viously described on 5×10^{-3} *M* solutions of **1a** in trifluoroacetic acid. Typical light intensities were on the order of 2.4×10^{-6} einsteins/15 ml min.[16] The product analysis was by uv at 261.5 nm while that for loss of starting material was measured at 295.0 nm; an isosbestic point was observed at 280.0 nm. The quantum yield measurements were independent of conversion between 0.25 and 7.0% giving average quantum yields of $\Phi_{2a} = 0.42 \pm 0.10$ and $\Phi_{3a} = 0.49 \pm 0.05$.

(16) Potassium ferrioxolate actinometry was employed: C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., London*, **235**, 518 (1956).

Registry No.—**1a**, 35202-17-6; **1b**, 35202-18-7; **1c**, 35202-19-8; **1d**, 35202-20-1; **3b**, 35202-21-2; **3c**, 35340-32-0; **3d**, 35202-22-3; **6b**, 35202-23-4; **6c**, 35202-24-5; **6d**, 35202-25-6; **7b**, 35202-26-7; **7c**, 35202-27-8; **7d**, 35202-28-9; **8b**, 35202-29-0; **8c**, 35202-30-3; **8d**, 33258-76-3.

Acknowledgment.—We gratefully acknowledge partial support from the Eli Lilly Co., Indianapolis, Ind.

Alkali-Induced Reactions of *N*-Nitrosooxazolidones and *N*-Nitrosoacetylamino Alcohols Containing Cyclopropyl Groups[1]

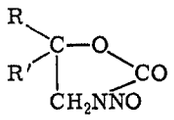
MELVIN S. NEWMAN* AND STANLEY J. GROMELSKI[2]

Evans Chemistry Laboratory of The Ohio State University, Columbus, Ohio 43210

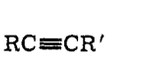
Received April 14, 1972

The reactions of 5-cyclopropyl-5-phenyl-3-nitrosooxazolidone (**6**), 5,5-dicyclopropyl-3-nitrosooxazolidone (**7**), and 5-cyclopropyl-5-methyl-3-nitrosooxazolidone (**8**) under alkaline conditions are described. When methanolic solutions of **6** are treated with aqueous hydroxide, about 90% yields of cyclopropylphenylacetylene (**9a**) are obtained. On similar treatment, **7** yields about 52% dicyclopropylacetylene (**9b**) together with about 21% 2,2-dicyclopropylvinyl methyl ether (**10b**), and **8** yields only 16% cyclopropylmethylacetylene (**9c**) together with about 64% a nearly 1:1 mixture of the *Z* and *E* forms of 2-cyclopropyl-1-propenyl methyl ether (**10c**). When a cyclohexene solution of **6** is added to a suspension of lithium ethoxide in cyclohexene, an 84% yield of **9a** is obtained. On similar treatment, **7** yields 64% **9b** and about 13% 7-(dicyclopropylmethylene)bicyclo[4.1.0]-heptane (**5b**), while **8** yields about 26% **9c** and 44% 7-(2-cyclopropylpropylidene)bicyclo[4.1.0]heptane (**5c**). Mechanisms which involve unsaturated carbonium ions and unsaturated carbenes are advanced to explain the results. Treatment of a cyclohexene–pentane solution (containing a small amount of Aliquat, a long chain quaternary ammonium chloride) of 2-(*N*-nitrosoacetylamino)-1,1-dicyclopropylethanol (**17**) with 50% sodium hydroxide afforded a 64% yield of **5b**. Similar treatments of 1-(*N*-nitrosoacetylamino)-2-cyclopropyl-2-propanol (**18**) yielded 52% **5c**.

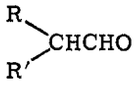
The reactions of 5,5-disubstituted-3-nitrosooxazolidones (**1**) with bases in polar media have been studied.[3a] When one or both R groups are phenyl, acetylenes (**2**) are formed. When alkyl groups are involved, disubstituted aldehydes (**3**) and/or rearranged ketones (**4**) are formed. If the reactions are carried out in cyclohexene with lithium ethoxide, substituted ethylidenecyclopropanes (**5**) are produced.[3b]



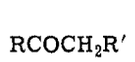
1



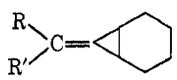
2



3

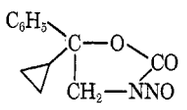


4

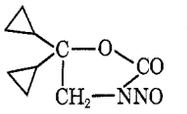


5b, R = R′ = Δ
c, R = Δ; R′ = CH_3

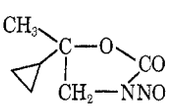
The present work was undertaken to find out how compounds such as **1** with cyclopropyl groups would behave under similar conditions. Cyclopropyl groups were chosen because they are between aryl groups and alkyl groups[4] in their tendency to participate in reactions involving cationic intermediates. Accordingly, 5-cyclopropyl-5-phenyl-3-nitrosooxazolidone (**6**), 5,5-dicyclopropyl-3-nitrosooxazolidone (**7**), and 5-cyclopropyl-5-methyl-3-nitrosooxazolidine (**8**) were prepared by procedures similar to those described,[3] and were treated with bases under the two different sets of reaction conditions discussed below.



6

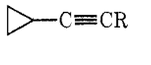


7

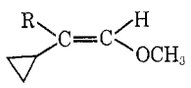


8

I. Treatment with Methanolic Potassium Hydroxide.—When methanolic solutions of the nitrosooxazolidones at room temperature were treated with methanolic potassium hydroxide, vigorous reactions occurred to yield mainly cyclopropylphenylacetylene (**9a**) from **6**, dicyclopropylacetylene (**9b**), and 2,2-dicyclopropylvinyl methyl ether (**10b**) from **7**, and cyclopropylmethylacetylene (**9c**) and both isomers of 2-cyclopropyl-1-propenyl methyl ether (**10c**) from **8**. The results are listed in Table I.



9a, R = C_6H_5
b, R = Δ
c, R = CH_3



10b, R = Δ
c, R = CH_3

These results seem best explained by assuming that the intermediate (A), similar to one previously postulated,[3b] undergoes a trans elimination *via* rotamers B and C to yield the isomeric intermediates D and E as shown in Scheme I. Each of these can give rise to

(1) This work was supported largely by Grant G-12445X from the National Science Foundation.

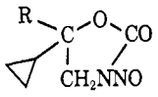
(2) This work was taken from the Ph.D. thesis presented by S. Gromelski to The Ohio State University, 1971.

(3) (a) M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.*, **73**, 4199 (1951); (b) M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, **34**, 1220 (1969).

(4) Y. E. Rhodes and T. Takino, *J. Amer. Chem. Soc.*, **92**, 5270 (1970).

TABLE I

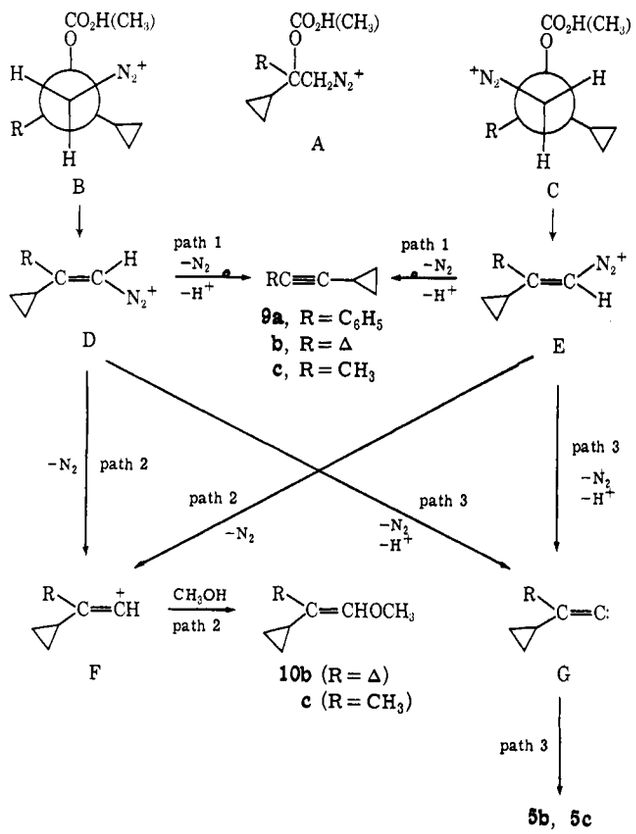
ALKALINE DECOMPOSITION OF NITROSOOXAZOLIDONES CONTAINING CYCLOPROPYL GROUPS



Compd	Method		Product	Yield, %
6 (R = C_6H_5)	*a*		**9a**	90[c]
	b			84
7 (R = ◁)	*a*		**9b**	52[d]
			10b[e]	21[d]
	b	**9b**		64[d]
			5b	13
				64[f]
8 (R = CH_3)	*a*		**9c**	16
			(*Z*)-**10c**[g]	33[h]
			(*E*)-**10c**[g]	31[h]
	b	**9c**		26
			5c	44
				52[i]

[a] Treatment of methanolic nitrosooxazolidones with aqueous methanolic hydroxide, method I in text. [b] Treatment of nitrosooxazolidones with lithium ethoxide in cyclohexene, method II in text. [c] Isolated yield. [d] Determined by glpc. [e] Isolated by glpc. [f] Obtained by treatment of **17** with base using Stark's procedure.[15] [g] See ref 20 for nomenclature. [h] Relative amounts of *Z* and *E* forms determined by nmr.[19] [i] Obtained from **18**.

SCHEME I



an acetylene by migration of the group trans to the diazo group with loss of nitrogen and a proton (path 1). Alternately, D and E may lose nitrogen to yield F (path 2), or nitrogen and a proton to yield G (path 3).[3b,5] Because of other studies,[6] we believe the path involving F is involved in the reactions which take place in methanol. The unsaturated carbonium ions (F) react with methanol to yield **10b** and the isomeric ethers **10c**. Since the steric requirements of methyl and cyclopropyl groups in F are probably nearly the same, the fact that about equal amounts of the isomeric ethers **10c** are obtained (see Table I) is readily understood. When the R groups in **1** are *tert*-butyl and methyl, the isomer in which the methoxy group is trans to the *tert*-butyl group predominates.[7] The acetylenes may be formed directly from D and E or from F.

To rationalize our results pertaining to the relative amounts of acetylene and vinyl ether formed, we assume that a phenyl group has a larger steric effect than a cyclopropyl group and the latter a slightly larger effect than a methyl group. We also assume that rearrangement of a phenyl group in intermediates of type D, E, and F occurs more readily than that of a cyclopropyl group and that methyl has little, if any, tendency to migrate because no 2-butyne is formed on treatment of the dimethyl analog of **8** with base.

Judging from the fact that the amount of vinyl ether formed increases in going from **6** to **7** to **8**, the preference of the intermediates D and E to decompose by path 2 rather than by path 1 is inversely related to the migration tendencies of the groups originally attached at the 5 position in the nitrosooxazolidones **6–8**. Unfortunately, no information can be gained about the relative migration aptitudes of phenyl and cyclopropyl[8] in this reaction because, even if the amount of phenyl migration could be determined by isotopic labeling of **6**, the result would probably hinge on the proportions of D and E formed and not on migration aptitudes. Presumably, D would be present in larger amount than E in the case where R = C_6H_5, since B should be favored over C because of steric reasons. However, there seems to be little chance to prepare the stereoisomeric intermediates D and E by other means as all attempts to nitrosate a pure trans unsaturated urethane RCH=CHNHCO$_2$H$_5$ failed.[9]

Finally, it should be noted that the treatment of 5,5-disubstituted nitrosooxazolidones (**1**) containing one or more cyclopropyl groups constitutes a new and effective synthesis of arylcyclopropylacetylenes[10] and of dicyclopropylacetylene.[11]

II. Treatment with Lithium Ethoxide in Cyclohexene.—When solutions of **6**, **7**, and **8** in cyclohexene were added to a stirred suspension of lithium ethoxide in cyclohexene the products listed in Table I were obtained. These reaction conditions were chosen because they favor the formation of unsaturated car-

(5) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964, pp 89–90.

(6) M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, **93**, 7564 (1970).

(7) Unpublished results by W. Liang.

(8) Studies on the products formed by rearrangement of a series of substituted *p*-tosylhydrazones of formula (R)$_3$CCH=NNHSO$_2$C$_7$H$_7$ *via* a carbenic intermediate, (R)$_3$CCH: led to the following migratory aptitudes, C_6H_5 (41.0), Δ (12.6), CH_3 (4.5): Unpublished results by H. Shechter and A. Kraska. See the Ph.D. thesis of A. Kraska, The Ohio State University, 1971.

(9) Unpublished experiments by Dr. Zia ud Din.

(10) Compare J. K. Crandall and D. J. Keyton, *Chem. Commun.*, 1069 (1968).

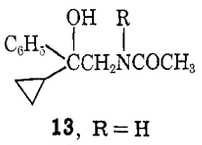
(11) G. Kobrick and D. Merkel, *Angew. Chem., Int. Ed. Engl.*, **9**, 243 (1970).

bene.[3b,12] As can be seen from the results reported in Table I, the amount of acetylene formed in these reactions is roughly the same as that obtained in the methanolic potassium hydroxide experiments. We believe that acetylene formation proceeds essentially by way of B → C and D → E as discussed above in part I, with the difference that the competition in decomposition of D and E is now between paths 1 and 3. The proportions which go through the unsaturated carbenes (G) yield the substituted bicyclo[4.1.0]-heptanes (**5b**, **5c**).

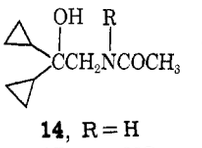
In the case of **6**, only path 1 is followed to afford an 84% yield of **9a**. In the cases of both **7** and **8**, path 3 is followed to a slightly greater extent to yield 7-(dicyclopropylmethylene)bicyclo[4.1.0]heptane (**5b**, R = R′ = △) and 7-(2-cyclopropylpropylidene)bicyclo-[4.1.0]heptane (**5c**, R = △, R′ = CH_3) than is path 2 in the cases in which the vinyl ethers **10b** and **10c** are formed.

Small amounts of dicyclopropyl ketone (**11**) and of cyclopropyl cyclopropylmethyl ketone (**12**) were isolated in studies on **7** under both of the above reaction conditions. Since similar products had been obtained in related work,[13] we studied the alkaline decomposition of **7** in water–glyme with and without added lithium nitrate. When lithium nitrate was absent, the yields of **9b**, **11**, and **12** were 48, 26, and 5.8%, respectively. When the solvent was saturated with lithium nitrate, no **9b** was formed and **11** and **12** were obtained in 31 and 27% yields, respectively. Thus, the yield of rearranged ketone (**12**) is markedly increased by lithium nitrate as in the previous work[13] (see ref 13 for comments).

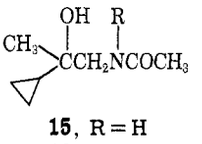
Since an improved method for generating unsaturated carbenes has recently been developed here,[14] the oxazolidones which served as precursors to **6**, **7**, and **8** were hydrolyzed to the corresponding amino alcohols which were acetylated to the acetylamino alcohols **13–15**, which were nitrosated to yield **16–18**. Treatment of cyclohexene–pentane solutions of **17** and **18** containing a small percent of a quaternary ammonium chloride with sodium hydroxide by the Starks procedure[15] afforded good yields of the corresponding bicycloheptane derivatives **5b** and **5c**. Thus, the formation of bicyclo[4.1.0]heptanes is favored by following the nitrosoacetylamino alcohol route,[14] whereas the formation of acetylenes is best carried out by starting with nitrosooxazolidones (**1**).[3a] However, in the case of **16**, an 89% yield of cyclopropyl-



13, R = H
16, R = NO



14, R = H
17, R = NO



15, R = H
18, R = NO

phenylacetylene (**9a**) was isolated with no trace of a bicycloheptane observed. Hence, when a phenyl group is present, the formation of acetylene is predominant regardless of the method.

(12) M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **91**, 6461 (1969).
(13) M. S. Newman and C. D. Beard, *ibid.*, **92**, 4309 (1970).
(14) M. S. Newman and Z. ud Din, *Syn. Commun.*, **1**, 247 (1971).
(15) C. M. Starks, *J. Amer. Chem. Soc.*, **93**, 195 (1971).

Experimental Section[16]

Reformatsky Reactions.—Improved yields of hydroxy esters used in this work were obtained when only one equivalent of activated zinc[17] was used instead of the usual excess and when ether–benzene was the solvent instead of benzene alone. The mixture was held at reflux until the zinc disappeared and no longer. In a typical reaction 30 ml of benzene was distilled from a three-necked flask containing 38 g (0.58 g-atom) of zinc[17] and 200 ml of benzene. A solution of 85 g of cyclopropyl phenyl ketone in 170 ml of dry ether was added and the mixture was heated to reflux. After a small addition of methyl α-bromoacetate and an induction period of 1 hr, 89 g (0.58 mol) of bromo ester was added in portions so that the reaction was not too vigorous. After all the zinc had disappeared (2–3 hr in all), the solution was cooled and treated with 130 ml of 1:1 acetic acid–water. The aqueous layer was reextracted several times with ether–benzene and the combined organic layers were washed with 130 ml of 1:1 ammonium hydroxide–water. The reaction mixture was then worked up as usual to yield 109 g (85%) of methyl 3-cyclopropyl-3-phenyl-3-hydroxypropionate,* bp 102–105° (0.3 mm).

Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.9; H, 7.3. Found: C, 70.7; H, 7.2.

In a similar way, methyl 3,3-dicyclopropyl-3-hydroxypropionate,* bp 57–60° (0.4 mm), and methyl 3-cyclopropyl-3-hydroxybutyrate,* bp 75–77° (8 mm), were obtained in 72 and 76% yields, from dicyclopropyl ketone and cyclopropyl methyl ketone, respectively.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.2; H, 8.8. Found: C, 64.9; H, 8.9.

Anal. Calcd for $C_8H_{14}O_3$: C, 60.8; H, 8.9. Found: C, 60.6 H, 9.0.

Synthesis of Oxazolidones.—In a typical reaction sequence 3-cyclopropyl-3-phenyl-3-hydroxypropionate was converted into 5-cyclopropyl-5-phenyloxazolidone as follows. To a solution of 5.0 g (0.023 mol) of hydroxy ester in 2.5 ml of absolute methanol was added 1.1 g (0.034 mol) of anhydrous hydrazine. The resulting solution (exothermic reaction) was allowed to stand overnight and the solvent was removed on a rotary evaporator. A solution of the oily residue in 88 ml of 0.5 *N* hydrochloric acid was slowly treated at 0–5° with 1.73 g (0.025 mol) of sodium nitrite in 20 ml of water. Benzene–chloroform (1:1) was added together with a little urea. The organic layer was separated and added dropwise to refluxing benzene. After all gas evolution had ceased, the cooled solution yielded a solid which was recrystallized from benzene–pentane to yield 3.5 g (78%) of 5-cyclopropyl-5-phenyl-2-oxazolidone,* mp 119.5–120.5°.

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.9; H, 6.4; N, 6.9. Found: C, 70.6; H, 6.7; N, 7.0.

In a similar way, 5,5-dicyclopropyl-2-oxazolidone,* mp 80.5–81.5°, and 5-cyclopropyl-5-methyl-2-oxazolidone,* mp 58.5–59.5°, were obtained in 73 and 75% yields, respectively.

Anal. Calcd for $C_9H_{13}NO_2$: C, 64.6; H, 7.8; N, 8.4. Found: C, 64.6; H, 7.9; N, 8.3.

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.6; H, 7.8; N, 9.9. Found: C, 59.4; H, 7.8; N, 9.8.

Preparation of 6, 7, and 8.—In a typical procedure a solution of 1.05 g (0.016 mol) of nitrosyl chloride[18] in 15 ml of pure acetic anhydride was added slowly to a solution of 3.0 g (0.015 mol) of 5-cyclopropyl-5-phenyl-2-oxazolidone in 30 ml of dry pyridine held at 0–5°. After 1 hr the mixture was poured on ice. A benzene–ether extract was washed with 10% hydrochloric acid and worked up in the usual way. The yellow oily residue was

(16) All melting and boiling points are uncorrected. Microanalyses by M-H-W Laboratories, Garden City, Mich., and Chemalytics, Tempe, Ariz. Ir spectra were recorded on a Perkin-Elmer Infracord. Nmr spectra were taken in CCl_4 and recorded on an A-60 instrument, Varian Associates, Palo Alto, Calif., and are reported as τ relative to tetramethylsilane as 10.0. A Varian Aerograph, Model 1200, flame ionization detector gas chromatograph was used for glpc. The phrase "worked up as usual" means that, after the organic solution was washed with water and saturated salt solution and dried by passage through a cone of anhydrous $MgSO_4$, the solvents were removed on a rotary evaporator. The nmr spectra of all compounds marked with an asterisk are recorded in the Ph.D. thesis of S. Gromelski, OSU, 1971, and are consistent with the structures proposed.
(17) L. F. Fieser and W. S. Johnson, *ibid.*, **62**, 576 (1940).
(18) Obtained in a 12-oz metal cylinder from Matheson Gas Products, Joliet, Ill.

taken up in chloroform and filtered through silica gel. On concentration and recrystallization of the solid from chloroform–pentane there was obtained 3.03 g (89%) of **6**, mp 51–52°.

Anal. Calcd for $C_{12}H_{12}N_2O_3$: C, 62.1; H, 5.2. Found: C, 62.4; H, 5.3.

In a similar way, 5,5-dicyclopropyl-2-oxazolidone was converted in 96% yield into **7**, a yellow oil: ir (neat) 6.6 μ, 1515 cm^{-1} (N=O), 5.5 μ, 1818 cm^{-1} (C=O); nmr (in CCl_4) τ 6.30 (s, 2, CH_2N), 8.45–9.00 (m, 2, c-$CHCH_2CH_2$), and 9.25–9.60 (m, 8, c-$CHCH_2CH_2$). Because **7** was unstable and a liquid, no attempt was made to prepare an analytical sample. All yields of products were calculated by assuming the oil was 100% **7**. Similarly, **8** was obtained in 95% yield as a yellow oil: ir (neat) 6.58, 5.48 μ, nmr (CCl_4) τ 6.30 (s, 2, CH_2N), 8.42 (s, 3, CH_3), 8.52–8.95 (m, 1, c-$CHCH_2CH_2$), 9.30–9.65 (m, 4, c-$CHCH_2CH_2$). The oil was stable enough to send for analysis.

Anal. Calcd for $C_7H_{10}N_2O_3$: C, 49.4 H, 5.9; N, 16.4. Found: C, 49.7; H, 5.7; N, 16.4.

2-Acetylamino-1,1-dicyclopropylethanol* (**14**).—To a solution of 2 g of potassium hydroxide in 3 ml of water was added 1.0 g (6 mmol) of 5,5-dicyclopropyl-2-oxazolidone. The mixture was held at reflux for 30 min and was then cooled (N_2 to prevent access of CO_2 from air). A solution of the organic layer in 5 ml of absolute methanol was treated during 10 min with 0.7 g (6.8 mmol) of pure acetic anhydride. The mixture was then refluxed for 30 min and volatile material removed on a rotary evaporator. The residue was recrystallized from benzene–pentane to yield 0.95 g (87%) of **14**, mp 95–96°.

Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.6; H, 9.3; N, 7.6. Found: C, 65.5; H, 9.4; N, 7.4.

2-(*N*-Nitrosoacetylamino)-1,1-dicyclopropylethanol* (**17**).—A stirred slurry of 0.44 g (2.4 mmol) of **14**, 0.62 g of freshly fused potassium acetate, 0.06 g of phosphorus pentoxide, and 3 ml of glacial acetic acid was maintained at 15–20° while a solution of 0.48 g (7.3 mmol) of nitrosyl chloride in 3 ml of acetic acid was added dropwise during 10 min. After 2 hr at 15–20° the mixture was poured on ice and a cold methylene chloride extract was washed with cold saturated potassium carbonate solution until the washings were slightly basic. The cold methylene chloride layer was evaporated under a pressure of 0.4 mm to constant weight. There was obtained 0.45 g (89%) of **17** as a yellow oil: ir (neat) 2.75, 5.78, and 6.55 μ; nmr ($CDCl_3$) τ 5.95 (s, 2, CH_2N), 7.18 (s, 3, $COCH_3$), 7.55 (s, 1, OH), 8.90–9.50 (m, 2, c-$CHCH_2CH_2$), 9.50–9.90 (m, 8, c-CCH_2CH_2).

1-Acetylamino-2-cyclopropyl-2-propanol* (**15**).—As in the case of **14**, 5-cyclopropyl-5-methyl-2-oxazolidone was converted into **15**, bp 118–119° (0.3 mm), mp 62–64°, in 83% yield. The sublimed analytical sample of **15** melted at 63.5–65.0°.

Anal. Calcd for $C_8H_{15}NO_2$: C, 61.2; H, 9.5; N, 8.9. Found: C, 61.2; H, 9.6; N, 8.9.

1-(*N*-Nitrosoacetylamino)-2-cyclopropyl-2-propanol* (**18**).—As above for **17**, 1.0 g of **15** was converted into 0.96 g (81%) of **18**, a yellow oil: ir (neat) 2.75, 5.72, and 6.58 μ; nmr ($CDCl_3$) τ 6.05 (s, 2, CH_2N), 7.20 (s, 3, $COCH_3$), 7.35 (s, 1, OH), 8.93 (s, 3, CCH_3), 9.10–9.60 (m, 1, c-$CHCH_2CH_2$), 9.60–9.95 (m, 4, c-$CHCH_2CH_2$). Both **17** and **18** were used shortly after they were made.

2-Acetylamino-1-cyclopropyl-1-phenylethanol (**13**).—As in the case of **14**, 5-cyclopropyl-5-phenyl-2-oxazolidone was converted into **13**, mp 120.5–121.0°, in 75% yield.

Anal. Calcd for $C_{13}H_{17}NO$: C, 71.3; H, 7.8; N, 6.4. Found: C, 71.2; H, 8.0; N, 6.2.

2-(*N*-Nitrosoacetylamino)-1-cyclopropyl-1-phenylethanol (**16**).—As in the case of **17**, a 95% yield of **16** (mp 72–74°; ir bands at 6.62, 5.72, and 2.70 μ) was obtained after crystallization from benzene–pentane.

Decomposition of Nitroso Compounds in Methanolic Potassium Hydroxide.—The apparatus consisted of a one-neck round-bottom flask equipped with a magnetic stirrer and a pressure equalizing dropping funnel connected to a gas collecting device. A strong (about 50%) solution of potassium hydroxide in water was added dropwise to a stirred solution of the nitroso compound (about 0.005 mol) in 20 ml of methanol at room temperature. After about 3 min the evolution of nitrogen was complete (usually quantitative). The mixture was stirred for 15 min and poured into water. The products were isolated by ether extraction and the ether removed by atmospheric distillation through a small packed column. The residue was analyzed by glpc using methyl cyclopropyl ketone as standard. Each of the products was isolated by preparative glpc using an $8^3/_4 \times {}^3/_8$ in. column containing 15% SE-30 (a silicone gum) on 60–80 mesh Chromosorb W (diatomaceous earth) at 125–150° and identified as described below.

Cyclopropylphenylacetylene (**9a**).—In a run involving 0.01 mol of **6**, **9a** was isolated as the only volatile product in 90% yield as a colorless oil: bp 71–72° (1 mm); ir 4.48 μ; nmr (CCl_4) τ 2.45–2.95 (m, 5, ArH), 8.45–8.85 (m, 1, c-$CHCH_2CH_2$), 9.15–9.45 (m, 4, c-$CHCH_2CH_2$).

Anal. Calcd for $C_{11}H_{10}$: C, 92.9; H, 7.1. Found: C, 92.9; H, 7.1.

Cyclopropylmethylacetylene (**9c**).—Obtained from runs with **8** **9c** was a colorless liquid: ir 4.45 μ; nmr (CCl_4) τ 8.28 (d, J = 2 Hz, 3, CH_3), 8.90–9.15 (m, 1, $CHCH_2CH_2$), 9.25–9.55 (m, 4, $CHCH_2CH_2$) on glpc at 125°.

Anal. Calcd for C_6H_8: C, 90.0; H, 10.0. Found: C, 90.0; H, 10.0.

2-Cyclopropyl-1-methoxy-1-propene (**10c**).—The stereoisomers of **10c** were obtained as one fraction by glpc at 125° which had a longer retention time than **9c**. The ir spectrum had a strong band at 8.2 μ and the nmr (CCl_4) showed bands at τ 4.26 (m, 1, =CH), 6.5 (s, 3, OCH_3), 8.52 (s, 3, =CCH_3), 8.76 (s, 3, =CCH_3) 9.35–9.80 (m, 5, c-$CHCH_2CH_2$). Integration of the methyl resonances showed that the isomer in which the CH_3O group is trans to the methyl group (τ 8.76),[19] the *Z* isomer,[20] was 48% and the *E* isomer (methyl group 8.52) was 52%.

Anal. (of *Z* and *E* forms). Calcd for $C_7H_{12}O$: C, 75.0; H, 10.7. Found: C, 75.2; H, 10.6.

On treatment of this mixture with 2,4-DNPH reagent[21] a 2,4-dinitrophenylhydrazone [mp 132.5–133.5°; nmr (CCl_4) τ 0.85–2.20 (m, 4, NH, ArH), 2.38 (d, J = 5 Hz, 1, CH=N), 8.10–8.40 (m, 1, $CHCH$=N), 8.72 (d, J = 6 Hz, 3, CH_3CH), 9.10–9.80 (m, 5, c-$CHCH_2CH_2$)] was obtained.

Anal. Calcd for $C_{12}H_{14}N_4O_4$: C, 51.8; H, 5.0; N, 20.1. Found: C, 51.6; H, 5.0; N, 20.3.

Dicyclopropylacetylene (**9b**).—This acetylene was isolated by preparative glpc as the first fraction in runs using **7**. In analytical runs in which methylcyclopropyl ketone was the standard, about 52–53% yields of **9b** [ir (neat) 3.28, 3.38, and 7.0 μ; nmr (CCl_4) τ 8.80–9.20 (m, 1, c-$CHCH_2CH_2$), 9.25–9.60 (m, 4, c-$CHCH_2CH_2$)] were obtained.

Anal. Calcd for C_8H_{10}: C, 90.6; H, 9.4. Found: C, 90.4; H, 9.4.

2,2-Dicyclopropyl-1-methoxyethylene (**10b**).—This vinyl ether was obtained as the fraction with the longest retention time on glpc analysis of the products obtained from **7**. In analytical runs in which methylcyclopropyl ketone was used as internal standard 21–22% yields of **10b** [mol wt 138 (mass spectrum); ir (neat) 8.2 μ (=COC); nmr (CCl_4) τ 4.24 (s, 1, =CH), 6.45 (s, 3, OCH_3), 9.10–9.80 (m, 10, c-$CHCH_2CH_2$)] were obtained.

Anal. Calcd for $C_9H_{14}O$: C, 78.3; H, 10.2. Found: C, 78.4; H, 10.4.

Compound **10b** was further characterized by treatment with 2,4-DNPH[21] to yield a yellow 2,4-dinitrophenylhydrazone: mp 143–144.5°; nmr (CCl_4) 0.74–2.22 (m, 4, NH, ArH), 2.40 (d, J = 6 Hz, 1, CH=N), 8.20–8.50 (m, 1, $CHCH$=N), 9.10–9.80 (m, 10, c-$CHCH_2CH_2$).

Anal. Calcd for $C_{14}H_{16}N_4O_4$: C, 55.3; H, 5.3; N, 18.4. Found: C, 55.6; H, 5.6; N, 18.4.

Dicyclopropyl ketone was identified by comparison (ir, nmr, glpc retention time) with an authentic sample.

Cyclopropyl cyclopropylmethyl ketone was obtained by glpc (longer retention time than dicyclopropyl ketone) as a colorless oil: mol wt 124 (mass spectrum); ir (neat) 5.9 μ; nmr (CCl_4) τ 7.60 (d, J = 7 Hz, 2, $COCH_2CH$), 7.80–8.25 (m, 1, c-$COCHCH_2CH_2$), 9.00–9.35 (m, 4, c-$COCHCH_2CH_2$), 9.40–9.95 (m, 5, c-$CH_2CHCH_2CH_2$); semicarbazone mp 114–115°, alone and mixed with the semicarbazone of the ketone prepared in 45% yield from the reaction of cyclopropylmagnesium bromide with

(19) This assignment was made by Dr. C. Meyers, Southern Illinois University.

(20) J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Reid, *J. Amer. Chem. Soc.*, **90**, 509 (1968), and ref 1b therein.

(21) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley, New York, N. Y., 1964, p 253.

cyclopropylacetonitrile. The mass spectra and ir were identical.[22,23]

Decomposition of Nitrosoacetylamino Alcohols in Cyclohexene.—In a typical experiment a solution at 10–15° of 0.74 (0.004 mol) of **18** in 10 ml each of pentane and cyclohexene containing 0.2 g of Aliquat 336[24] was treated slowly with a solution of 1 g of sodium hydroxide in 1 ml of water.[15] After 15 min the theoretical amount of nitrogen had been collected and the mixture was allowed to come to room temperature. The mixture was washed with water. The organic layer was filtered through a cone of anhydrous magnesium sulfate and concentrated to about 4 ml by fractionation through a small packed column. There was no evidence (glpc) for the presence of **9c** in the distillate or the concentrate. Further fractionation afforded 0.33 g (52%) of **5c**, bp 48° (0.4 mm), identical with the sample prepared from **8**.

In a similar experiment a 64% yield of **5b**, bp 74° (0.4 mm), was obtained from **17**.

Registry No.—**5b**, 35200-94-3; **5c**, 35200-95-4; **6**, 35200-96-5; **7**, 35200-97-6; **8**, 35200-98-7; **9a**, 21777-85-5; **9b**, 27998-49-8; **9c**, 35201-01-5; **10b**, 34189-07-6; **10b** 2,4-DNP, 35200-78-3; (*Z*)-**10c**, 35200-79-4; (*E*)-**10c**, 35200-80-7; **10c** 2,4-DNP, 35200-81-8; **13**, 35200-82-9; **14**, 35200-83-0; **15**, 35200-84-1; **16**, 35249-60-6; **17**, 35200-85-2; **18**, 35200-86-3; methyl 3-cyclopropyl-3-phenyl-3-hydroxypropionate, 35200-87-4; methyl 3,3-dicyclopropyl-3-hydroxypropionate, 35200-88-5; methyl 3-cyclopropyl-3-hydroxybutyrate, 35200-89-6; 5-cyclopropyl-5-phenyl-2-oxazolidinone, 35200-90-9; 5,5-dicyclopropyl-2-oxazolidinone, 35200-91-0; 5-cyclopropyl-5-methyl-2-oxazolidinone, 35200-92-1; cyclopropyl cyclopropylmethyl ketone, 14113-96-3.

(22) L. Michiels, *Bull. Cl. Sci., Acad. Roy. Belg.*, **10**, (1912) [C 1105 (1912)], report mp 82–83° for the semicarbazone of the ketone prepared by reaction of cyclopropyl cyanide with cyclopropylmethylmagnesium bromide. We believe their ketone was not the expected one.

(23) The nmr spectrum for cyclopropylmethyl ketone, reported by M. Hanack and H. M. Ensslin, *Ann.*, **697**, 100 (1966), has a quartet at τ 7.5 which is not present in the pure sample that we obtained.

(24) Methyl tricaprylammonium chloride obtained from General Mills Chemicals, Kankakee, Ill.

A Direct Synthesis of Benzo[*b*]thiophene-2-carboxylate Esters Involving Nitro Displacement

JAMES R. BECK

Eli Lilly and Company, Greenfield Laboratories, Greenfield, Indiana 46140

Received May 11, 1972

Facile, one-step synthesis of methyl benzo[*b*]thiophene-2-carboxylates from *o*-nitrobenzaldehydes and methyl 3-aminobenzo[*b*]thiophene-2-carboxylates from *o*-nitrobenzonitriles are described. Both reactions involve nucleophilic displacement of activated nitro functions followed by base-catalyzed ring closures.

The first synthesis of benzo[*b*]thiophene-2-carboxylic acid was reported by Friedländer and Lenk.[1] The acid was formed by a series of reactions involving alkylation of *o*-mercaptobenzaldehyde with chloroacetic acid followed by ring closure in fused alkali. Modifications of this procedure were used in the preparation of 5-nitrobenzo[*b*]thiophene-2-carboxylic acid[2–4] and 5,6-dimethoxybenzo[*b*]thiophene-2-carboxylic acid.[5,6] A further modification of this general ring-closure principle, but starting with *o*-methylmercaptoacetophenone, has been reported recently by Ruwet and Renson.[7] The disadvantages of these approaches have been the inaccessibility of the starting materials and the low overall yields obtained. A second method, reported by Campaigne and Cline[8] and improved upon by Chakrabarti and coworkers,[9] involved oxidative cyclization of β-aryl-α-mercaptoacrylic acids and gave high yields especially in aryl systems containing methoxyl functions. A related synthesis was reported by Ruwet and Renson.[10]

An even less accessible group of compounds has been the 3-aminobenzo[*b*]thiophene-2-carboxylic acids. Friedländer and Laske[11] reported the synthesis of the parent compound by a sequence involving alkylation of *o*-mercaptoaniline with chloroacetic acid, diazotization, displacement by cyanide ion, and, finally, fusion with alkali. More recently, a synthesis of ethyl 3-aminobenzo[*b*]thiophene-2-carboxylate was reported by Carrington and coworkers.[12] This compound was prepared by a ring-opening rearrangement of 3-chloro-1,2-benzisothiazole.[13] The generality of these methods again suffers from inaccessibility of starting materials.

The author wishes to report facile, one-step syntheses of both methyl 3-aminobenzo[*b*]thiophene-2-carboxylates from *o*-nitrobenzonitriles and methyl benzo[*b*]-thiophene-2-carboxylates from *o*-nitrobenzaldehydes. The ease of nucleophilic displacement of activated nitro functions in aromatic systems has been known for some time, and scattered examples of its utility occur throughout the chemical literature. Bunnett and coworkers[14] studied the relative displacement rates by piperidine in substituted 2,4-dinitrobenzenes. They found the rate of nitro displacement was more than 200 times that of chlorine and was nearly equal to fluorine. In similar studies, Bolto and Miller,[15] using methoxide ion as the nucleophile, established the following order of ease of displacement: $SMe_2^+ > NMe_3^+ > F > NO_2 > Cl$. In the reactions to be discussed, advantage is taken of this

(1) P. Friedländer and E. Lenk, *Ber.*, **45**, 2083 (1912).
(2) L. F. Fieser and R. G. Kennelly, *J. Amer. Chem. Soc.*, **57**, 1611 (1935).
(3) K. Fries, H. Heering, E. Hemmecke, and G. Siebert, *Ann.*, **527**, 83 (1937).
(4) F. G. Bordwell and C. J. Albisetti, Jr., *J. Amer. Chem. Soc.*, **70**, 1955 (1948).
(5) J. Sićе and M. Mednick, *ibid.*, **75**, 1628 (1953).
(6) D. G. Bew and G. R. Clemo, *J. Chem. Soc.*, 1314 (1953).
(7) A. Ruwet and M. Renson, *Bull. Soc. Chim. Belg.*, **79**, 75 (1970).
(8) E. Campaigne and R. E. Cline, *J. Org. Chem.*, **21**, 39 (1956).
(9) R. M. Chakrabarti, N. B. Chapman, and K. Clarke, *Tetrahedron*, **25**, 2781 (1969).
(10) A. Ruwet and M. Renson, *Bull. Soc. Chim. Belg.*, **79**, 593 (1970).
(11) P. Friedländer and A. Laske, *Ann.*, **351**, 412 (1907).
(12) D. E. L. Carrington, K. Clarke, and R. M. Scrowston, *Tetrahedron Lett.*, 1075 (1971).
(13) A. Reissert, *Ber.*, **61**, 1680 (1928).
(14) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *J. Amer. Chem. Soc.*, **79**, 385 (1957).
(15) B. A. Bolto and J. Miller, *Aust. J. Chem.*, **9**, 74 (1956).