL, **75**, 4756 (1953).

[11] H. D. Zook, J. March and D. F. Smith, *ibid.*, **81**, 1617 (1959).

[12] W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, **24** 416 (1959).

[13] All analyses by Galbraith Laboratories, Knoxville, Tenn. Melting points are corrected.

[14] Bromoacetic acid is quite hygroscopic. Redistilled commercial material was stored in a desiccator when not in use. When making a run, the product was weighed out as rapidly as possible and then quickly covered with solvent in a corked flask to avoid absorption of water and lowering of yield.

[15] During this addition, ammonia fumes evolved both by ammonia remaining dissolved in the ether and by reaction of the acid with lithium amide would generally cause formation of some precipitate of the ammonium salt of the acid in the stem of the addition funnel. This could be reduced somewhat by bubbling dry nitrogen gas through the reaction mixture for 2–3 minutes before adding the acid. However, as the yield appeared to be nearly the same whether this was done or not, the nitrogen purging was omitted in the majority of the runs, care being taken during the addition to regulate the stopcock so that a fairly rapid and nearly constant rate of addition was maintained. At completion of addition, any solid salt adhering to the upper walls of the flask or addition joint was transferred to the reaction mixture as rapidly as possible with minimum exposure to air.

to be seeded and scratched to induce crystallization after each attempted recrystallization. Three recrystallizations from benzene–ligroin (66–75°) gave white blocks, m.p. 103–109°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47; neut. equiv., 218.2. Found: C, 71.74; H, 6.48; neut. equiv., 218.2.

α-Methyl-β-(*p*-chlorobenzoyl)-butyric Acid (X).—The product as obtained was apparently a mixture of diastereoisomers. The material was originally a thick, gray oil which on scratching set up to a gray-white solid. Three recrystallizations from benzene–ligroin (66–75°) yielded short, white needles, m.p. 125–129°.

Anal. Calcd. for $C_{12}H_{13}ClO_3$: C, 59.88; H, 5.44; neut. equiv., 240.7. Found: C, 59.69; H, 5.63; neut. equiv., 241.5.

Attempted Displacement between Acetophenone and *t*-Butyl Bromoacetate by Lithium Amide.—To 0.26 mole of lithium acetophenone in ether was added 0.13 mole of *t*-butyl bromoacetate[16] and the reaction mixture refluxed and stirred for 10 hours. At the end of this period the ether layer was washed with water and saturated sodium bicarbonate solution. Ether was removed from the dried solution and the residue distilled *in vacuo* to yield 5.2 g. (17%) of recovered acetophone, 1.0 g. (4%) of material boiling in the range for the glycidic ester, 2.2 g. (7%) of material boiling in the correct range for the desired γ-keto ester product, and 16.0 g. of high boiling, tarry residue which decomposed on attempted further distillation. Acidification of the bicarbonate extracts yielded 9.0 g. of a brown, thick oil which resisted all attempts at crystallization. Since the yield of desired γ-keto ester was so low, no attempts were made to further characterize the material boiling in the correct range for this product.

Qualitatively similar results were obtained when equimolar portions of lithium acetophenone and *t*-butyl bromoacetate were refluxed in ether for 10 hours.

Influence of the Metallic Cation on Product Yields.—For experiments in which combinations of different cations were used, 0.075 mole of dry lithium, sodium or potassium iodoacetate was added to an ether solution or suspension of 0.15 mole of the alkali acetophenone by means of Gooch tubing connecting the reaction flask and an erlenmeyer flask containing the iodoacetate salt. The addition was manual by shaking, and consumed about 5 minutes. The reaction was then completed in the usual manner.

Sodium and potassium iodoacetate were commercial materials which were dried *in vacuo*. **Lithium iodoacetate** was prepared by stirring a solution of 0.18 mole of iodoacetic acid and 0.17 mole of lithium hydroxide in 90 ml. of acetone and 5 ml. of water for 18 hours, filtering off the voluminous white precipitate, washing with acetone, and then drying at 115° for 20 hours and at room temperature *in vacuo* for 48 hours; yield 30 g. (93%). When a 1.448-g. sample of this product was heated for 264 hours in a drying oven at 120°, a 0.025-g. loss in weight occurred. This is less than 20% of the loss in weight required for one molecule of water of hydration and may be due to slight decomposition of the product. Attempts to determine loss of weight by drying at 230° produced decomposition to yield free iodine within 5 minutes.

Solubility Determinations.—Alkali acetophenones were made by preparing solutions or suspensions of 0.10 mole of the alkali acetophenone in 130 ml. of ether in the usual manner. Filter-aid was added, and the mixture filtered rapidly with slight suction. The ether was evaporated from the filtrate first by rotation under a water aspirator, and then by drying at room temperature under 10 mm. pressure for 15 minutes. The residue (an orange supercooled glass in the case of lithium acetophenone, an orange powder with sodium acetophenone) was weighed to determine the amount of dissolved alkali acetophenone (see Discussion). Since the sodium and lithium salts were completely soluble in the medium in the concentrations employed in the general procedure, attempts were made to measure the limiting solubility with these salts by employing twice the concentrations normally used. Although experimental difficulties in these concentrations made evaluation somewhat difficult, it appeared that the lithium salt was still completely soluble in these concentrations (1.4–1.6 *M*), while the sodium salt was just at or slightly over its solubility limit (approximately 1.1 *M*).

Alkali iodoacetates were made by refluxing 0.015 mole of alkali iodoacetate in 100 ml. of ether for 15 minutes, filtering with suction by means of Filter-aid, and treating as above to determine the amount of soluble residue (see Discussion). The soluble material was extremely small in all cases, and that which did dissolve was not similar in appearance to the original salt, but was a fragrant liquid which may have resulted from self-esterification of a small portion of the salt during the heating with ether.

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant (NSF G-4206) which supported this research.

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[16] C. R. Hauser, B. E. Hudson, B. Abramovitch and J. C. Shivers, *Org. Syntheses*, **24**, 19 (1944).

[CONTRIBUTION FROM THE BRANCH OF COAL-TO-OIL RESEARCH, DIVISION OF SOLID FUELS TECHNOLOGY, BUREAU OF MINES, BRUCETON, PA.]

Carboxylation of Diphenylacetylene with $Ni(CO)_4$ in Alkaline Medium

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RECEIVED DECEMBER 11, 1959

Treatment of diphenylacetylene with a saturated solution of NaOH in methanol in the presence of excess nickel carbonyl yields α-phenyl-*trans*-cinnamic acid and 1,2,3,4-tetraphenylbutadiene. It is shown that a nickel carbonyl anion, $[Ni_3(CO)_8]^{-2}$, is formed and is probably the source of carbon monoxide in this reaction.

The stoichiometric[1,2] and semi-catalytic[3] carboxylation of acetylenes with $Ni(CO)_4$ to give acrylic acid derivatives is always carried out in the presence of an acid. However, little is known about the function of the acid or the nature of the carbon monoxide transfer agent. We now have found that carboxylation of diphenylacetylene can be carried out in alkaline solution and that in this case a nickel carbonyl anion is the source of carbon monoxide.

When diphenylacetylene is shaken with a saturated solution of NaOH in methanol in the presence of excess nickel carbonyl and the dark red reaction mixture acidified, α-phenyl-*trans*-cinnamic acid and 1,2,3,4-tetraphenylbutadiene are obtained in 25 and 67% yield, respectively, based on the amount of diphenylacetylene used. It is conceivable that the intermediate in this carboxylation is an acetylene nickel carbonyl anion containing carbon monoxide

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[1] W. Reppe, *Ann.*, **582**, 1 (1953).

[2] E. R. H. Jones, T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, 230 (1950); 348 (1951); 766 (1951).

[3] H. T. Neher, E. H. Specht and A. Neuman to Rohm & Haas Co., U. S. Patent 2,582,911, Jan. 15, 1952.