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THE REACTIONS OF ω-IODOALKYNES WITH NICKEL TETRACARBONYL–POTASSIUM t-BUTOXIDE

J. K. CRANDALL* and W. J. MICHAELY
Department of Chemistry, Indiana University, Bloomington, Indiana 47401 (U.S.A.)

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SUMMARY

The reactions of ω-iodoalkynes n-$C_4H_9C{\equiv}C(CH_2)_nI$ ($n=3,4,5$) with $Ni(CO)_4$–KO-t-Bu have been studied. The $n=3$ and $n=5$ compounds yield the esters n-$C_4H_9C{\equiv}C(CH_2)_nCO_2$-t-Bu as the major products whereas the $n=4$ system yields a mixture of the cyclic esters t-butyl-2-(1-cyclopentenyl)hexanoate and t-butyl-2-cyclopentylidenehexanoate in good yield.

INTRODUCTION

Cyclization reactions involving organometallic species of the type $RC{\equiv}C(CH_2)_nM$ have recently been examined in several laboratories[1,2,3,4]. We have been particularly concerned with comparing different organometallic systems as to the range and facility of intramolecular addition reactions as well as the orientation and stereochemistry of such processes. Nickel carbonyl systems were especially attractive for study since reaction occurs with alkyl halides under relatively mild conditions[5]. Furthermore, alkyne groups show a propensity for coordination with nickel carbonyl compounds, a characteristic which might be expected to facilitate interaction between this function and remote carbon–nickel bonds. The reaction selected for study was that first used by Corey and Hegedus[6] for the conversion of reactive organic halides into their homologous t-butyl esters by treatment with $Ni(CO)_4$–KO-t-Bu.

RESULTS

The reactions of the ω-iodoalkynes I with the complex[7] formed from $Ni(CO)_4$ and KO-t-Bu were performed using a 1/3/6 ratio of I/KO-t-Bu/$Ni(CO)_4$. The $Ni(CO)_4$ was added to freshly prepared KO-t-Bu in t-BuOH and the mixture was stirred at room temperature until a dark brown color developed (~15 min). The alkyl iodide was then added and the reaction mixture was heated to reflux for several hours in a stream of argon to remove excess $Ni(CO)_4$ prior to work-up (*caution*, see Experimental). Dehydrohalogenation was the major reaction if I was added prior to development of the brown color.

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The reaction of 1-iodo-5-decyne (I, $n=4$) gave a 77% isolated yield of a mixture of three t-butyl esters in a ratio of 22/39/39 in addition to several hydrocarbon products. The esters were identified as t-butyl 2-(1-cyclopentenyl)hexanoate (II), t-butyl 2-cyclopentylidenehexanoate (III) and t-butyl-6-undecynoate (IV, $n=4$), respectively, on the basis of their spectral characteristics which are detailed in the Experimental section. Treatment of either II or III with KO-t-Bu leads to an equilibrium mixture of the two compounds in a 5/2 ratio. This observation effectively rules out the isomeric cyclic structure V and its double-bond isomer, since a balanced equilibrium is not compatible with this pair of isomers[8]. The percentage of cyclic products is high (95%) when the reaction is allowed to proceed at room temperature. Cyclization appears to be completed rapidly since little change is caused by subsequent heating longer than 15 min. prior to work-up. Heating the reaction mixture during or immediately after the addition of I resulted in a larger percentage of straight-chain ester. Interestingly when the brown complex is heated and then cooled to room temperature prior to the addition of I a smaller amount of cyclic products was formed. This indicates that the initial complex is transformed to an inactive, or less effective cyclization reagent upon heating.

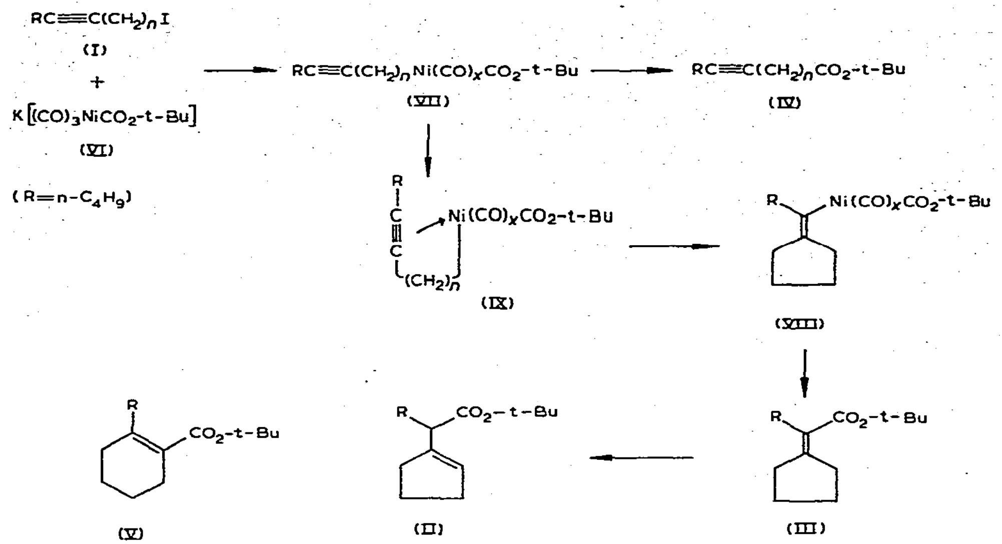
The reaction of 1-iodo-4-nonyne (I, $n=3$) gave a number of products but the straight-chain ester IV ($n=3$) was the predominant one even under optimum cyclization conditions. A similar situation obtains with 11-iodo-5-undecyne (I, $n=5$) which gave t-butyl-7-dodecynoate (IV, $n=5$) as the major product.

DISCUSSION

The observation of cyclic esters in the reaction of I with $Ni(CO)_4$–KO-t-Bu suggests that an intermediate organometallic species is formed which is capable of intramolecular addition to the remote triple bond. This is most easily rationalized in terms of displacement of iodide from I by a nucleophilic species such as VI leading to an acyclic organonickel VII. Competitive with a reductive-elimination[9] mode of decomposition of VII resulting in the straight-chain ester, is a rearrangement process which produces VIII, the organometallic precursor of the cyclic esters. The π-complex IX is a conceptually attractive intermediate in the VII to VIII transformation. (This π-complex can, of course, also lead to IV). Unfortunately, the competition between the irreversible reductive-elimination step leading to the acyclic ester and cyclization to VIII is favorable towards the latter only in the $n=4$ case, although cyclic esters are probably among the unidentified minor products from the other two starting materials. This situation severely limits the synthetic potential of the cyclization reaction. The use of activated acetylenes or of modified metal–ligand systems may, however, aid cyclization. The regiospecific cyclization to yield III instead of the isomeric possibility V is a common feature of such intramolecular additions, which is presumably dictated by conformational restraints imposed on the system by the linking hydrocarbon chain.

EXPERIMENTAL

Nuclear magnetic resonance spectra were recorded with Varian A-60, HR-100 and HA-220 spectrometers on samples in carbon tetrachloride solutions. Mass



spectra were obtained with AEI-MS9 and CH-7 Varian-MAT spectrometers. Analytical gas chromatography (GLPC) was performed on a Varian Aerograph Model 1200 (hydrogen flame detector) chromatograph equipped with a disk integrator utilizing the following columns: 10 ft × 1/8 in 15% or 30% Carbowax 20M on 60–80 Chromosorb W. Preparative GLPC utilized a Varian A-90P instrument, with 10 ft × 3/8 in 20% Carbowax 20M on 60–80 Chromosorb W, and 20 ft × 3/8 in 30% Carbowax 20M on 60–80 Chromosorb W as columns. Nickel Carbonyl (Matheson Co.) was used without further purification. Preparations of the alkynyl iodides will be described in a subsequent publication.

Caution: Nickel tetracarbonyl is extremely toxic! This coupled with its high volatility make it imperative that all operations utilizing $Ni(CO)_4$ be carried out in a very efficient hood and, insofar as possible, in systems closed to the atmosphere. Protective gloves and clothing are also advisable to prevent direct contact with the skin from vapors or spills. Exiting gases from reaction systems should be washed effectively with conc. HNO_3 to destroy any excess $Ni(CO)_4$[10].

Reactions of l-iodo-5-decyne with $Ni(CO)_4$–KO-t-Bu

A dried three-neck flask, equipped with a condenser, a pressure equilizing addition funnel and a rubber septum, was flushed with argon and 125 ml of anhydrous t-butanol (distilled from sodium) was added. To the refluxing t-butanol was added 1.2 g of potassium. After the potassium had dissolved, the solution was cooled to room temperature and 3 ml of $Ni(CO)_4$ was condensed into the calibrated addition funnel and added. Upon stirring for 15 minutes, the solution turned dark brown. The solution was brought to reflux and 2.63 g of I ($n=4$) was added by syringe. The solution was refluxed for 6 h, while an argon stream was passed through the system to remove excess $Ni(CO)_4$. The effluent gas was bubbled through two conc. HNO_3 wash bottles to destroy excess $Ni(CO)_4$. The solution was diluted with pentane and filtered, (*caution*: the black precipitate is pyrophoric), and the filtrate was washed with water and dried. GLPC of the crude mixture showed 18% of two C_{10} hydrocarbons in a 7/1 ratio (tentatively identified by GLPC retention times as 1-decen-5-yne and 5-decyne. The solvent was removed and vacuum distillation of the residue gave 1.85 g (77%), b.p. 107–109° (1 mm), of a 22/39/39 mixture of three esters which was separated by GLPC. The first component was t-butyl 2-(1-cyclopentenyl)-hexanoate (II): IR 3.42, 5.78, 7.35, 8.0 and 8.7μ; NMR (220) δ 5.43 (m, 1), 2.92 (t, 1, J=7 Hz), 2.28 (q, 4, J=7 Hz), 1.93–1.60 (m, 4), 1.60–1.10 (m, 4), 1.40 (s, 9), 0.90 (t, 3, J=7 Hz); mass spectrum (70 eV) *m/e* (rel. intensity) 238 (0.1), 182(32), 137(24), 127(24), 126(28), 95(34), 81(64), 57(100). (Found C, 75.68; H, 11.10. $C_{15}H_{26}O_2$ calcd.: C, 75.58; H, 10.99%.)

The second component was t-butyl 2-cyclopentylidenehexanoate (III): IR 3.41, 5.88, 6.12, 7.35, 7.84, 8.67 and 9.06 μ; NMR δ 2.1 (m, 6), 1.8–1.1 (m, 8), 1.40 (s, 9), 0.90 (t, 3, J=7 Hz); UV λ_{max} 231 nm (ε=23300); mass spectrum (70eV) *m/e* (rel. intensity) 238(0.1), 182(12), 139(72), 81(50), 80(58), 57(100). (Found: *m/e*, 238.1928. $C_{15}H_{26}O_2$ calcd.: *m/e*, 238.1933.)

The third component was t-butyl-6-undecynoate (IV, n=4): IR 3.44, 5.79, 7.35, and 8.74 μ; NMR δ 2.65 (t, 2, J=7 Hz), 2.20 (t, 4, J=7 Hz), 1.85–1.10 (m, 8), 1.43 (s, 9), 0.90 (t, 3, J=7 Hz). Mass spectrum (70 eV) *m/e* (rel. intensity) 238 (0.1), 182(100), 165(29), 139(67), 121(29), 94(24), 92(27), 57(50). (Found: C, 75.63; H, 10.85. $C_{15}H_{26}O_2$ calcd.: C, 75.58; H, 10.99%.)

Reaction of 1-*iodo*-4-*nonyne with* $Ni(CO)_4$–*KO-t-Bu*

The reaction was identical to that described above except that the solution was refluxed for 1 h before 2.49 g of I(n=3) was added. Work-up gave a crude mixture which GLPC showed to be 61% of a major product and 39% of eleven unidentified compounds. Distillation gave 1.19 g (53%) of crude t-butyl-5-decynoate (IV, n=3): b.p. 112–114° (3 mm), IR 3.43, 5.79, 7.35, 8.00 and 8.71 μ; NMR (220) δ 2.25 (t, 2, J=7.5 Hz), 2.12 (m, 4), 1.70 (quint., 2, J=7.5 Hz). 1.60–1.20 (m, 4), 1.43 (s, 9), 0.91 (t, 3, J=7 Hz). (Found: C, 74.73; H, 10.55. $C_{14}H_{24}O_2$ calcd.: C, 74.95, H, 10.78%.)

Reaction of 11-*iodo*-5-*undecyne with* $Ni(CO)_4$–*KO-t-Bu*

Using the same procedure with 2.35 g of I(n=5) gave a crude mixture whose GLPC analysis showed one major product (75%) and eight minor products (25%). Distillation gave 1.40 g (65%) of crude t-butyl 7-dodecynoate (IV, n=5): b.p. 108–111° (0.5 mm), IR 3.42, 5.78, 7.35, 8.00 and 8.73 μ; NMR (220) δ 2.1 (m, 6), 1.7–1.3 (m, 10), 1.49 (s, 9), 0.90 (t, 3, J=7 Hz). (Found: C, 76.09; H, 11.11. $C_{16}H_{28}O_2$ calcd.: C, 76.14; H, 11.18%.)

Reaction of III with KO-t-Bu

To 10 mg of potassium dissolved in 3 ml t-butanol was added 35 mg of III. The solution was refluxed under an argon atmosphere for 12 h. After cooling to room temperature, the solution was diluted with pentane and washed three times with water. After drying and concentrating the mixture, GLPC analysis showed a 64/36 mixture of III/II.

Reaction of II with KO-t-Bu

To 22 mg of potassium t-butoxide in 4 ml of t-butanol was added 42 mg of II. The solution was refluxed under argon for 12 h. After normal workup GLPC analysis showed it to be a 58/42 mixture of III/II.

Small-scale reactions of 1-iodo-5-decyne

Several reactions were run on approximately one-quarter the scale of the preparative reactions. Reactions were run in a 4-necked, round-bottom flask equipped with a reflux condenser, a pressure-equilizing addition funnel, a thermometer and a septum cap for injecting the organic iodides. The condenser and the pressure equilizing addition funnel were both connected to an argon line and the effluent was passed through two conc. HNO_3 wash bottles. The molar ratios of $Ni(CO)_4$, KO-t-Bu, and I were 6/3/1; only the timing of the addition of the reagents and the temperature were varied. In a reaction in which the $Ni(CO)_4$–KO-t-Bu mixture was stirred for 0.25 h before and 0.25 h after the addition of the alkyl halide and then heated to reflux for 6 h to remove excess $Ni(CO)_4$, the crude product showed a ratio of 39/55/5 of II/III/IV. A similar reaction in which CO was bubbled through the reaction gave essentially identical results. Extending the reaction period to 6 h at room temperature after the alkyl halide addition gave a 41/56/3 ratio of the same products. If the reaction was heated to reflux immediately after the alkyl halide addition the ratio was 22/39/39. Heating the reagent mixture for 1.25 h prior to alkyl halide addition at the reflux temperature of 84° gave a 31/36/29 ratio. In a similar reaction except that the reaction was cooled prior to alkyl halide addition and allowed to react for 0.25 h prior to reheating the ratio was 29/33/38 with unreacted starting material remaining.

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