Schmidt rearrangement of chromanones

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The mechanism of the Schmidt rearrangement has been examined in the conversion of chromanones to 1,4- and 1,5-benzoxazepinones. With substituents in the 6-, 7-, or 8-position, only electronic effects prevail resulting in the exclusive formation of 1,4-benzoxazepinones. Steric effects come into play with increasing bulk of substituents in the 5-position of the chromanone. Results now presented favor more than one pathway for the products to arise. Nuclear magnetic resonance spectra have been used to distinguish between the isomeric 1,4- and 1,5-benzoxazepinones.

Several new chromanones have been synthesized.

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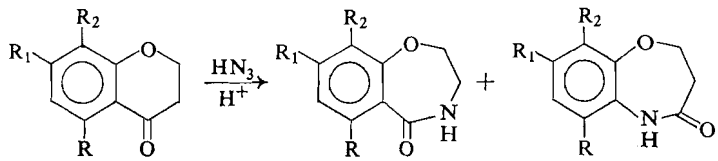


SCHEME 1

1*a*: R = R_1 = CH_3; R_2 = H
b: R = R_2 = CH_3; R_1 = H
c: R = ETHYL; R_1 = R_2 = H
d: R = R_2 = H; R_1 = ETHYL
e: R = R_2 = H; R_1 = *tert*-BUTYL

2*a*: R = R_1 = CH_3; R_2 = H
b: R = R_2 = CH_3; R_1 = H
c: R = ETHYL; R_1 = R_2 = H
d: R = R_2 = H; R_1 = ETHYL
e: R = R_2 = H; R_1 = *tert*-BUTYL

3*a*: R = R_1 = CH_3; R_2 = H
b: R = R_2 = CH_3; R_1 = H
c: R = ETHYL; R_1 = R_2 = H

The mechanism of Schmidt rearrangement has been a subject of considerable attention during recent years. Smith (1, 2) suggested the iminodiazonium ion as an intermediate in this rearrangement but the universality of involvement of this intermediate has recently been questioned by Lansbury and Mancuso (3) who favor the iminium cation, because of the nonstereospecificity observed in their experiments. We have been interested in the synthesis of benzoxazepines by the Schmidt rearrangement of chromanones (4) and in this paper we present the results of our experiments in the context of the mechanism of this rearrangement.

Results

5,7-Dimethyl Chromanone[1]

Schmidt rearrangement of 5,7-dimethyl chromanone (**1***a*) gave a 60% yield of a solid (m.p. 119–124°) which was shown by nuclear magnetic resonance (n.m.r.) spectra to be a mixture of 6,8-dimethyl-2,3-dihydro-1,4-benzoxazepin-5-(4*H*)-one (**2***a*) and 6,8-dimethyl-2,3-dihydro-1,5-benzoxazepin-4(5*H*)-one (**3***a*) in a ratio of 46:54, (Scheme 1).

In the n.m.r. spectrum (Fig. 1) of the crude reaction product, peaks from the two isomers are distinctly discernible. The triplets at δ 4.5 and δ 2.75 are assignable respectively to the C-2 and C-3 methylenes of **3***a* while the triplet at δ 4.3 and the quartet[2] at δ 3.35 represent the C-2 and C-3 methylenes of **2***a*. Of the two sharp singlets, the one integrating to 9 protons is assignable to the methyls at C-6 and C-8 positions of **3***a* and at C-8 of **2***a*. The C-6 methyl of **2***a* appears as a singlet at δ 2.45 being deshielded by the amide carbonyl.

These isomeric lactams were separated by column chromatography to give **2***a*, m.p. 155°, and **3***a*, m.p. 141°, in a ratio of 46:54 respectively and were also identified individually by n.m.r. The spectrum of **3***a* showed two triplets at δ 4.5

[1]Lockhart and Evans (5) reported that in three trials, Schmidt reaction of **1***a* gave only 6,8-dimethyl-2,3-dihydro-1,5-benzoxazepin-5(4*H*)one, m.p. 123–125°, in 5% yield.

[2]A sextet (or a multiplet) would be expected from additional NH participation in spin–spin coupling of the C-3 methylene protons. However, in all these cases it appears as a quartet only.

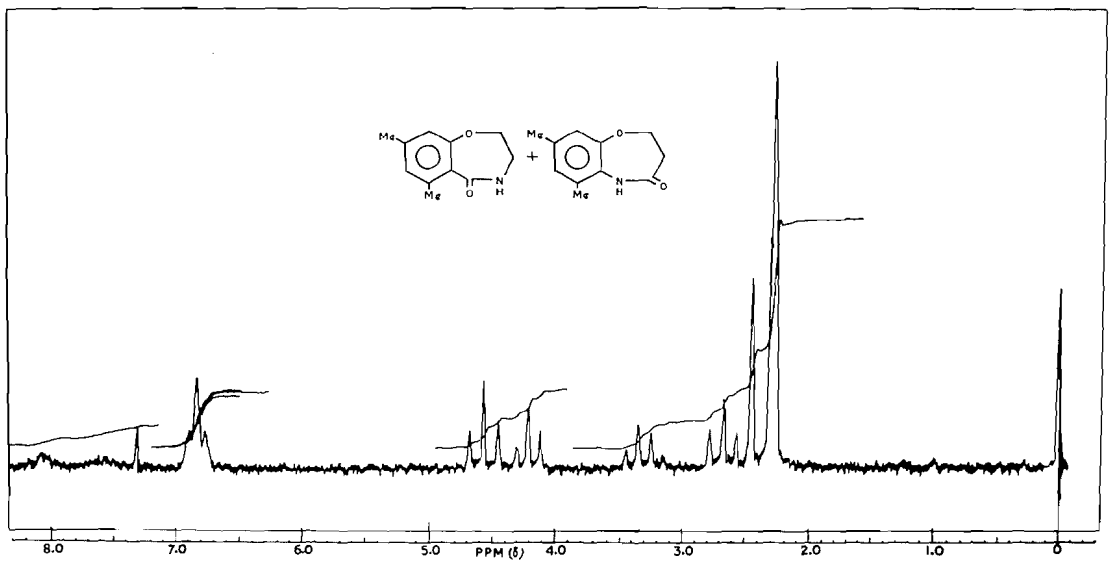


FIG. 1. Nuclear magnetic resonance spectrum of crude product from Schmidt reaction on 5,7-dimethyl chromanone (**1***a*).

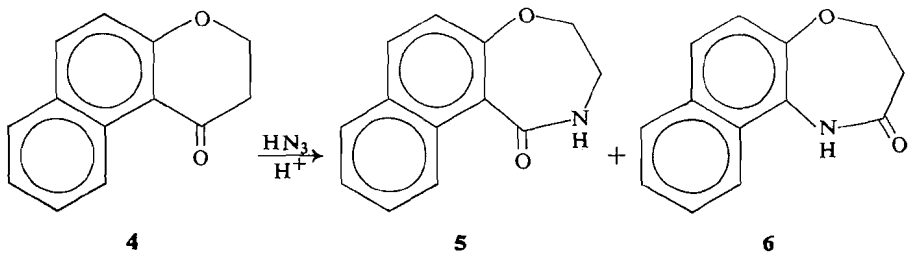
(—O—CH_2) and δ 2.75 (—CH_2—CO—) and a sharp singlet (6H) at δ 2.3 for the two methyl groups besides the broad NH absorption at δ 8.5. In contradistinction, the spectrum of **2***a* showed a quartet at δ 3.35 assignable to —NH—CH_2— arising from the participation of the adjacent NH proton in spin–spin coupling. The triplet centered at δ 4.3 represents the C-2 methylene proton while the singlets at δ 2.45 and δ 2.3 arise from the C-6 and C-8 methyls respectively.

5,8-Dimethyl Chromanone

To obtain additional evidence that the bulk of the methyl group in the 5-position only affects the course of the Schmidt reaction, 5,8-dimethyl chromanone was rearranged. The product (57% yield) was a mixture of two isomeric lactams separated and identified as 6,9-dimethyl-2,3-dihydro-1,4-benzoxazepin-5(4*H*)-one, m.p. 150° (**2***b*) and 6,9-dimethyl-2,3-dihydro-1,5-benzoxazepin-4(5*H*)-one, m.p. 135–136° (**3***b*) in a ratio of 45:55 respectively. The n.m.r. spectra (see Experimental) of the individual isomers fully corroborate the structure assigned.

2,3-Dihydronaphth(2,1-b)pyran-1-one (4)

Schmidt reaction afforded a solid, m.p. 116°, shown by n.m.r. to consist of 1,4- and 1,5-isomeric products in a ratio of 40:60 respectively. Column chromatography enabled separation into 3,4-dihydronaphth(1,2-*f*)(1,4)oxazepin-1-(2*H*)-one (**5**), m.p. 143–144°, and 3,4-dihydronaphth(2,1-*b*)(1,4)oxazepin-2(1*H*)-one (**6**), m.p. 156° (Scheme 2). The structures were confirmed by n.m.r. spectra, the basis of distinction again being the NH participation in spin–spin coupling of the C-3 methylene protons. The spectrum of **6** (Fig. 2) consists of two triplets at δ 2.75



4 **5** **6**

SCHEME 2

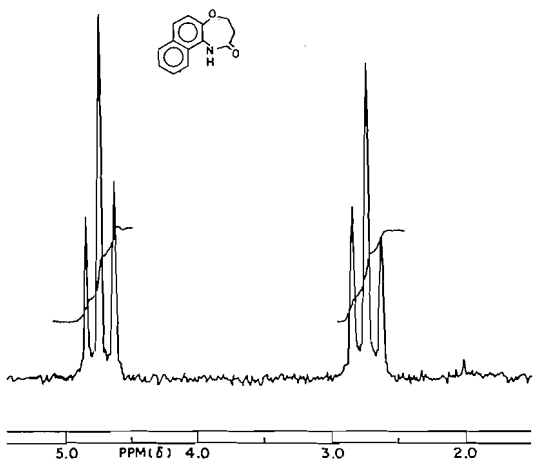


FIG. 2. Nuclear magnetic resonance spectrum (part) of 3,4-dihydronaphth(2,1-*b*)(1,4)oxazepin-2(1*H*)-one (**6**).

(—CO—CH_2—) and δ 4.75 (—O—CH_2—) the aromatic multiplet (6H) in the region δ 7.2–8.2 and a broad absorption (—NH—CO—) at δ 8.85 while that of **5** (Fig. 3) shows a quartet at δ 3.35 (—N—CH_2—) and a triplet at δ 4.35 (—O—CH_2—) assignable respectively to the C-3 and C-4 methylenes, the other features being similar.

The availability of 1-nitro-2-naphthol made possible an independent synthesis of **6**. 1-Nitro-2-naphthol on treatment with β-chloropropionic acid gave β-(1-nitro-2-naphthoxy)-propionic acid. Catalytic reduction to the amino derivative followed by cyclization under pressure at elevated temperature afforded 3,4-dihydronaphth-(2,1-*b*)(1,4)oxazepin-2(1*H*)-one (m.p. 156°) identical with the Schmidt reaction product in all respects.

5-Ethyl Chromanone

The synthesis of this chromanone was achieved as follows. Cyanoethylation of *m*-ethylphenol gave β-(*m*-ethylphenoxy)-propionitrile which upon hydrolysis followed by cyclization with phosphorus pentoxide in refluxing benzene resulted in the formation of both 5-ethyl chromanone and 7-ethyl chromanone in a ratio of 4:6 determined by gas–liquid chromatography (g.l.c.). This mixture was efficiently fractionated in a Piros–Glover M8480 spinning band micro still into 5-ethyl chromanone (**1***c*), b.p. 97.5°/1 mm and 7-ethyl chromanone (**1***d*), b.p. 113°/1 mm, identified on the basis of the respective n.m.r. spectrum. These new chromanones were converted into the corresponding oximes, the n.m.r. spectra (see Experimental) of which confirm the structures assigned to **1***c* and **1***d*.

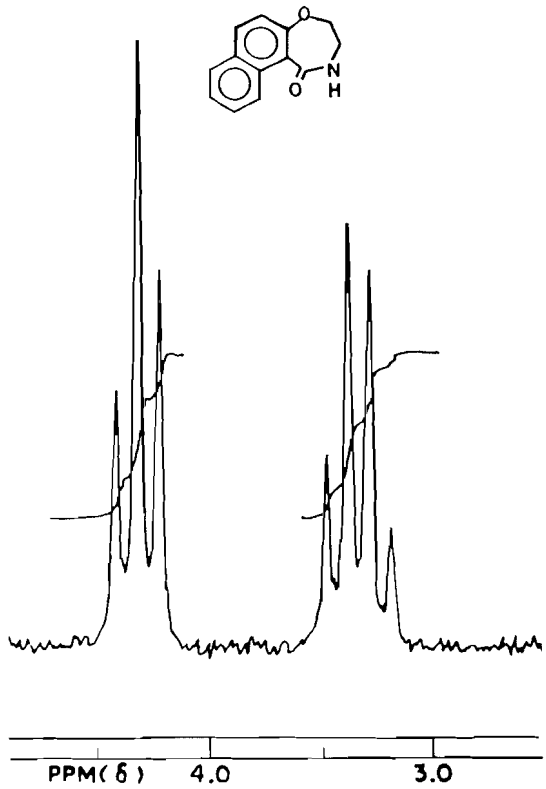


FIG. 3. Nuclear magnetic resonance spectrum (part) of 3,4-dihydronaphth(1,2-*f*)(1,4)oxazepin-1(2*H*)-one (**5**).

Schmidt rearrangement of 5-ethyl chromanone (**1***c*) gave a mixture of 6-ethyl-2,3-dihydro-1,4-benzoxazepin-5(4*H*)-one (**2***c*) and 6-ethyl-2,3-dihydro-1,5-benzoxazepin-4(5*H*)-one (**3***c*) in a ratio of 22:78 respectively (Scheme 1).

7-Ethyl Chromanone

Nuclear magnetic resonance spectra (Fig. 4) of the crude product from Schmidt rearrangement of this compound (**1***d*) indicated the exclusive presence of 8-ethyl-2,3-dihydro-1,4-benzoxazepin-5(4*H*)-one (**2***d*), m.p. 89°. The quartet (2H) at δ 2.7 and the triplet (3H) at δ 1.2 arise from the C-8 ethyl group while the quartet (2H) at δ 3.5 and the triplet (2H) at δ 4.4 are assignable to the C-3 and C-2 methylenes respectively. The deshielded C-6 aromatic proton appears as an AB type doublet at δ 7.95 ($J_{6,7}$ = 8 c.p.s.) while the C-7 proton is the doublet at δ 7.0 one limb

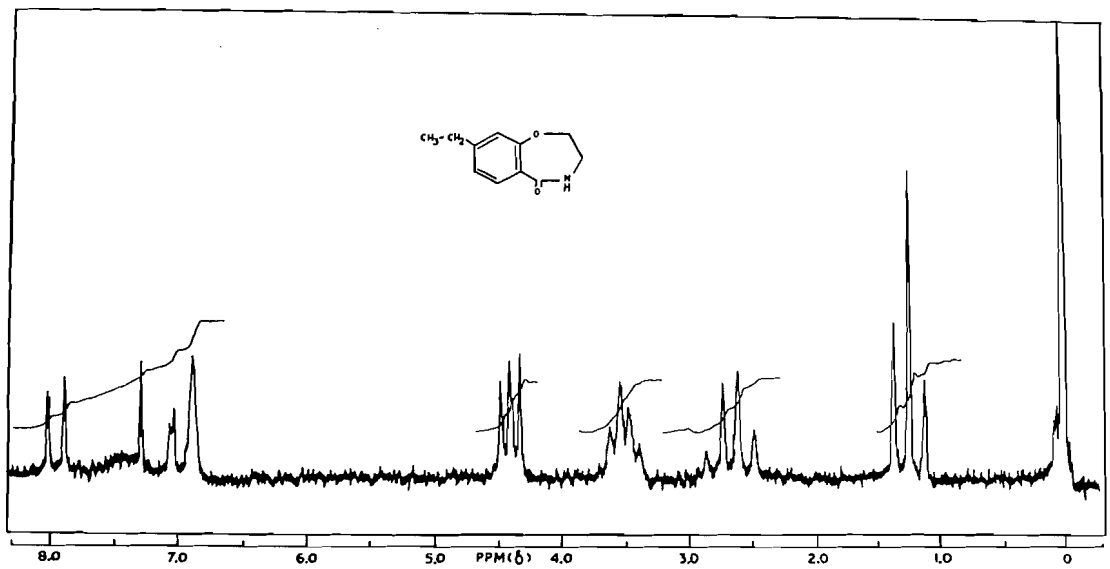


FIG. 4. Nuclear magnetic resonance spectrum of crude product from Schmidt reaction on 7-ethyl chromanone (**1***d*).

of which is merged with that of the C-9 proton. The broad absorption at δ 7.4 represents the NH.

5,7-Di-t-butyl Chromanone

Cyanoethylation of 3,5-di-*t*-butyl phenol gave β-(3,5-di-*t*-butyl phenoxy)-propionitrile, which on acid-catalyzed hydrolysis and cyclization with phosphorus pentoxide in benzene gave 5,7-di-*t*-butyl chromanone. In two trials, Schmidt rearrangement did not occur and the starting material was recovered unchanged as confirmed by g.l.c., infrared, and n.m.r.

However, when cyclization of β-(3,5-di-*t*-butyl phenoxy)-propionitrile was earlier attempted by using polyphosphoric acid at 180°, an interesting product was encountered in which one *t*-butyl group had been lost.[3] The structure of this new product was assigned as 7-*t*-butyl chromanone (**1***e*) on the basis of its n.m.r. spectrum. Schmidt rearrangement of this chromanone gave only one product identified as 8-*t*-butyl-2,3-dihydro-1,4-benzoxazepin-5(4*H*)-one (**2***e*), m.p. 162°. The n.m.r. spectrum showed one *t*-butyl group at δ 1.35 and a 2-proton signal at δ 3.55 and δ 4.4, assignable to C-3 (NH—CH_2) and C-2 (O—CH_2) methylenes respectively. In the aromatic region, the deshielded C-6 proton appeared as an AB-type doublet at δ 8.0 ($J_{6,7}$ = 8 c.p.s.), the C-9 proton *meta* coupled ($J_{7,9}$ = 2 c.p.s.) at δ 7.05 while the C-7 proton *ortho* coupled to C-6 ($J_{6,7}$ = 8 c.p.s.) and *meta* coupled to C-9 ($J_{7,9}$ = 2 c.p.s.) appeared at δ 7.15, the NH proton being a broad signal in the region δ 7.4–7.9.

The results obtained in these experiments are summarized in Table I.

Discussion

In an earlier publication (4) we had reported the Schmidt reaction on various derivatives of chromanones carrying alkyl, alkyloxy, and halogen substituents in 6- and 8-positions, the product in every case being a derivative of 1,4-benzoxazepin-5-one. Results now presented[4] show that an alkyl group in the 7-position of chromanone does not also alter the course of the reaction, the product being again a derivative of 1,4-benzoxazepin-5-one (Scheme 1). The bulk of the substituents in the 5-position, however, does

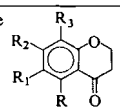
[3]Lansbury and Mancuso (3) reported an instance of de-*t*-butylation during the Beckmann rearrangement of 8-*t*-butyl,5-bromo-1-tetralone oxime in polyphosphoric acid at 110–120°.

[4]All experiments described here were carried out using concentrated sulfuric acid and sodium azide. An experiment using sodium azide and polyphosphoric acid at 60° also gave one product, 2,3-dihydro-1,4-benzoxazepin-5(4*H*)-one (as seen by n.m.r.), resulting from exclusive alkyl bond migration.

TABLE I

Migratory aptitudes in Schmidt rearrangement of chromanones*

No.	Chromanone R_3	R_2	R_1	R	Yield %	Isomer ratio % aryl migration	% alkyl migration
1	H	H	H	H	78	0	100
2	H	CH_2—CH_3	H	H	55	0	100
3	H	C—$(CH_3)_3$	H	H	51	0	100
4	H	CH_3	H	CH_3	60	54	46
5	CH_3	H	H	CH_3	57	55	45
6	2,3-Dihydronaphtho (2,1-*b*)pyran-1-one				50	60	40
7	H	H	H	CH_2—CH_3	45	78	22
8	H	C—$(CH_3)_3$	H	C—$(CH_3)_3$	—	No reaction	

*Compounds of structure 

influence the course of reaction since the major product in these cases arises by aryl bond migration, namely, the derivatives of 1,5-benzoxazepin-4-one (Table I).

In chromanones unsubstituted in the 5-position only electronic effect (4, 5) prevails. Conjugation arising out of the lone pair of electrons on ethereal oxygen atom would stabilize the aryl bond[5] by imparting a partial double bond character. Since the benzenoid character of the benzene ring is lost, a phenonium type of intermediate which would favor aryl bond migration is not possible. Alkyl bond migration therefore results. The involvement of iminodiazonium ion **9** (Scheme 3, R = H) as the intermediate is consistent with conjugation with the benzene ring while the azidohydrin **7** (carbonyl carbon being of sp^3 nature) would remove conjugation with the benzene ring and thereby with ethereal oxygen.

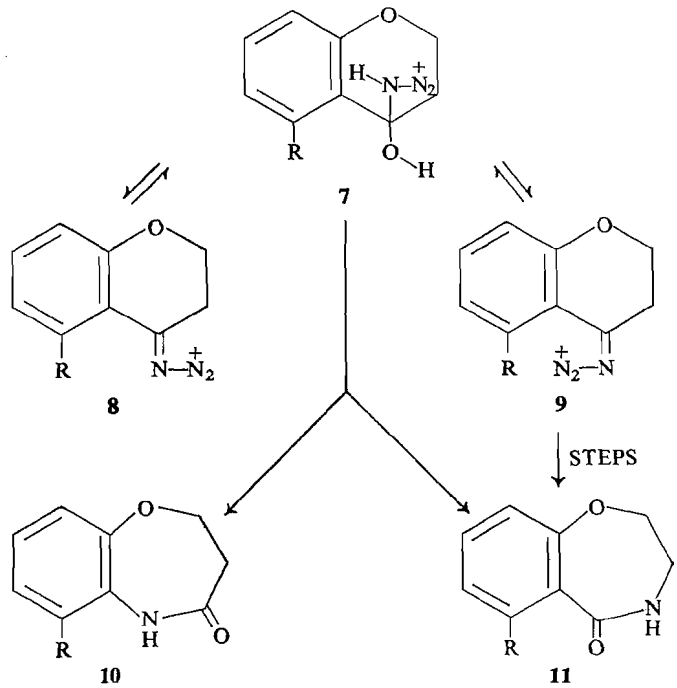
It is seen from Table I that as the bulk of the 5-position increases there is a corresponding increase in the quantity of the product arising from aryl bond migration, namely, derivatives of 1,5-benzoxazepin-4-one. A scrutiny of the models of 2,3-dihydronaphth(2,1-*b*)pyran-1-one (**4**) and 5-ethyl chromanone (**1***c*) shows that if iminodiazonium ion were to be considered, due to enhanced steric repulsion the relative population in the equilibrium of the iminodiazonium ion **9** (Scheme 3) would be extremely low. Then 40 and 20% of sterically non-favored alkyl bond migration may arise by direct rearrangement of the azidohydrin **7**. It is conceivable that when R = H the dehydration step of the azidohydrin **7** to the iminodiazonium ions **8** or **9** is favored, whereas this dehydration will not be sterically favored, when R = CH_3 etc., since in the iminodiazonium ion the C = N is coplanar with the benzene ring and the 5-alkyl substituent, whereas in the azidohydrin the hydroxyl and the azido groups would be above and below the plane of the ring. Steric resistance to iminodiazonium ion formation may thus allow rearrangement of the azidohydrin to become dominant. The increase in aryl bond migration with increase in the bulk of the substituent in the 5-position of chromanone may be attributed to a preference by the diazo nitrogens of the azido group (due to non-bonded interaction with the substituent in the 5-position of chromanones) for a conformation which is *trans* to the aryl bond. The dissimilarity in our results (7) (when R = CH_3,C_2H_5) from Beckmann rearrangement on corresponding chromanone oximes[6] under similar conditions, and nonformation of tetrazoles[7] also indicates that an intermediate of the type of azidohydrin and not iminodiazonium ion is involved.

Steric and electronic effects thus influence the course of Schmidt rearrangement. Our evidence

[5]If such a stabilization were not to exist, then by virtue of the phenyl participation, the aryl bond should migrate as observed in the case of tetralones (1, 3).

[6]Beckmann rearrangement of chromanone oximes shows that a methyl or bulkier group in 5-position leads to exclusive aryl bond migration.

[7]We were unable to isolate any tetrazole using the conditions reported by Dimaio and Permutti (6).



SCHEME 3

leads us to the conclusion that the products can be derived either through the iminodiazonium ion or when the latter is not sterically favored through the azidohydrin. In other words, more than one pathway, different but consistent, are possible. A similar conclusion was arrived at by Dimaio and Permutti (6) from their work on Schmidt rearrangement of *cis*-8-methyl-hydrindan-1-one.

Experimental

All melting points were determined by the capillary method and are uncorrected. Petroleum ether refers to the fraction of boiling range 40–60°. Infrared spectra were recorded on a Perkin–Elmer model F221 spectrometer equipped with sodium chloride optics and n.m.r. spectra were recorded on a Varian A-60 instrument in $CDCl_3$ solutions with TMS as the internal standard.

Synthesis of Chromanones

5,7-Dimethyl chromanone (5) and 2,3-dihydronaphth-(2,1-*b*)pyran-1-one[8] were prepared as reported in the literature.

Only typical procedures are reported here; all experiments were carried out using essentially these procedures.

Cyanoethylation of Phenols

The phenol (0.1 mole) was added to acrylonitrile (0.12 mole) containing sodium (1.5% on the weight of the phenol). The mixture was heated in an autoclave for 4–6 h at 125–135°, cooled, extracted in chloroform, and washed with 5% sodium hydroxide solution till free from the phenol. Drying over sodium sulfate and removal of solvent gave the desired nitrile. The following were prepared by this method.

β-*(3,6-Dimethyl phenoxy)-propionitrile*, yield 74%, b.p. 154°/11 mm; $\nu_{C\equiv N}$(Nujol) 2250 cm^{-1}.

Anal. Calcd. for $C_{11}H_{13}ON$: C, 75.4; H, 7.5; N, 8.0. Found: C, 75.3; H, 7.1; N, 7.9.

β-*(m-Ethylphenoxy)-propionitrile*, yield 63%, b.p. 128°/9 mm; $\nu_{C\equiv N}$ (film) 2245 cm^{-1}.

Anal. Calcd. for $C_{11}H_{13}ON$: C, 75.4; H, 7.5; N, 8 0. Found: C, 75.1; H, 7.4; N, 7.7.

β-*(3,5-Di-t-butyl phenoxy)-propionitrile*, yield 58%, m.p. 81°; $\nu_{C\equiv N}$(film) 2220 cm^{-1}.

Anal. Calcd. for $C_{17}H_{25}ON$: C, 78.7; H, 9.7; N, 5.4. Found: C, 78.6; H, 9.6; N, 5.2.

Hydrolysis of β-*Phenoxy Propionitrile*

A mixture of the nitrile (0.22 mole) and concentrated hydrochloric acid (0.2 mole) was stirred and refluxed for 5–8 h. As the reaction mixture became hot the solid dissolved, but as hydrolysis proceeded a precipitate appeared. The reaction mixture was cooled and diluted with water. The solid β-phenoxy propionic acid thus obtained was filtered and purified by dissolving in sodium bicarbonate solution, reprecipitation with hydrochloric acid, and crystallization from a suitable solvent.

The following acids were thus synthesized starting with appropriate β-phenoxy propionitriles.

β-*(3,6-Dimethylphenoxy)propionic acid*, yield 90%, m.p. 97°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3; Found: C, 67.7; H, 7.0.

[8]Chakravarti and Dutta (8) refer to this compound as 1-benzo-(*f*)-chromanone.

β-*(m-Ethyl phenoxy)propionic acid*, yield 85%, m.p. 112°.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3. Found: C, 67.8; H, 7.0.

β-*(3,5-Di-t-butylphenoxy)propionic Acid*

Hydrolysis of β-(3,5-di-*t*-butyl phenoxy)-propionitrile with concentrated hydrochloric acid at reflux temperature for 30 h gave back the starting nitrile. However, hydrolysis occurred under pressure.

The nitrile (12 g) was heated in an autoclave with concentrated hydrochloric acid (150 ml) for 10 h, cooled, and taken up in chloroform. Drying and removal of solvent gave 10 g (83%) of β-(3,5-*t*-butyl phenoxy)propionic acid, m.p. 97° (from petroleum ether); $\nu_{C=O}$ (KBr) 1705 cm^{-1}.

Anal. Calcd. for $C_{17}H_{26}O_3$: C, 73.3; H, 9.4. Found: C, 73.1; H, 9.1.

Cyclization of β-phenoxy propionic acids to the chromanones was carried out as reported by Chakravarti and Dutta (8). New chromanones thus prepared were the following.

6,8-Dimethyl chromanone, yield 56%, b.p. 118°/4 mm; $\nu_{C=O}$ (film) 1675 cm^{-1}.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.9. Found: C, 75.1; H, 6.8.

5- and 7-Ethyl chromanones, the mixture (4:5) of 5- and 7-ethyl chromanones was separated in an M-8480 Piros–Glover spinning band micro still, the take-off rate being 1 ml/h and at a reduced pressure of 1 mm. Two fractions were collected at 97.5 and 113°.

5-Ethyl chromanone, b.p. 97.5°/1 mm; $\nu_{C=O}$ (film) 1680 cm^{-1}.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.1; H, 6.8. Found: C, 74.9; H, 6.6.

5-Ethyl chromanone oxime, m.p. 70°; δ ($CDCl_3$) 7.3 (b, 1H, hydroxy), 6.7–7.2 (m, 3H, aromatic), 4.2 (t, 2H, O—CH_2), 3.1 (m, 4H, C-3 methylene and methylene of C-5 ethyl group), 1.2 (t, 3H, methyl of C-5 ethyl group) p.p.m.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.1; H, 6.9; N, 7.3. Found: C, 69.0; H, 6.7; N, 7.1.

7-Ethyl chromanone, b.p. 113°/1 mm; $\nu_{C=O}$ (film) 1683 cm^{-1}.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.1; H, 6.8. Found: C, 74.7; H, 6.5.

7-Ethyl chromanone oxime, m.p. 111°; δ ($CDCl_3$) 8.2 (b, 1H, hydroxy), 7.9 (d, 1H, deshielded C-5 proton), 7.0 (d, 1H, C-6 proton), 6.85 (b, 1H, C-8 proton), 4.4 (t, 2H, C-2 methylene); 2.9 (t, 2H, C-3 methylene), 2.7 (q, 2H, methylene of C-7 ethyl group), 1.25 (t, 3H, methyl of C-7 ethyl group) p.p.m.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.1; H, 6.9; N, 7.3. Found: C, 68.8; H, 6.7; N, 7.0.

5-7-Di-t-butyl chromanone, yield 35%, b.p. 180–182°/5 mm; $\nu_{C=O}$ (film) 1670 cm^{-1}; δ ($CDCl_3$) 1.3 (s, 9H, C-7 *t*-butyl group), 1.5 (s, 9H, C-5 *t*-butyl group), 2.8 (t, 2H, C-3 methylene), 4.4 (t, 2H, C-2 methylene), 6.9–7.1 (b, 2H, aromatic) p.p.m.

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.4; H, 9.3. Found: C, 78.3; H, 9.1.

7-t-Butyl Chromanone

β-(3,5-Di-*t*-butylphenoxy)propionitrile (15 g) was heated with polyphosphoric acid (220 g) at 180–185° for 2.5 h. Pouring the reaction mixture into crushed ice and extraction with chloroform gave 7.5 g (50%) of 7-*t*-butyl chromanone, b.p. 140°/11 mm; $\nu_{C=O}$ (film) 1675 cm^{-1}; δ ($CDCl_3$) 7–8 (m, 3H, aromatic); 4.4 (t, 2H, C-2 methylene), 2.95 (t, 2H, C-3 methylene), 1.3 (s, 9H, protons of C-7 *t*-butyl group) p.p.m.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9. Found: C, 76.3; H, 7.8.

Schmidt Rearrangement[9]

Reactions were carried out under the same conditions as reported by us earlier (4).

5,7-Dimethyl chromanone (**1***a*) gave 60% yield of a crude product, m.p. 119–124°. Thin-layer chromatography using chloroform – petroleum ether (1:9) solvent system showed two spots. This crude mixture (2 g) was separated on a silica gel column. Elution first with chloroform – petroleum ether (1:9) gave 1 g of a white compound (**3***a*), m.p. 141°; elution next with chloroform gave 0.91 g of a compound (**2***a*), m.p. 155°. Similar proportions of **3***a* (2.04 g) and **2***a* (1.9 g) were obtained on separation of 4 g of the crude reaction mixture from another experiment.

Compound **3***a* was identified as *6,8-dimethyl-2,3-dihydro-1,5-benzoxazepin-4(5H)-one*, m.p. 141°; $\nu_{C=O}$ (KBr) 1650 cm^{-1}.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.1; H, 6.9; N, 7.1. Found: C, 68.7; H, 6.6; N, 7.1.

Compound **2***a* was identified as *6,8-dimethyl-2,3-dihydro-1,4-benzoxazepin-5(4H)-one*, m.p. 155°; $\nu_{C=O}$ (KBr) 1660 cm^{-1}.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.1; H, 6.9; N, 7.1. Found: C, 68.9; H, 6.7; N, 6.9.

5,8-Dimethyl chromanone (**1***b*) gave 57% yield of a crude mixture, m.p. 114–117°. The reaction product (2 g) was separated on a silica gel column. Elution, first with chloroform – petroleum ether (2:8) gave 1 g of a white compound (**3***b*), m.p. 135–136°; elution then by chloroform gave 0.89 g of a compound (**2***b*), m.p. 150°.

Compound **3***b* was identified as *6,9-dimethyl-2,3-dihydro-1,5-benzoxazepin-4(5H)-one*, m.p. 135–136°; $\nu_{C=O}$ (KBr) 1670 cm^{-1}; δ ($CDCl_3$) 8.4 (b, 1H, NH), 6.9 (s, 2H, C-7 and C-8 protons), 4.55 (t, 2H, C-2 methylene); 2.65 (t, 2H, C-3 methylene), and 2.25 (s, 6H, for C-6 and C-9 methyl groups) p.p.m.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.1; H, 6.9; N, 7.3. Found: C, 68.9; H, 6.6; N, 7.2.

Compound **2***b* was identified as *6,9-dimethyl-2,3-dihydro-1,4-benzoxazepin-5(4H)-one*, m.p. 150°; $\nu_{C=O}$ (KBr) 1650 cm^{-1}.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.1; H, 6.9; N, 7.3. Found: C, 69.0; H, 6.7; N, 7.3.

2,3-Dihydronaphth(2,1-b)pyran-1-one (**4**) gave a 50% yield of a mixture of isomeric amides (2 g) m.p. 116°, which was separated over a silica gel column. Elution with chloroform – petroleum ether (3:7) gave 1.1 g of compound **6**, m.p. 156°; elution next by chloroform gave 0.8 g of compound **5**, m.p. 143–144°.

Compound **6** was identified as *3,4-dihydronaphth(2,1-b)-(1,4)-oxazepin-2(1H)-one*, m.p. 156°; $\nu_{C=O}$ (KBr) 1675 cm^{-1}.

[9]The acidic layer was examined in each case for possible presence of hydrolytic cleavage products of the benzoxazepinones formed but none were found. In only one case a small quantity of aniline was present which may have arisen from decomposition of hydrazoic acid or as suggested by us earlier (9).

Anal. Calcd. for $C_{13}H_{11}O_2N$: C, 73.2; H, 5.2; N, 6.6. Found: C, 73.1; H, 5.2; N, 6.5.

Compound **5** was identified as *3,4-dihydronaphth-(1,2-f)(1,4)-oxazepin-1(2H)-one*, m.p. 143–144°; $\nu_{C=O}$ (KBr) 1655 cm^{-1}.

Anal. Calcd. for $C_{13}H_{11}O_2N$: C, 73.2; H, 5.2; N, 6.6. Found: 73.1; H, 5.0; N, 6.4.

7-Ethyl chromanone (**1***d*) gave *8-ethyl-2,3-dihydro-1,4-benzoxazepin-5(4H)-one* (**2***d*), m.p. 89° in 55% yield.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.1; H, 6.9; H, 7.3. Found: C, 68.7; H, 6.7; N, 7.1.

5-Ethyl chromanone (**1***c*) gave a 45% yield of a mixture of isomeric amides, m.p. 120° which consisted of *6-ethyl-2,3-dihydro-1,4-benzoxazepin-5(4H)-one* (**2***c*) and *6-ethyl-2,3-dihydro-1,5-benzoxazepin-4(5H)-one* (**3***c*) in a ratio (22:78).

7-t-butyl chromanone (**1***e*) gave 50% yield of 8-*t*-butyl-1,4-benzoxazepin-5(4*H*)-one (**2***e*), m.p. 162°; $\nu_{C=O}$ (KBr) 1645 cm^{-1}.

Anal. Calcd. for $C_{13}H_{17}O_2N$: C, 71.2; H, 7.8; N, 6.4. Found: C, 70.9; H, 7.8; N, 6.5.

5,7-Di-t-butyl chromanone was recovered unchanged in two experiments as borne out by g.l.c., infrared, and n.m.r.

Synthesis of 3,4-Dihydronaphth(2,1-b)(1,4)oxazepin-2(1H)-one

β-*(1-Nitro naphthoxy)propionic Acid*

1-Nitro-2-naphthol (38 g) was dissolved in aqueous potassium hydroxide (30%, 60 ml) and heated on a water bath. To this was added in small portions, during 2 h, a solution of β-chloropropionic acid (26 g) neutralized with sodium bicarbonate. The reaction mixture was further heated for 3 h, cooled, acidified with hydrochloric acid, and extracted with ether. The ether solution was extracted with aqueous sodium bicarbonate. Neutralization of the alkaline layer with hydrochloric acid gave 13 g (25%) of β-(1-nitro naphthoxy)propionic acid, m.p. 101°; $\nu_{C=O}$ (KBr) 1700 cm^{-1}.

Anal. Calcd. for $C_{13}H_{11}O_5N$: C, 59.8; H, 4.3; N, 5.4. Found: C, 59.7; H, 4.1; N, 5.1.

β-*(1-Amino naphthoxy)propionic Acid*

β-(1-Nitro naphthoxy)propionic acid (6.5 g) was mixed with 10% palladium-on-charcoal (350 mg) in absolute ethanol (150 ml) and hydrogenated at room temperature for 3 h. Filtration of the catalyst and removal of solvent gave 5 g (87%) of β-(1-amino naphthoxy)propionic acid, m.p. 88°.

Anal. Calcd. for $C_{13}H_{13}O_3$: C, 67.5; H, 5.7; N, 6.1. Found: C, 67.4; H, 5.6; N, 6.0.

3,4-Dihydronaphth(2,1-b)(1,4)oxazepin-2(1H)-one (**6**)

β-(1-Amino naphthoxy)propionic acid (4.6 g) on heating *in vacuo* (5 ml) at 150° for 3 h gave 2 g (48%) of 3,4-dihydronaphth(2,1-*b*)(1,4)oxazepin-2(1*H*)-one, m.p. 156°; $\nu_{C=O}$ (KBr) 1675 cm^{-1}. This was identical in every respect with the Schmidt rearrangement product (mixture melting point, 156°; t.l.c., same R_f value, infrared spectra were superimposable).

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