Szwarc suggested essentially the same experiment, in addition to clarifying the Bamford mechanism.

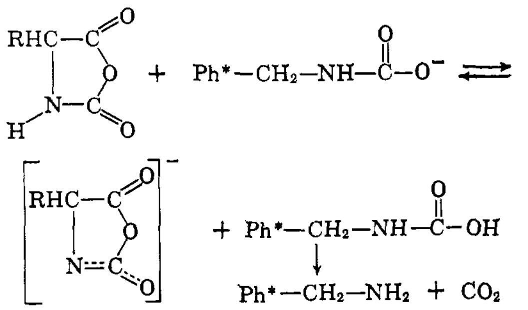
Radioactive (^{14}C) benzylamine (3 g., 0.5 mcurie, supplied by Nuclear Research Chemicals, Inc.) was converted to the sodium N-benzylcarbamate using carbon dioxide and a sodium methoxide–methanol solution as described previously.[4] The carbamate was dissolved in anhydrous methanol and standardized by titrating the carbon dioxide evolved upon addition of sulfuric acid.

The preparation and purification of γ-benzyl-L-glutamate NCA and method of polymerization, measurement of kinetics, determination of molecular weight, and radioactive counting have also been discussed previously.[4]

Polymerizations of γ-benzyl-L-glutamate NCA with both radioactive and nonradioactive carbamate in tetrahydrafuran solutions showed the same results. The rates were high, giving an average k_p at 25° of about 3.0 l./mole sec. This value is close to that observed with sodium methoxide initiation. Of prime importance, however, is the fact that only 2.5–3.0% of the radioactivity was found in the isolated polymer. Thus, we conclude that the mixed anhydride mechanism cannot be valid. The Bamford–Szwarc mechanism has not been positively proven but it is now clearly the best possibility.

Additional support for this interpretation comes from the observation of a large induction period and a degree of polymerization significantly higher than the anhydride/initiator ratio (*A*/*I*). If nucleophilic carbamate ion were the propagating species no induction period would be observed because the initiation step would be by-passed. Also, since each molecule of carbamate would produce one growing chain, the *A*/*I* would be nearly equal to the degree of polymerization.

The carbamate ion can remove weakly acidic protons in spite of its weak basicity because subsequent decarboxylation of the resulting carbamic acid continuously shifts the following equilibrium to the right:



We can explain the appearance of the small amount of radioactivity in the polymer from initiation by radioactive benzylamine, produced as above. Such a polymerization would follow slow kinetics, leading to the incorporation of only a small amount of activity in the polymer.

A very good analogy can be drawn between this activated monomer propagation mechanism and that of the anionic polymerization of caprolactam as presented by Wichterle.[6]

Work in progress on N-substituted NCA's indicates that a different polymerization mechanism is operative. A complete report of our findings, in which we will include our investigations on radioactive primary, secondary, and tertiary amine initiators, will appear shortly.

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Electrochemical Syntheses. V. The Synthesis of Methyl Esters of α,β-Unsaturated Carboxylic Acids from Olefins and Carbon Monoxide

Sir:

Although various reactions of olefins with carbon monoxide have been reported,[1-3] the synthesis of α,β-unsaturated carboxylic acids or esters from olefins and carbon monoxide has been unsuccessful as yet.

We wish to report here the first direct synthesis of methyl esters of α,β-unsaturated carboxylic acids from olefins and carbon monoxide by a unique electrochemical method in the presence of a platinum–carbonyl complex

$$C_6H_5CR{=}CH_2 + CO + CH_3O^- \xrightarrow[{[Pt_x(CO)_y]^n}]{\text{anode}} C_6H_5CR{=}CHCOOCH_3$$

$$R = H,\ CH_3,\ C_6H_5$$

The electrolysis was carried out by using a platinum plate (2 × 3 cm.^{2}) as the anode in a cylindrical glass cell placed in an autoclave (500 cc.) under a pressure of 70 kg./cm.^{2} of carbon monoxide in the following way. First, by using a platinum plate (2 × 3 cm.^{2}) as the cathode, the platinum carbonyl complex[4] was produced in methanol solution containing sodium methoxide (metallic sodium, 0.5 g., in 90 g. of methanol) by electrolysis for 5–10 hr. Then, by using a copper plate (2 × 3 cm.^{2}) as the cathode, the electrolysis was carried out in the presence of olefins and carbon monoxide for 16 hr. The current was controlled at approximately 1.0 amp. and the temperature was kept at −10 to −15°.

The electrolysis of styrene (15.6 g., 0.15 mole) in the presence of platinum–carbonyl complex (1.5 g. of Pt) under these conditions gave methyl *trans*-cinnamate (I), m.p. 35–36° (5.0 g., 21%), which was contaminated with methyl β-methoxy-β-phenylpropionate (II, 3.9 g., 13%), methyl β-phenylpropionate (III, 0.4 g., 1%), and styrene glycol dimethyl ether (IV, 5.7 g., 23%).

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(4) When the electrolysis of methanol containing sodium methoxide (metallic sodium, 0.5 g., in 90 g. of methanol) was carried out by using two platinum plate electrodes (2 × 3 cm.^{2}) in the presence of carbon monoxide (70 kg./cm.^{2}) for 5–10 hr (1.0 amp., 16–45 v.), the platinum plate used as the cathode was easily dissolved into the solution to give a platinum–carbonyl complex, which was isolated by the removal of methanol from the electrolyzed solution under dry nitrogen atmosphere. This carbonyl complex is very air sensitive and greenish blue.

Table I. Electrolytic Carbomethoxylation of Styrene[a]

Pt–carbonyl complex, g. (wt. of Pt)	Total yield of esters, %[b]	Dimethyl ether, % IV	Ester, % I	II	III
0.9	23	32	14	8	1
1.5	35	23	21	13	1
2.8	43	10	17	16	10

[a] Fifteen grams (0.15 mole) of styrene was used. [b] Based on styrene used.

When α-methylstyrene (17.7 g., 0.15 mole) was used in the presence of platinum–carbonyl complex (2.9 g.), methyl *trans*-β-methylcinnamate (V) was obtained as the main product, in 18% yield (4.5 g.), along with methyl 3-phenyl-3-butenoate (VI, 2.7 g., 11%), methyl β-methyl-β-phenylpropionate (VII, 0.6 g., 2%), and α-methylstyrene glycol dimethyl ether (VIII, 2.5 g., 9.3%). Moreover, in the case of 1,1-diphenylethylene (18.0 g., 0.10 mole) in the presence of platinum–carbonyl complex (1.0 g.), methyl β-phenylcinnamate (IX) was obtained as the main product (7.6 g., 30%), along with 1,1-diphenylethylene glycol dimethyl ether (X, 5.0 g., 25%).

Infrared spectroscopic, gas chromatographic, and elemental analyses, and, in part, n.m.r. data and also mixture melting points (as free acids, with authentic specimens), were used to identify these compounds.

In these electrochemical reactions, it may be assumed that the formation of unsaturated esters proceeds by the addition[5] of the Pt–$COOCH_3$ group in the platinum–carbonyl complex to the olefinic double bond *via* anodic process. The above consideration was supported by the following experimental results: (a) Without the platinum–carbonyl complex, the electrolysis of styrene gave dimethyl ether (IV[6]) as the sole product (23%). (b) In the absence of electric current, the reaction of these olefins with the platinum–carbonyl complex gave no products for 16 hr. at 0 to 150°. (c) The electrolysis with both the catholyte and anolyte containing the platinum–carbonyl complex, styrene, and sodium methoxide in separated compartments under nitrogen atmosphere resulted in the formation of the esters I and II in the anode compartment while no product was detected in the cathode compartment. (d) With the increase in the concentration of the platinum–carbonyl complex, the yield of these esters increased; on the contrary, that of dimethyl ether (IV) decreased, as shown in Table I. (e) These esters were obtained by the catalytic amount of the platinum–carbonyl complex, as shown in Table I. (f) Interestingly, the infrared spectrum of the platinum–carbonyl complex isolated from the electrolyzed solution[4] has characteristic absorption bands at about 1642, 1280, and 1180 cm.$^{-1}$, besides absorption bands at about 2015 (v.s.) and 2145 cm.$^{-1}$ (w.) (the terminal carbonyl group) and at about 1860 (m.s.) and 1840 cm.$^{-1}$ (m.s.) (the bridged carbonyl group). The former strong absorption bands may be due to the ester group attached to platinum, as has been reported in other metal carbonyl compounds.[7]

The structure of this carbonyl complex and the mechanism of these noble electrochemical syntheses are under investigation, and detailed description of this and further work will be reported shortly.

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[5] The addition of a metal–carbon σ-bond to an olefinic double bond has recently been reported by several workers; for example, (a) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 3116 (1963); (b) R. F. Heck, *ibid.*, **85**, 3383 (1963); (c) J. B. Wilford, P. M. Treichel and F. G. A. Stone, *J. Organometal. Chem.* (Amsterdam), **2**, 119 (1964); J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 93 (1965).

[6] Dimethyl ether derivatives would be produced by the reaction of the methoxy radical with olefins, as has been reported before: T. Inoue and S. Tsutsumi, *Bull. Chem. Soc. Japan*, **38**, 661 (1965).

[7] T. Kruck and M. Noack, *Ber.*, **97**, 1693 (1964).

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Oligonucleotide Synthesis on a Polymer Support[1,2]

Sir:

With the objective of simplifying procedures for the stepwise synthesis of complex substances such as polynucleotides and polypeptides, we undertook a study of chemical reactions on insoluble supports. In a previous paper it was shown that functional groups on styrene–divinylbenzene popcorn polymer are available for many conventional chemical reactions and that a dipeptide may be prepared on and removed from this polymer.[3] The present communication reports experiments illustrating the use of a polymer support in the synthesis of oligonucleotides.

The general scheme is typified by the preparation of deoxycytidylyl-(3′→5′)-thymidine (V) outlined in Chart I. All reactions on the polymer support (a–f) were carried out at room temperature. In the initial step (a) 5 g. of polymer acid chloride, Ⓟ$_c$–COCl,[3b,4] was stirred with 2.8 g. (6.0 mmoles) of 5′-O-trityldeoxycytidine[5] in 50 ml. of dry pyridine for 2 days. Methanol was then added to convert residual acid chloride to ester, and the solid polymer (6.3 g.) was separated by filtration (1.2 g. of trityldeoxycytidine was recovered from the solvent). Phosphorylation (b) was effected by stirring 12 g. of I (from two experiments) with pyridinium β-cyanoethyl phosphate[6] (obtained from 5.1 g., 15 mmoles, of the barium salt trihydrate) and 6.2 g. of dicyclohexylcarbodiimide for 7 days. After filtration, treatment with 50% aqueous pyridine (c), and successive washing with methanol, ethanol, 1:1 ethanol–cyclohexane, and ether, a portion of the polymer (9.5 g.) was stirred with 2.5 g. (11 mmoles) of mesitylenesulfonyl chloride[7] (d) in 100 ml. of pyridine for 1 day. The polymer was then removed and mixed with 2.1 g. (9 mmoles) of dry thymidine (e)

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[1] Part II in a series on Nucleotide Chemistry. Paper I: R. L. Letsinger, J. Fontaine, V. Mahadevan, D. A. Schexnayder, and R. E. Leone, *J. Org. Chem.*, **29**, 2615 (1964).

[2] This research was supported by the Division of General Medical Sciences, National Institutes of Health, Grant 10265.

[3] (a) R. L. Letsinger and M. J. Kornet, *J. Am. Chem. Soc.*, **85**, 3045 (1963); (b) R. L. Letsinger, M. J. Kornet, V. Mahadevan, and D. M. Jerina, *ibid.*, **86**, 5163 (1964).

[4] The polymer had 1.0 mmole of acid chloride groups/g.

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[7] H. G. Khorana, J. P. Vizsolyi, and R. K. Ralph, *ibid.*; **84**, 414 (1962); T. M. Jacob and H. G. Khorana, *ibid.*, **86**, 1630 (1964).