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.

---

[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

BY HEINZ W. STERNBERG, RAYMOND MARKBY AND IRVING WENDER

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 nicke 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

---

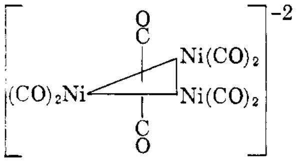
[1] W. Reppe, *Ann.*, **582**, 1 (1953).

[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.

and acetylene combined in a new ligand. Complexes containing carbon monoxide and acetylene as part of a negative ion have been reported previously. An example is the anion $[FeC_{10}H_2O_4]^{-2}$ in which two carbon monoxide groups and one acetylene are combined in a ligand.[4-7] A similar complex may be the intermediate in this carboxylation in the presence of alkali. This intermediate is probably formed from the reaction of acetylene with a nickel carbonyl anion, $[Ni_3(CO)_8]^{-2}$, whose presence was demonstrated by these experiments.

When nickel carbonyl is shaken with a saturated solution of NaOH in methanol the solution becomes dark red.[8] Addition of water to the reaction mixture causes separation into a clear dark red solution and a voluminous dark brown precipitate. The aqueous solution contains a nickel carbonyl anion which has a Ni/CO ratio of 3/8. It is stable in the absence of air and can be precipitated with $[Ni\text{-}(o\text{-phenanthroline})]^{++}$ cation. By analogy with the corresponding $[Fe_3(CO)_{11}]^{-2}$ anion, it is assumed that this nickel carbonyl anion is trinuclear and has a charge of −2. This anion by analogy with the recently elucidated[9] structure of $(C_5H_5)_3Ni_3(CO)_2$[10] may have structure A. The



(A)

anion $[Ni_3(CO)_8]^{-2}$ is obtained in about 50% yield based on the amount of $Ni(CO_4)$ used. Previous attempts to prepare a nickel carbonyl anion by treating $Ni(CO)_4$ with either aqueous alkali or a methanolic solution of $NaOCH_3$ had failed.[11]

That the anion $[Ni_3(CO)_8]^{-2}$ can act as a source of carbon monoxide in the carboxylation of diphenylacetylene was demonstrated: Nickel carbonyl was treated with methanol saturated with NaOH and the dark red reaction product containing $[Ni_3(CO)_8]^{-2}$ ion diluted with methanol and extracted with petroleum ether to remove any unreacted $Ni(CO)_4$. Diphenylacetylene was added and the mixture shaken for several days. At the end of this period no $[Ni_3(CO)_8]^{-2}$ ion could be detected in the reaction mixture. Acidification of the reaction mixture yielded 58% 1,2,3,4-tetraphenylbutadiene and 30% α-phenyl-*trans*-cinnamic acid based on the amount of diphenylacetylene used.

The formation of tetraphenylbutadiene may be due to dimerization of diphenylacetylene within a nickel carbonyl diphenylacetylene complex. In the case of iron such complexes as $(CO)_8Fe_3(C_6H_5C_2C_6H_5)_2$ and $(CO)_6Fe_2(C_6H_5C_2C_6H_5)_2$ have been isolated from the interaction of $Fe_3(CO)_{12}$ with diphenylacetylene.[12,13] In the presence of alkali these iron complexes decompose with formation of tetraphenylbutadiene.[13] Similarly, the intermediates formed from $[Ni_3(CO)_8]^{-2}$ and diphenylacetylene may decompose readily in the strongly alkaline reaction mixture to give tetraphenylbutadiene.

Experimental[14]

Formation of Tetraphenylbutadiene and α-Phenylcinnamic Acid by Treating Diphenylacetylene with $Ni(CO)_4$ and a Saturated Solution of NaOH in Methanol.—To a solution of 18 g. (0.45 mole) of NaOH in 75 ml. of methanol contained in a flask was added 5 g. (0.028 mole) of diphenylacetylene. Very little, if any, diphenylacetylene dissolved in the methanolic NaOH solution. To this mixture was added under helium about 5 ml. (0.04 mole) of $Ni(CO)_4$. The flask was stoppered and attached to a mechanical shaker. Immediately after the shaker was started, the solution turned light brown and after a few hours dark red. After the flask had been shaken for a total of 80 hours, 250 ml. of water was added and the reaction mixture was acidified. Treatment of the acid-insoluble material with aqueous $NaHCO_3$ gave an acidic (1.55 g.) and a neutral (3.35 g.) fraction. The neutral portion, after crystallization from petroleum ether (90–100°) and finally methanol, yielded white crystals which melted at 183.0–183.5° (lit.[15] m.p. 182.5–183.0°). The melting point was not depressed by admixture of an authentic sample of 1,2,3,4-tetraphenylbutadiene prepared according to Smith and Hoehn.[15]

Anal. Calcd. for $C_{28}H_{22}$: C, 93.81; H, 6.19; mol. wt., 358. Found: C, 94.05; H, 6.08; mol. wt. (ebull. in benzene), 349.

The acidic portion, after crystallization from methanol-water, yielded white needles of α-phenyl-*trans*-cinnamic acid which melted at 173.5–174.0° (lit.[16] 174°). The melting point was not depressed by admixture of an authentic sample of *trans*-α-phenylcinnamic acid prepared according to Fieser.[17]

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.40; mol. wt., 224. Found: C, 80.65; H, 5.51; mol. wt. (ebull. in benzene), 257.

Preparation of a Solution Containing $[Ni_3(CO)_8]^{-2}$ Ion.—Five ml. (0.04 mole) of $Ni(CO)_4$ was added to 75 ml. of a saturated solution of NaOH in methanol and the mixture shaken under helium for a total of 80 hours. To the dark red reaction mixture was added 250 ml. of oxygen-free water, the mixture shaken for one hour and then allowed to stand overnight to allow any unreacted $Ni(CO)_4$ or solid material to settle out. An aliquot of the clear, dark red aqueous solution was analyzed for Ni. Another aliquot was neutralized with acetic acid, decomposed with a solution of I_2 in aqueous KI,[18] and the evolved gas analyzed for CO. On the basis of these analytical data the aqueous solution contained Ni and CO in a ratio of 3.00/7.77. This indicated the presence of an anion with a Ni/CO ratio of 3/8. To determine whether this anion could be precipitated as a $[Ni(o\text{-Phen})_3]^{++}$ salt, a third aliquot was treated with an aqueous solution of $Ni(o\text{-phen})_3Cl_2$ and neutralized with acetic acid. The voluminous, dark red brown precipitate, presumably $[Ni(o\text{-phen})_3][Ni_3(CO)_8]$, was filtered, washed with

---

(4) W. Reppe and H. Vetter, *Ann.*, **582**, 133 (1952).

(5) H. W. Sternberg, R. A. Friedel, R. Markby and I. Wender, THIS JOURNAL, **78**, 3621 (1956).

(6) R. Clarkson, E. R. H. Jones, P. C. Wailes and M. C. Whiting, *ibid.*, **78**, 6206 (1956).

(7) A. A. Hock and O. S. Mills, *Proc. Chem. Soc.*, 233 (1958).

(8) The use of a saturated solution of NaOH in methanol was suggested by E. O. Brimm and M. A. Lynch, Jr.; presented at the 121st Meeting of the A.C.S. in Buffalo, N. Y., March, 1952.

(9) A. A. Hock, O. S. Mills and G. Robinson, "The Structures of Some Organo-Transition-metal Complexes," presented at the International Conference on Co-ordination Chemistry, London, April 6–11, 1959.

(10) The possibility of a structural similarity between $[Fe(CO)_{11}]^{-2}$ and $(C_5H_5)_3Ni_3(CO)_2$ was pointed out by O. S. Mills, A. A. Hock and G. Robinson in a paper, "The Structures of Some Polynuclear Organometallic Complexes," presented at the 17th International Congress of Pure and Applied Chemistry, Munich, Aug. 30–Sept. 6, 1959.

(11) W. Hieber and H. Kaufmann, *Z. anorg. u. allgem. Chem.*, **204**, 174 (1932).

(12) W. Huebel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959).

(13) G. N. Schrauzer, THIS JOURNAL, **81**, 5307 (1959).

(14) Microanalyses and molecular weight determinations by Huffman, Microanalytical Laboratories, Wheatridge, Colo.

(15) L. I. Smith and H. H. Hoehn, THIS JOURNAL, **63**, 1184 (1941).

(16) H. E. Zimmerman and L. Ahramjian, *ibid.*, **81**, 2086 (1959).

(17) L. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 182.

(18) H. W. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**, 174 (1952).

oxygen-free water and decomposed with a solution of I_2 in pyridine. The amount of evolved CO corresponded to a Ni/CO ratio of 3.00/7.95. The amount of nickel present in the aqueous solution, presumably as $[Ni_3(CO)_8]^{-2}$, corresponded to 57% of the nickel in the $Ni(CO)_4$ used as a starting material.

Formation of Tetraphenylbutadiene and α-Phenylcinnamic acid, by Treating Diphenylacetylene with a Solution Containing $[Ni_3(CO)_8]^{-2}$.—Five ml. (0.04 mole) of $Ni(CO)_4$ was added to 75 ml. of a saturated solution of NaOH in methanol and the mixture shaken under helium for a total of 80 hours. The dark red mixture was diluted with 100 ml. of methanol and the solution extracted with petroleum ether to remove any unreacted $Ni(CO)_4$. Five grams (0.028 mole) of diphenylacetylene was added to the solution and the mixture shaken for a total of 80 hours. The absence of $[Ni_3(CO)_8]^{-2}$ in the reaction mixture was demonstrated by adding oxygen-free water to a sample of the reaction mixture. The addition of water caused separation into a dark brown precipitate, probably tetraphenylbutadiene and polymeric nickel carbonyls, and a colorless aqueous solution. No precipitate formed on addition of $Ni(o\text{-phen}_3)_3Cl_2$ to this solution. The reaction mixture was acidified and the precipitate separated into a neutral and acidic fraction by treatment with aqueous $NaHCO_3$.

The neutral fraction, 1,2,3,4-tetraphenylbutadiene, weighed 2.9 g., corresponding to a yield of 57.8%; the acidic fraction, α-phenyl-*trans*-cinnamic acid, weighed 1.9 g., corresponding to a yield of 30.3%.

Acknowledgment.—This work was carried out in coöperation with International Nickel Company.

[COMMUNICATION NO. 2063 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK CO.]

Polyesteramides

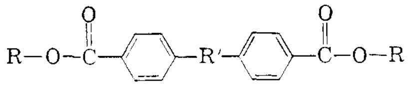
BY T. M. LAAKSO AND D. D. REYNOLDS

RECEIVED OCTOBER 31, 1959

Polyesteramides have been prepared by the condensation of glycols with bis-esters having the general structure, ROOCR'NHCOR'COOR and ROOCR'NHCOR''CONHR'COOR, where R is alkyl, R' is phenylene and R'' is alkylenes The amide links are stable under condensation conditions when R' is aromatic and when R' is aromatic with R'' aliphatic. Physical properties are tabulated.

Introduction

After Whinfield and Dickson[1] demonstrated that aryl-*p*-dicarboxylic acids react with glycols to give crystalline polymers having high melting points, many *p*-substituted dicarboxylic acids were prepared and converted to polyesters. Polyesters have been prepared from compounds having the general formula shown, where R' has been varied widely.[2]



Since the amide group is a contributing factor to the desirable properties of polyamides, it was of interest to study polyesters composed of aromatic nuclei linked through the *p*-positions by chains possessing amide linkages. Numerous polyesteramides have been described in the literature,[3] but, for the most part, they are aliphatic. They have been prepared by the reaction of a dibasic acid or its ester with amino alcohols, or with a mixture of a diamine and a glycol. In some cases amino acids were used. When free amines are used in such condensations, it is difficult to avoid color formation. We have prevented this by using esters of the general structure ROOCR'NHCOR'COOR and ROOCR'NHCOR''CONHR'COOR, which contain a preformed amide link.

The stability of the amide linkage, and as a direct result the color of the final polymer, is dependent upon the nature of R' and R''. When R' is aromatic, as in the case of 4,4'-dicarbethoxybenzanilide, the linkage is very stable and light-colored polymers are obtained. When R' is aromatic with R'' aliphatic, *e.g.*, bis-[N-*p*-carbethoxyphenyl]-sebacamide, the amide linkage is likewise stable. In all cases where R' was aliphatic with R'' aromatic, there was decomposition accompanied by the liberation of free amine which produced colored products.

This paper is concerned with polyesteramides prepared by the condensation of glycols with: (i) 4,4'-dicarbethoxybenzanilide, (ii) 4,4'-dicarbethoxybenzanilide plus 4,4'-dicarbutoxydiphenyl sulfone, (iii) bis-[N-*p*-carbethoxyphenyl]-sebacamide, (iv) bis-[N-*p*-carbethoxyphenyl]-azelamide, and (v) bis-N-*p*-carbethoxyphenyl]-suberamide.

Experimental

Diethyl terephthalate (m.p. 42–44°, lit. 43–44°) was prepared by the esterification of terephthalic acid according to the procedure of Koelsch.[4]

Ethyl hydrogen terephthalate (m.p. 170–171°, lit. 168–170°) was prepared according to the procedure of Cohen and de Pennington.[5]

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 62.0; H, 5.1. Found: C, 62.1; H, 5.1.

***p*-Carbethoxybenzoyl Chloride.**—Ethyl hydrogen terephthalate (5820 g., 30 moles) and 6720 g. (56.46 moles) of thionyl chloride were mixed together in a 12-liter flask equipped with a reflux condenser. The reaction mixture was heated gently on a steam-bath until a homogeneous solution was obtained. The excess thionyl chloride was distilled and the residue fractionated through an 18-inch column filled with glass helices; yield 95%, b.p. 134° (6 mm.).

---

[1] J. R. Whinfield and J. T. Dickson, British Patent 578,079 (1946).

[2] (a) J. T. Dickson, British Patent 579,462 (1946); (b) R. H. Griffith and J. H. G. Plant, British Patent 643,388 (1950); (c) A. R. Lowe, British Patent 604,075 (1948); (d) J. G. Cook, J. T. Dickson, H. P. W. Huggill and A. R. Lowe, British Patent 604,074 (1948); (e) E. R. Wallsgrove and F. Ruder, British Patent 636,429 (1950); (f) J. R. Whinfield and J. T. Dickson, U. S. Patent 2,465,319 (1949); (g) L. J. Tyler, U. S. Patent 2,601,646 (1952).

[3] W. H. Carothers, U. S. Patent 2,071,250 (1937); E. L. Martin, U. S. Patent 2,359,867 (1944); E. L. Kropa, U. S. Patents 2,440,516 (1948), 2,463,977 (1949); E. A. Lasher, U. S. Patent 2,475,034 (1949). British Patents: R. E. Christ, 561,108 (1944); Wingfoot Corporation, 571,017 (1945); J. Drewitt and G. Harding, 621,977 (1949); Am. Viscose Corporation, 671,141 (1952).

[4] C. F. Koelsch, "Organic Syntheses," H. Adkins, editor, Vol. 26, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 95.

[5] J. B. Cohen and H. S. de Pennington, *J. Chem. Soc.*, **113**, 57 (1918).