= cyclopentanecarbonyl), 72917-14-7; **30** (R = Me), 72917-15-8; **31** (R = cyclopentanecarbonyl), 72917-16-9; **31** (R = cyclopentylmethyl), 72917-17-0; **31** (R = cyclopentylmethyl) HCl, 72982-83-3; **32** (R = benzyl), 72917-18-1; **33** (R = benzyl), 72917-19-2; **34** (R = benzyl), 72917-20-5; **35** (R = benzyl), 72917-21-6; **35** (R = benzyl) HCl, 72982-84-4; **36** (R = benzyl), 72982-85-5; **36** (R = benzyl) HCl, 73035-71-9; **37**, 72917-22-7; **38** (R = H), 72917-23-8; **38** (R = Me), 72917-24-9; spiro[5*H*-5,9b-*o*-benzenobenz[*e*]isoindole-3,1′-cyclohexane], 72917-25-0; spiro[cyclohexane-1,1′(3*H*)-2*H*-dibenzo[3,4:7,8]cycloocta[1,2-*c*]pyrrole], 72917-26-1; cyclopentanecarbonyl chloride, 4524-93-0; 4,6-dihydro-3*H*-6,10b-*o*-benzenobenz[*h*]isoquinoline, 72917-27-2; 2-methyl-2,3,4,9-tetrahydro-4a,9-methano-4a*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyridine, 72917-28-3; 2-(cyclopentanecarbonyl)-2,3,4,9-tetrahydro-4a*H*-4a,9-methanodibenzo[3,4:6,7]cyclohepta[1,2-*c*]pyridine, 72917-29-4; 9-anthraceneacetyl chloride, 72917-30-7; *N*-benzylpropargylamine, 1197-51-9; 11-methylene-9,10-dihydro-9,10-ethanoanthracene, 19978-14-4; 1-(chlorosulfonyl)-8,12-dihydro-3*H*-3a,8-methanodibenzo[3,4:6,7]cyclohepta[1,2-*b*]pyrrol-2(1*H*)-one, 72925-73-6; chlorosulfonyl isocyanate, 1189-71-5.

Notes

Intramolecular Diels–Alder Additions. 3. Additions to Isoindole

Engelbert Ciganek

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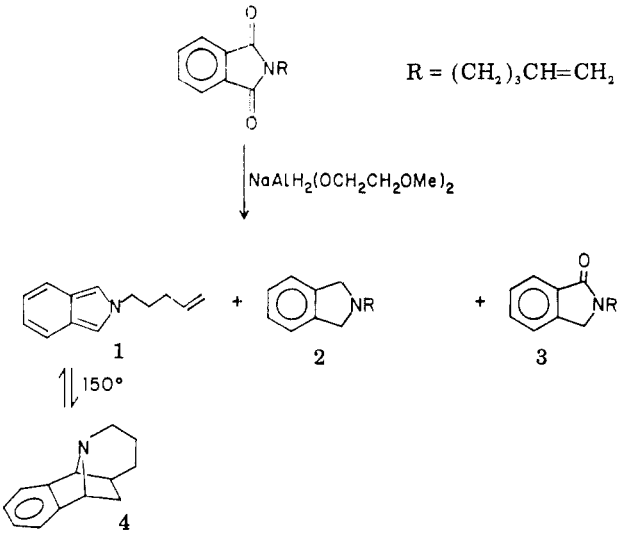
In the first two papers[1] of this series, we described intramolecular Diels–Alder additions to anthracene and acridine and some rearrangements of 9,12-bridged ethenoanthracenes. In this note we report an intramolecular Diels–Alder addition to isoindole.[2]

N-4-Pentenylisoindole (**1**) was prepared by reduction of *N*-4-pentenylphthalimide with sodium bis(2-methoxyethoxy)aluminum hydride.[3] The desired product was contaminated by the isoindoline **2** and the isoindolinone **3**.



Removal of **2** by acid extraction left a mixture of ca. 70% of the isoindole **1** and 30% of **3**. Heating this mixture in toluene to 150 °C for 8 h resulted in partial cyclization of **1** to 1,2,3,4,6,10b-hexahydro-1,6-methanopyrido[2,1-*a*]isoindole (**4**); the ratio of **1** and **4**, as determined by NMR spectroscopy, was ca. 1:1. At 200 °C under otherwise identical conditions, the ratio of **1** and **4** was about 2.3:1, indicating that at elevated temperatures **1** and **4** were in equilibrium. Slow fractional distillation of the equilibrium mixture at 160–180 °C (bath temperature) resulted in almost complete conversion to the lower boiling cyclized isomer **4**. No cyclization was observed in the case of *N*-5-hexenylisoindole [$(CH_2)_4CH{=}CH_2$ in place of pentenyl group on **1**].

Experimental Section

***N*-4-Pentenylisoindole (1).** A mixture of 32.5 g of potassium phthalimide, 33 g of 5-bromo-1-pentene, and 150 mL of anhydrous dimethylformamide was stirred at 127 °C (bath temperature) overnight. Most of the solvent was removed under vacuum. Ice was added to the residue, and the product was collected by filtration, washed with water, and dried to give 35.79 g of crude *N*-4-pentenylphthalimide as a low-melting solid; it was used without further purification.

A 70% solution of sodium bis(2-methoxyethoxy)aluminum hydride in benzene (100 mL) was added over a period of 45 min to a mechanically stirred solution of 28.5 g of *N*-4-pentenylphthalimide in 180 mL of benzene, keeping the temperature at 15–20 °C. After being stirred at room temperature for 1 h, the mixture was cooled, and 100 mL of a 25% aqueous sodium hydroxide solution was added slowly. The layers were separated, and the aqueous phase was extracted twice with benzene. The combined organic phases were washed with water and then extracted with several portions of 5% sulfuric acid to remove the *N*-4-pentenylisoindoline (**2**, 9.3 g after reconversion to the free base). Removal of the solvent gave 13.2 g of a dark liquid consisting of ca. 70% of *N*-4-pentenylisoindole (**1**) and 30% of *N*-4-pentenylisoindolin-1-one (**3**). It was short-path distilled (95–150 °C bath temperature, 0.5 μm) to give 10.43 g of a yellow liquid, still containing most of the isoindolinone impurity. The products had the following NMR spectra (in $CDCl_3$). For **1**: τ 2.5–3.5 (m, 6), 3.9–4.8 (m, 1), 4.9–5.4 (m, 2), 6.1 (t, J = 6.5 Hz, 2), 8.0–8.6 (m, 4). For **2**: τ 3.0 (s, 4), 2.9–3.5 (m, 1), 4.8–5.2 (m, 2), 6.2 (s, 4), 7.4 (t, J = 7 Hz, 2), 7.7–8.6 (m, 4). For **3**: τ 2.3–3.4 (m, 4), 4.0–4.7 (m, 1), 5.0–5.4 (m, 2), 5.9 (s, 2), 6.6 (t, J = 7 Hz, 2), 7.8–9.0 (m, 4).

1,2,3,4,6,10b-Hexahydro-1,6-methanopyrido[2,1-*a*]isoindole (4). The crude *N*-4-pentenylisoindole (**1**) was distilled slowly through a spinning-band column at 160–180 °C (bath temperature) (0.3 mm), giving 7.41 g (80%) of essentially pure **4** in four fractions: bp 90–92 °C (0.3 mm); n^{24}_D 1.5745–1.5773. The purest fraction had the following: n^{24}_D 1.5765; NMR (in $CDCl_3$) τ 2.8–3.2 (m, 4), 5.8 (d, J = 4.5 Hz, 1), 6.1 (s, 1), 6.8–7.2 (m, 2), 7.9–9.1 (m, 7). The methiodide melted at 147–147.5 °C dec after crystallization from isopropyl alcohol: NMR (in $CDCl_3$) τ 2.3–2.8 (m, 4), 4.1 (d, J = 4 Hz, split further, 1), 4.3 (s, slightly split, 1), 5.5–6.1 (m, 2), 6.9 (s, 3), 7.1–9.1 (m, 7).

Anal. Calcd for $C_{14}H_{18}IN$: C, 51.39; H, 5.51; N, 4.28. Found: C, 51.53; H, 5.59; N, 4.30.

(1) Parts 1 and 2, E. Ciganek, *J. Org. Chem.*, companion papers in this issue.

(2) For intermolecular Diels–Alder additions to isoindoles, see: J. C. Emmett and W. Lwowski, *Tetrahedron*, **22**, 1011 (1966); J. E. Shields and J. Bornstein, *Chem. Ind. (London)*, 1404 (1967).

(3) D. I. Garmaise and A. Ryan, *J. Heterocycl. Chem.*, 413 (1970).

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Continuation of the distillation gave another 1.31 g of 4 containing small amounts of 1 and 3; the pot residue was mostly *N*-4-pentenylisoindolin-1-one (3).

Registry No. 1, 72893-85-7; 2, 72893-86-8; 3, 72905-19-2; 4, 72905-20-5; 4 methiodide, 72905-21-6; 5-bromo-1-pentene, 1119-51-3; *N*-4-pentenylphthalimide, 7736-25-6.

Rearrangement of 2,2,6,6-Tetramethyl-4-piperidone in Phase-Transfer Catalyzed Reactions[1]

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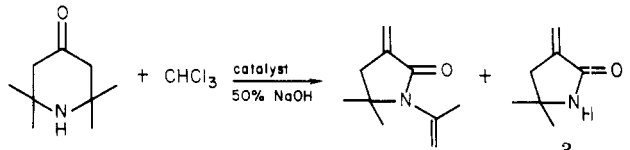
We recently described a novel synthesis of 1,3,3,5,5-pentasubstituted 2-piperazinones[2] from N[1],2,2-trisubstituted 1,2-ethanediamines, ketones, and chloroform by a phase-transfer[3] catalyzed reaction. We proposed that trichloromethide ion is the reactive species while dichlorocarbene involvement is minimal at most.[2] We now report a novel rearrangement of 2,2,6,6-tetramethyl-4-piperidone (1) to *N*-isopropenyl-3,3-methylene-5,5-dimethyl-2-pyrrolidinone (2) and 3,3-methylene-5,5-dimethyl-2-pyrrolidinone (3) which occurs when 1 is reacted with excess chloroform and 50% aqueous NaOH in the presence of a phase-transfer catalyst, where trichloromethide ion rather than dichlorocarbene[4] is still believed to play a dominant role.

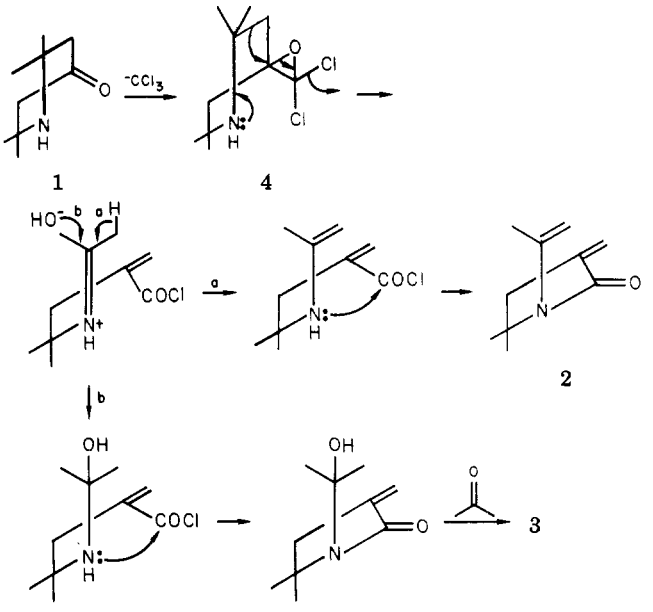


1 2 3

catalyst	ratio[5]	
1, $PhNH_2NEt_3^+Cl^-$	78	22
2, 18-crown-6	90	10
3, 18-crown-6/1.0 piperidine	21	79

The reaction proceeds essentially quantitatively to the products in a few hours at 0–5 °C. When 1 equiv of piperidine is added to the reaction (see reaction 3), the ratio of 2 to 3 changes drastically, although 2 and 3 still make up most of the product (85–90%). This suggests that dichlorocarbene, being an electrophile, is quite unlikely as an intermediate because it would react with the stronger base piperidine[6] much faster than with 1. 2 and 3 are not interchangeable under the reaction conditions, and adding piperidine to reactions 1 and 2 does not cause the conversion of 2 to 3 after their formation. We outline a possible mechanism in Scheme I featuring $^-CCl_3$ as the reactive species which forms the dichlorooxirane 4 with 1.

Scheme I



Experimental Section

^1H NMR spectra were recorded on a Varian A-60 spectrometer. ^{13}C NMR spectra were recorded on a Bruker HX90E spectrometer. $CDCl_3$ was used as solvent and Me_4Si was added as internal standard in all NMR samples. Infrared spectra were obtained on a Perkin-Elmer 467 spectrometer. Mass spectra were recorded on a Varian MAT311A mass spectrometer. Microanalyses were performed by Huffman Lab, Inc., Wheatridge, CO.

***N*-Isopropenyl-3,3-methylene-5,5-dimethyl-2-pyrrolidinone (2).** 2,2,6,6-Tetramethyl-4-piperidone hydrate[7] (5.20 g, 30 mmol), chloroform (11.94 g, 100 mmol), and 18-crown-6 (0.40 g, 1.5 mmol) were placed in a 100-mL 3-neck flask immersed in a refrigerated circulating bath. The temperature was kept below 5 °C while 50% aqueous NaOH (24 g, 300 mmol) was added dropwise in 25 min. The solution was stirred at 5 °C for 7 h after the addition and then water was added until all solids dissolved. The two layers were separated and the aqueous layer was extracted with two 25-mL portions of $CHCl_3$. The combined organic layers were washed with one 10-mL portion of H_2O, dried, and concentrated under vacuum, 15 mL of hexane was added, the mixture was stirred, and the small amount of solid which formed was filtered off. The filtrate was concentrated and distilled to give 3.5 g (71%) of a clear oil at 63–7 °C (0.2 mm): IR (neat) 1680, 1655, 1640 cm^{-1}; ^1H NMR δ 1.35 (s, 6 H), 2.01 (d, 3 H), 2.70 (t, 2 H), 4.89 (s, 1 H), 5.20 (q, 1 H), 5.32 (dt, 1 H), 6.00 (dt, 1 H); ^{13}C NMR δ 22.04 (q), 28.15 (q), 29.48 (t), 42.12 (s), 114.60 (t), 115.51 (t), 139.47 (s), 140.18 (s), 166.35 (s); mass spectrum, *m/e* 165 (M^+). Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 71.35; H, 8.93; N, 8.42.

3,3-Methylene-5,5-dimethyl-2-pyrrolidone (3). The procedure was as above except that 2.55 g (30 mmol) of piperidine was mixed with the reactants before the addition of 50% NaOH. The obtained crude product was stirred with 15 mL of hexanes to yield 1.95 g (52%) of a slightly yellowish solid after filtration. Recrystallization from heptane–toluene afforded colorless crystals: mp 139–142 °C; IR (KBr) 3180, 1680, 1645 cm^{-1}; ^1H NMR δ 1.32 (s, 6 H), 2.61 (t, 2 H), 5.33 (m, 1 H), 5.97, (t, 1 H); ^{13}C NMR δ 29.67 (q), 41.83 (t), 53.92 (s), 115.64 (t), 141.09 (s), 169.89 (s); mass spectrum, *m/e* 125 (M^+). Anal. Calcd for $C_7H_{11}NO$: C, 67.17;

(1) Lai, J. T. Presented in part at the 179th National Meeting of the American Chemical Society, TX, March, 1980.
(2) Lai, J. T. *J. Org. Chem.*, **1980**, *45*, 754.
(3) (a) Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis"; Springer-Verlag: New York, 1977. (b) Stark, C. M.; Liotta, C. "Phase Transfer Catalysis: Principles and Techniques"; Academic Press: New York, 1978.
(4) An independent observation for the isolation of 2 from 1 under similar conditions was published: Lind, H.; Winkler, T. *Tetrahedron Lett.* **1980**, 119.
(5) Determined by GC by their relative peak heights. A 6 ft × $^3/_{16}$ in. 10% OV-17 on Chromosorb W column was used.
(6) No appreciable amount of *N*-formylpiperidine which would otherwise be formed from piperidine and dichlorocarbene can be detected. Cf. (a) Graefe, J.; Frohlich, I.; Muhtstadt, M. *Z. Chem.* **1974**, *14*, 34. (b) Makosza, M.; Kacprowice, A. *Rocz. Chem.* **1975**, *49*, 1627.
(7) Eastman Kodak; a simple distillation will remove most of the color.

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