E stereochemistry, the opposite was demonstrated earlier for α-bromoethylide reactions, which showed high stereoselectivity for Z isomers.

Experimental Section

^{1}H NMR spectra were recorded at 60 MHz with a Hitachi Perkin-Elmer R20B instrument (tetramethylsilane as internal standard, $CDCl_3$ as solvent). Analytical GLC was performed on a Varian Aerograph Series 1800 preparative instrument using a 10 ft × 0.25 in. column packed with 10% SE30 on Chromosorb W support, operated at 115 °C. Elemental analyses were performed by the Australian Microanalytical Service, CSIRO, Victoria, Australia.

Materials. Triphenylphosphine, carbon tetrabromide, tetrahydrofuran, and dichloromethane[6] were purified as reported previously.[3] Allyl bromide was freshly distilled and stored over 5A molecular sieves.

Synthesis of Phosphonium Salt 2c. A typical preparation is as follows. Into a 250-mL three-necked flask fitted with a mechanical stirrer, low temperature thermometer, and pressure-equalized dropping funnel was introduced a solution of purified carbon tetrabromide (33.2 g, 0.1 mol) in *dry* dichloromethane[6] (100 mL) under a nitrogen blanket. While the mixture was stirred and dry ice–acetone cooled (−5 to 0 °C), a solution of triphenylphosphine (52.4 g, 0.2 mol) in dry dichloromethane was rapidly added (10 min) via the dropping funnel and stirring continued until a heavy precipitate appeared (~15 min). After the flask contents were cooled to −30 °C, allyl bromide (14.5 g, 0.12 mol) in dry dichloromethane (20 mL) was added dropwise to the gently stirred solution (30 min) and stirring then continued overnight at 2 °C. The product, a cream-colored suspension in a pale yellow solution, was poured with rapid stirring into aqueous potassium bicarbonate (120 mL of a 2 M solution; 0.24 mol). When the gassing had finished, a small volume of ethanol (~25 mL) was added to completely dissolve the solid, the organic layer was separated and dried ($MgSO_4$), and the solvent was removed. Trituration of the resulting solid material with benzene (100 mL) to remove Ph_3PO followed by dissolution of the crude **2c** in the minimum volume of CH_2Cl_2–EtOH (9:1) and reprecipitation with hot ethyl acetate furnished 34.0 g (61%) of **2c**, mp 187–189 °C. A further crop of ~4.0 g of product, mp 179–182 °C, was obtained on concentration of the mother liquor. Drying was effected at 65 °C in a vacuum oven (~0.5 mmHg): ^{1}H NMR δ 3.4 (2 H, m), 5.2–6.0 3 H, m), 7.7–8.2 (15 H, m). Anal. Calcd for $C_{22}H_{20}Br_3P$: C, 47.60; H, 3.6; Br, 43.20. Found: C, 47.6; H, 3.6; Br, 43.4.

Procedure for Wittig Reactions. As described previously, ylide generation was carried out by dropwise addition of n-BuLi in hexane to a 10% excess of **2c** suspended in THF mechanically stirred at −40 °C. After the mixture was stirred an additional 30 min at this temperature, the aldehyde in a small volume of THF was added at −55 to −60 °C. Workup involved slow warming to room temperature, being stirred for 30 min, filtration, concentration, extraction (hexane), and column chromatography (silica gel, hexane eluent). Removal of solvent rendered **6** and **7** as colorless oils.

4-Bromoundeca-1,4-diene (6): ^{1}H NMR δ 0.7–1.5 (11 H, m), 3.1 (2 H, d, J = ~6 Hz), 4.8–5.2 (2 H, m), 5.4–5.9 (1 H, m), 5.5 (1 H, t, $J_{allylic}$ > 1 Hz, Z isomer), 5.8 (1 H, t, $J_{allylic}$ < 1 Hz, E isomer). Anal. Calcd for $C_{11}H_{19}Br$: C, 57.2; H, 8.3; Br, 34.6. Found: C, 56.9; H, 8.2; Br, 33.4.

1-Phenyl-2-bromo-1,4-pentadiene (7): ^{1}H NMR δ 3.15–3.4 (2 H, d, J = ~6 Hz), 4.9–5.3 (2 H, m), 5.5–6.2 (1 H, m), 6.7 (1 H, brs, Z isomer), 6.95 (1 H, brs, E isomer), 7.1–7.3 (5 H, brs).

Acknowledgment. The author wishes to express his thanks to the University of Malaya for its financial support of this work under Vote F Grant No. F73/75.

Registry No. 2c, 71974-98-6; **6**, E isomer, 71987-45-6; **6**, Z isomer, 71974-99-7; **7**, E isomer, 71975-00-3; **7**, Z isomer, 71975-01-4; carbon tetrabromide, 558-13-4; triphenylphosphine, 603-35-0; allyl bromide, 106-95-6; $C_6H_{13}CHO$, 111-71-7; PhCHO, 100-52-7.

(6) Final drying over 3A molecular sieves gives superdry solvent: D. R. Burfield, G. H. Gan, and R. H. Smithers, *J. Appl. Chem. Biotechnol.*, **28**, 23 (1978).

N-(Ethoxycarbonyl)phthalimide. An Improved Procedure

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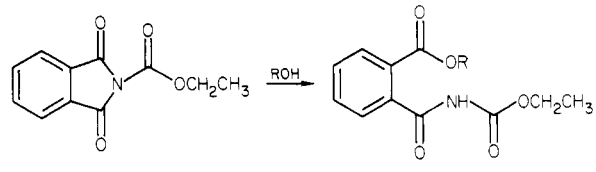
Received June 28, 1979

N-(Ethoxycarbonyl)phthalimide (1) has been known for some time as a reagent for the *N*-phthaloylation of primary amino groups.[1] The mild conditions under which it causes N-phthaloylation offers advantages over other methods.[2] Heating with phthalic anhydride can cause racemization of amino acids[2a,b] and formation of byproducts when used with amino alcohols.[2c] The advantages of protecting amino groups by formation of phthaloyl derivatives, compared, for example, with the use of benzylcarbonyl derivatives, also has been recognized for some time.[3] Yet Nefkens' reagent, **1**, has not achieved wide use as recently pointed out.[4] Low yields were experienced in the use of **1** to N-phthaloylate 2-aminoethanol compared with the phthalic anhydride fusion method.[5] In the course of our work on the asymmetric alkylation of polymer-bound imines,[6] we encountered difficulties in the N-phthaloylation of amino alcohols through the use of **1**. When we attempted to prepare **1** by Nefkens' procedure,[1] only impure product in low yields was obtained.

The procedure of Nefkens et al.,[1] involving the reaction of phthalimide and ethyl chloroformate in the presence of triethylamine, in our hands afforded **1**, after the purification steps described,[1] in 43% yield[7] which was contaminated to the extent of 10% with phthalimide which appears to cocrystallize with **1**.[8] The extent of contamination was indicated both by the NMR spectrum of the product mixture and by separation and isolation of the components through fractional crystallization of the mixture from chloroform.

The earlier report[1] states that **1** exhibited no reactivity towards water, alcohols, and acids. Ethanol was the



1 **2**

solvent used[1] for the purification of **1** by successive recrystallizations. We have found that **1** reacts in hot alcohols and is converted to the corresponding ethyl *N*-[2-(alkoxycarbonyl)benzoyl]carbamates, **2**.

(1) (a) G. H. L. Nefkens, G. I. Tesser, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **79**, 688 (1960); (b) G. H. L. Nefkens, *Nature (London)*, **185**, 309 (1960).

(2) (a) Y. F. Shealy, C. E. Opliger, and J. A. Montgomery, *J. Pharm. Sci.*, **57**, 757 (1968); (b) H. Sato, T. Kusumi, K. Inaye, and H. Kakisawa, *Bull. Chem. Soc. Jpn.*, **49**, 2815 (1976); (c) Z. W. Wicks, Jr., and G. Chen, *J. Org. Chem.*, **44**, 1244 (1979).

(3) J. C. Sheehan and V. S. Frank, *J. Am. Chem. Soc.*, **71**, 1857 (1949).

(4) S. O. DeSilva and V. Snieckus, *Can. J. Chem.*, **56**, 1621 (1978).

(5) S. Wolfe and S. K. Hasan, *Can. J. Chem.*, **48**, 3572 (1970).

(6) P. M. Worster, C. R. McArthur, and C. C. Leznoff, *Angew. Chem., Int. Ed. Engl.*, **18**, 221 (1979).

(7) While Nefkens et al.[1] reported 80% yield, it apparently was based on the weight of solid material obtained before the recrystallizations described in their procedure.

(8) The melting point of the product containing 10% phthalimide was the same as that reported[1] (79–80 °C; lit.[1] mp 80 °C).

0022-3263/80/1945-0174$01.00/0

Our modified procedure described below includes removal of excess phthalimide on the basis of its low solubility in chloroform, does not require, as in other procedures,[1,4] the formation of potassium phthalimide, avoids the use of protic solvents in the purification, and affords pure 1 in high yields.

Experimental Section[9]

Modified Procedure for *N*-(Ethoxycarbonyl)phthalimide. Ethyl chloroformate (115 mL, 1.29 mol) was added dropwise over a period of 90 min to a stirred solution of phthalimide (149.9 g, 1.02 mol) and triethylamine (160 mL, 1.15 mol) in dimethylformamide (500 mL) at 0–5 °C under argon. The reaction mixture was allowed to warm to room temperature and stand for 4 h. It then was slowly added to an agitated mixture of ice and water (3 L). The solid product was collected and extracted with two portions of chloroform (450 mL and then 50 mL). The extract was dried (Na_2SO_4), cooled overnight in the refrigerator, and filtered to remove phthalimide (mp 238 °C). The chloroform solution was concentrated to about 350 mL, diluted with petroleum ether (bp 60–80 °C; 350 mL) and allowed to stand at room temperature to give *N*-(ethoxycarbonyl)phthalimide (179 g, followed by two additional crops for a total of 212 g, 95% yield): mp 83 °C; IR (KBr) 1720, 1765, 1805 cm^{-1}; NMR ($CDCl_3$) δ 1.46 (t, 3 H, J = 7.2 Hz, OCH_2CH_3), 4.51 (q, 2 H, J = 7.2 Hz, OCH_2CH_3), 7.96 (d, 4 H, J = 2 Hz, aromatic H); UV λ_{max} (CH_3CN) 216 nm (ϵ 48 000), 263 (1400), 292 (1400); gas chromatographic analysis on a high-performance column (3% Carbowax on Chromosorb W (20 M); $^1/_8$ in. × 6 ft; 200 °C) exhibited one sharp peak. Anal. Calcd for $C_{11}H_9NO_4$: C, 60.28; H, 4.14; N, 6.39. Found: C, 60.36; H, 4.15; N, 6.32.

Alcoholysis of *N*-(ethoxycarbonyl)phthalimide (1). A. A solution of 1 (1.02 g, 4.66 mmol) in reagent-grade methanol (25 mL) was stirred and heated under reflux for 1 h and then concentrated under reduced pressure to afford a viscous oil (1.2 g). Crystallization from 2-propanol (20 mL) at −5 °C gave ethyl *N*-[2-(methoxycarbonyl)benzoyl]carbamate (**2**, R = CH_3): 765 mg, followed by additional crops for a total of 1.18 g, 100% yield; mp 86–87 °C; IR (KBr) 1680, 1718, 1760 cm^{-1}; NMR ($CDCl_3$) δ 1.17 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 3.89 (s, 3 H, OCH_3), 4.11 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 7.45 (m, 3 H, aromatic H), 8.00 (m, 1 H, aromatic H), 8.65 (br s, 1 H, exchangeable with D_2O, –CONHCO–). Anal. Calcd for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.22; N, 5.58. Found: C, 57.57; H, 5.24; N, 5.36.

B. In a similar manner, a solution of 1 in reagent-grade ethanol was heated under reflux for 2 h. Concentration gave an impure white solid (mp 60–70 °C) which by recovery of 1 by crystallization from 2-propanol appeared to be a mixture of 1 (65%) and ethyl *N*-[2-(ethoxycarbonyl)benzoyl]carbamate (**2**, R = CH_2CH_3; 35%) isolated as a clear viscous oil which could not be crystallized. The same proportions of 1 and **2** (R = CH_2CH_3) were indicated by treatment of the mixture with aqueous sodium bicarbonate solution for 8 h at 22 °C to convert 1 to sodium *N*-[2-(ethoxycarbonyl)benzoyl]carbamate and then extraction of the mixture with dichloromethane followed by concentration of the extract to afford **2** (R = CH_2CH_3) as a clear oil: IR (CCl_4) 3420 (NH), 1765 (C=O), 1720 (C=O), 1705 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.17 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 1.33 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 4.11 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 4.33 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 7.40 (m, 3 H, aromatic H), 7.95 (m, 1 H, aromatic H), 8.73 (br s, 1 H, exchangeable with D_2O, –CONHCO–); mass spectrum, m/e 265 (M^+).

Similarly, when a solution of 1 in ethanol was heated for 12 h, 1 was recovered (20%) and **2** (R = CH_2CH_3) was produced (80%). After 36 h, the proportions were ~2% 1 and ~98% **2** (R = CH_2CH_3).

C. In a similar manner, a solution of 1 in 2-propanol was heated for 2 h to produce a mixture of 1 (93%) and **2** (R = $CH(CH_3)_2$) (7%). After the mixture was heated in 2-propanol for 60 h, the proportions were 50% 1 and 50% **2** (R = $CH(CH_3)_2$). Ethyl *N*-[2-(2-propoxycarbonyl)benzoyl]carbamate (**2**, R = $CH(CH_3)_2$) was isolated as a clear viscous oil: IR (CCl_4) 3420 (NH), 1770 (C=O), 1720 (C=O), 1710 cm^{-1} (sh, C=O); NMR ($CDCl_3$) δ 1.20 (t, 3 H, J = 7.0 Hz, CH_2CH_3), 1.33 (d, 6 H, J = 6.0 Hz, $CH(CH_3)_2$), 4.11 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 5.20 (m, 7 peaks, 1 H, J = 6.0 Hz, $OCH(CH_3)_2$), 7.2–7.6 (7, 3 H, aromatic), 7.8–8.1 (m, 1 H, aromatic H), 8.48 (br s, 1 H, exchangeable with D_2O, –CONHCO–).

Acknowledgment. We thank the National Research Council of Canada and the Faculty of Science, York University, for financial support.

Registry No. 1, 22509-74-6; **2**, R = CH_3, 71964-88-0; **2**, R = CH_2CH_3, 71964-89-1; **2**, R = $CH(CH_3)_2$, 71964-90-4; phthalimide, 85-41-6; ethyl chloroformate, 541-41-3; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0.

(9) Melting points are uncorrected. Microanalyses were performed by A. B. Gygli, Toronto, Ontario, Canada. The NMR spectra were determined on an EM 360 Varian spectrometer, the IR spectra on an SP1000 Infrared Pye Unicam spectrometer, the UV spectra on a Hitachi Perkin-Elmer 340 spectrometer, and the gas chromatographic analyses on a Perkin-Elmer 990 gas chromatograph.

Efficient and General Synthesis of 1,3-Dithiole-2-thiones

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Received July 30, 1979

Recently we reported a novel synthesis of 1,3-dithiole-2-thiones with a variety of functional groups from sodium *tert*-butyl trithiocarbonate and propargyl halides.[1] Although this synthesis allowed the introduction of many substituents, some of which are unavailable by other methods, the limited availability of acetylenic halides precluded broad application of this technique.[2] We now report an expansion of the synthetic utility of sodium *tert*-butyl trithiocarbonate in the synthesis of 1,3-dithiole-2-thiones (**3**) by the acid-catalyzed ring closure of β-keto *tert*-butyl trithiocarbonates (**1**) which are readily available from α-halo ketones (Scheme I) and sodium *tert*-butyl trithiocarbonate. We also report the ring closure of acetylenic trithiocarbonate **4** with bromine to give the highly reactive 4-(bromomethyl)-1,3-dithiole-2-thione (**7**) (Scheme II).

Although specific preparations of 1,3-dithiolylium salts via the acid-catalyzed ring closures of substituted methyl trithiocarbonates have been disclosed, which would give compounds similar to **2**, the reported cyclizations are specific only for phenacyl-substituted methyl trithiocarbonates; acetonyl methyl trithiocarbonates were reported not to yield any 1,3-dithiolylium salts.[3] Since we have by our method isolated high yields of 4-methyl-1,3-dithiole-2-thione (**3c**) from acetonyl *tert*-butyl trithiocarbonates as well as other compounds such as **3b,e,f**, the mechanistic question arises: When is isobutylene lost, before or after cyclization? The actual intermediate leading to **3** may be **8** rather than **2**. Our experimental technique did not allow us to answer this mechanistic question.

However, an example of cyclization before loss of isobutylene was found when acetylenic trithiocarbonate **4** cyclized stereospecifically to salt **5**. This parallels the

(1) Haley, N. F. *Tetrahedron Lett.* **1978**, 5161.
(2) Recent syntheses of dithioles from acetylenes, carbon disulfide, and bis(amine) disulfides suffer from the same limitation. See: Grumwell, J. R. *J. Org. Chem.* **1978**, *43*, 2917.
(3) Hamilton, R. D.; Campaigne, E. *Chem. Heterocycl. Compd.* **1977**, *30*, 171.

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