JOURNAL
OF
THE CHEMICAL SOCIETY

PERKIN TRANSACTIONS I
Organic and Bio-organic Chemistry

Use of 2,3-Dichloropropene and 1,3-Dichlorobut-2-ene as Synthons for Heterocyclic Compounds: Synthesis of 2-Methylbenzo[*b*]furans, 2-Methylbenzo[*b*]thiophens, and 4-Methyl-2*H*-chromen †

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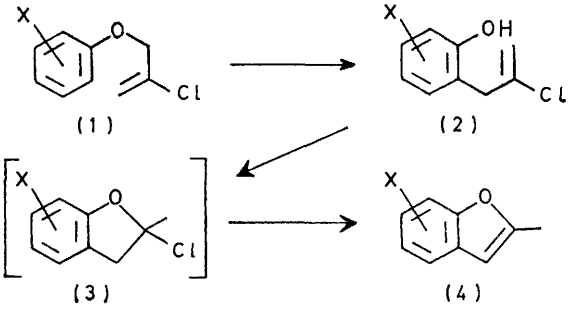
The aryl 2-chloroprop-2-enyl ethers (1a—g), prepared from the appropriate phenols by treatment with 2,3-dichloropropene, underwent smooth Claisen rearrangement to the 2-(2-chloroprop-2-enyl)phenols (2a—g), acid-catalysed cyclization of which afforded the 2-methylbenzo[*b*]furans (4a—g). The chloropropenyl thioethers (5a—e) yielded the 2-methylbenzo[*b*]thiophens (6a—e) directly when heated at 200 °C in *NN*-diethylaniline. Attempts to prepare 2-methylindoles by this method failed. 3-Chloro-1-phenoxybut-2-ene (7a) cyclized thermally to give 4-methyl-2*H*-chromen (9a). Similar attempts to prepare 1,2-dihydro-4-methylquinoline (12) and 4-methyl-2*H*-thiochromen (18) failed.

THE utility of chloro-olefins in carbocyclic chemistry has been well documented in recent years.[1] Reports of the use of vinyl halides in the synthesis of aziridines [2] and 2-methylindoles [3] prompted us to examine their potential in the synthesis of other heterocyclic systems.

One convenient synthesis of 2,3-dihydrobenzofurans involves the acid-catalysed cyclization of *o*-allylphenols.[4] In an effort to extend this synthesis to 2-methylbenzo[*b*]-furans we prepared several aryl 2-chloroprop-2-enyl ethers (1a—g). These were readily synthesized in high yield (Table 1) by treatment of the appropriate phenol with 2,3-dichloropropene and potassium carbonate in acetone heated under reflux. The ethers, when heated in *NN*-diethylaniline or *p*-di-isopropylbenzene, readily underwent Claisen rearrangement [5a] to give 2-(2-chloroprop-2-enyl)phenols, (2a—g), in high yield (Table 2). The phenols (2) were stable at 0 °C; however, after several weeks at room temperature extensive cyclization to the benzo[*b*]furan was observed.

The phenols (2a—g) were readily cyclized to the corresponding benzo[*b*]furans (4a—g) upon treatment with concentrated hydrochloric acid at 85—89 °C [Table 3, method (a)]. When base was excluded from the work-up of these reactions, the unstable intermediate (3) could be observed by n.m.r.



a; X = H b; X = *p*-Me c; X = *p*-OMe
d; X = *p*-Cl e; X = *o*-Me f; X = *o*-OMe
g; X = *o*-Cl

In the cyclization of the phenols (2a—e) the yields of (4a—e) ranged from 51 to 77%; in contrast, (2f and g) afforded only about 5% of the desired benzo[*b*]furan. Treatment of (2f and g) with trifluoroacetic acid [method

† Preliminary communication, W. K. Anderson and E. J. LaVoie, *J.C.S. Chem. Comm.*, 1974, 174.

[1] P. T. Lansbury, *Accounts Chem. Res.*, 1972, **5**, 311.

[2] A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1957, **79**, 1462; A. T. Bottini and R. E. Olsen, *ibid.*, 1962, **84**, 195; A. T. Bottini, B. J. King, and R. E. Olsen, *J. Org. Chem.*, 1963, **28**, 3241.

[3] B. McDonald, A. McLean, and G. R. Proctor, *J.C.S. Chem. Comm.*, 1973, 208.

[4] R. C. Elderfield and V. B. Meyer, in 'Heterocyclic Compounds,' vol. 2, ed. R. C. Elderfield, Wiley, New York, 1951, pp. 1—67.

[5] (*a*) C. D. Hurd and C. N. Webb, *J. Amer. Chem. Soc.*, 1936, **58**, 2190; (*b*) recently a similar cyclization with polyphosphoric acid has been described: I. R. Trehan, H. P. Singh, D. V. L. Rewal, and A. K. Bose, *J. Org. Chem.*, 1974, **39**, 2656.

(b)] did afford a moderate yield of (4f and g) (*ca.* 30%) Surprisingly, use of trifluoroacetic acid gave poor results in the cyclization of (2a—e).[5b]

Giraldi *et al.* have reported the cyclization of (2f) to (4f).[6] Under the conditions of this reaction (ethanolic potassium hydroxide at 120 °C) it is probable that (2f) was first converted into the acetylene, which cyclized to (4f) (*cf.* ref. 7).

The low yields obtained in the acid-catalysed cyclization of (2f and g) cannot be explained satisfactorily on the basis of either electronic or steric factors. In comparison with the *ortho*-isomers, both the *p*-chloro- and *p*-methoxy-compounds (2d and c) were readily cyclized to the corresponding benzo[*b*]furan. In fact (2c) was cyclized most rapidly and gave the highest yield of all the compounds studied. Thus electronic factors seem not to be responsible for the low yields observed. Steric factors also appear unimportant since the *o*- and *p*-methyl isomers (2e and b) were cyclized in almost identical yield.

Two factors which could influence the yield are hydrogen bonding and product decomposition. The phenolic hydroxy-group can hydrogen bond either to the olefinic bond [8] or to the *o*-chloro- or *o*-methoxy-group.[9,10] Thus, intramolecular hydrogen bonding between the phenol and the olefin could hold the molecule in an orientation

TABLE 1

Preparation of 3-aryloxy-2-chloropropenes (1)

Compound	B.p. (°C) [Torr] (lit. b.p.)	% Yield
(1a)	73 [3.3] (89—91 [12]) [a]	68
(1b)	48 [0.5]	65
(1c)	88 [0.4]	98
(1d)	78 [1.0]	67
(1e)	89 [1.3]	56
(1f)	78 [0.6] (133—136 [14]) [b]	67
(1g)	63 [0.3]	72

[a] Ref. 5*a*. [b] Ref. 6.

appropriate for cyclization, whereas hydrogen bonding to an *ortho*-substituent could disrupt this favoured orientation. Finally, acid-catalysed dimerization of the 2-methylbenzo[*b*]furan products may also account for the low yields observed from (2f and g).[11]

The method for the synthesis of benzo[*b*]furans was readily extended to benzo[*b*]thiophens.[12] Thus, several aryl 2-chloroprop-2-enyl sulphides (5a—e), prepared in high yield from the appropriate benzenethiol and 2,3-dichloropropene (Table 4), readily underwent cyclization to the corresponding benzo[*b*]thiophens (6a—e) (Table 5) when heated in *NN*-diethylaniline at 200 °C for 24 h. The increased nucleophilicity of benzenethiols [13] did not permit isolation or spectral observation of the presumed Claisen rearrangement product or any other intermediate.

(5) (6)

a; X = H b; X = *p*-Me c; X = *p*-OMe
d; X = *p*-Cl e; X = *o*-Cl

The *ortho*-chloro-compound (5e) did cyclize in good yield, unlike the benzo[*b*]furan counterpart, possibly because of the weak hydrogen bonding known to be associated with benzenethiols.[14]

TABLE 2

Preparation of substituted 2-(2-chloroprop-2-enyl)-phenols (2)

Compound	B.p. (°C) [Torr] (lit. b.p.)	% Yield
(2a) [a]	77 [0.9] (130—134 [12]) [b]	77 [c]
(2b)	90 [0.6]	85 [c]
(2c)	104 [1.0]	84 [d,e]
(2d)	125—127 [2.8]	90 [c]
(2e)	79—80 [0.25]	71 [c]
(2f)	117 [1.6] (149—150 [15]) [f]	92 [c]
(2g)	75 [0.45]	76 [d]

[a] The previously reported Claisen rearrangement of (1a) gave (2a) in 24% yield and 20% of (4a); under the conditions we employed, no significant conversion into 2-methylbenzo[*b*]-furan occurred. [b] Ref. 5*a*. [c] Reaction solvent *NN*-diethylaniline. [d] Reaction solvent *p*-di-isopropylbenzene. Reaction time 20 h. [f] Ref. 6.

TABLE 3

Preparation of substituted 2-methylbenzo[*b*]furans (4)

Compound	B.p. (°C) [Torr] (lit. b.p.)	% Yield (method)	Reaction time (h)
(4a)	73 [3.3] (98—100 [40]) [a]	56 (a)	7
(4b)	59 [1.0] (111—112 [27]) [a]	59 (a)	8
(4c)	92.5 [2.7] (123—125) [12]) [a]	77 (a)	4.5
(4d)	78 [1.0] (128—133 [25]) [b]	51 (a)	8
(4e)	60 [0.8] (215 [749]) [c]	57 (a)	8
(4f)	80 [2.0] (125—127 [15]) [d]	29 (b)	24
(4g)	55 [0.4]	28 (b)	24

[a] Ref. 11. [b] G. H. Coleman and R. H. Rigterink, U.S.P. 2,559,532 (*Chem. Abs.*, 1952, **46**, 3084). [c] K. V. Auwers, *Annalen*, 1921, **422**, 153. [d] Ref. 6.

TABLE 4

Preparation of 3-arylthio-2-chloropropenes (5)

Compound	B.p. (°C) [Torr]	% Yield
(5a) [a]	123—124 [5.0]	84 [b]
(5b)	91.5—92.5 [0.7]	77
(5c)	139 [3.4]	80
(5d)	97.5—98 [2.8]	77
(5e)	96—98 [0.7]	81

[a] Ref. 12. [b] Reaction time 3 h.

[6] P. N. Giraldi, A. Fojanesi, W. Logemann, G. P. Tosoline, E. Dradi, and M. Bergamaschi, *Arzneim.-Forsch.*, 1970, **20**, 676.

[7] C. E. Castro, E. J. Graughan, and D. C. Owsley, *J. Org. Chem.*, 1966, **31**, 4071; C. E. Castro and R. D. Stephens, *ibid.*, 1963, **28**, 2163; R. D. Stephens, and C. E. Castro, *ibid.*, p. 3313.

[8] A. W. Baker and A. T. Shulgin, *J. Amer. Chem. Soc.*, 1958, **80**, 5358; W. F. O'Hara, T. Hu, and L. G. Hepler, *J. Phys. Chem.*, 1963, **67**, 1933.

[9] G. Rossmy, W. Luttke, and R. Mecke, *J. Chem. Phys.*, 1963, **21**, 1606; W. J. Hurley, I. D. Kuntz, jun., G. E. Leroi, *J. Amer. Chem. Soc.*, 1966, **88**, 3199.

[10] J. H. Richards and S. Walker, *Trans. Faraday Soc.*, 1961, **57**, 399.

[11] T. Abe and T. Shimizu, *Nippon Kagaku Zasshi*, 1970, **91**, 753 (*Chem. Abs.*, 1970, **73**, 120436a).

[12] H. Kwart and M. H. Cohen, *Chem. Comm.*, 1968, 319.

[13] J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, 1962, **84**, 16.

[14] M. J. Copley, C. S. Marvel, and E. Ginsberg, *J. Amer. Chem. Soc.*, 1939, **61**, 3161; S. H. Marcus and S. I. Miller, *ibid.*, 1966, **88**, 3719; R. Mathur, E. D. Becker, R. B. Bradley, and N. C. Li, *J. Phys. Chem.*, 1963, **67**, 2190.

We attempted to extend this synthesis to include 2-methylindoles: thus, 3-anilino-2-chloropropene [15] was heated at 220 °C in *p*-di-isopropylbenzene. However, starting material was recovered even after the solution had been heated for several days with or without added sodium carbonate. *N*-(2-Chloroprop-2-enyl)-*N*-phenylacetamide also failed to rearrange under these conditions.

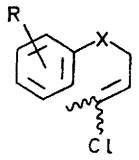
TABLE 5

Preparation of substituted 2-methylbenzo[*b*]thiophens (6)

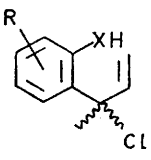
Compound	% Yield	B.p. (°C) [Torr] (lit. b.p.)	M.p. (°C) (lit. m.p.)
(6a)	75	63 [0.62] (153—154 [9]) [a]	51—52 (51—52) [a]
(6b)	67	77 [0.7] (177—179 [10]) [b]	45—46 (52—52.5) [b]
(6c)	54	110.5 [2.1]	97—98
(6d)	80	97.5—98 [2.8] (193—194 [10]) [b]	79.5 (72—73.5) [b]
(6e)	73	84 [0.8]	

[a] M. Pailer and E. Romberger, *Monatsh.*, 1960, **91**, 1070.
[b] R. P. Dickinson and B. Iddon, *J. Chem. Soc.* (*C*), 1971, 182.

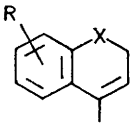
We next examined the potential of 1,3-dichlorobut-2-ene as a synthon for chromens, thiochromens, and dihydroquinolines. The aryl ethers (7a—c) were prepared from the corresponding phenols by treatment with 1,3-dichlorobut-2-ene. It was hoped that the ethers (7) would undergo a Claisen rearrangement to yield (8) and that the intermediate phenols would then cyclize through an S_N2' process to yield the chromens (9).



(7) X = O
(10) X = NH
(13) X = N·COCF$_3$
(16) X = S



(8) X = O
(11) X = NH
(14) X = N·COCF$_3$
(17) X = S



(9) X = O
(12) X = NH
(15) X = N·COCF$_3$
(18) X = S

a; R = H b; R = *p*-OMe c; R = *p*-NO$_2$

3-Chloro-1-phenoxybut-2-ene (7a) (mixture of *cis*- and *trans*-isomers) was heated under reflux in *NN*-diethylaniline (N_2) for 5 days to give 4-methyl-2*H*-chromen (9a) in 64% yield. In no instance was any of the phenol (8a) detected. When the ethers (7b and c) were heated under similar conditions, extensive polymerization resulted; neither the intermediate Claisen rearrangement products (8b or c) nor the desired chromens (9b or c) could be isolated. Similar decomposition resulted when (7b and c) were heated in the presence of potassium carbonate. The *cis*- and *trans*-isomers of (7c) were separated; however, both underwent decomposition when heated. This method may be of value in the synthesis of chromens which lack strong electron-donating or -withdrawing substituents on the aromatic ring. It does not appear to offer any real advantage over the more conventional approach with aryl but-2-ynyl ethers [16] and was not studied further.

We also attempted to employ 1,3-dichlorobut-2-ene in the synthesis of dihydroquinolines and thiochromens. Neither 1-anilino-3-chlorobut-2-ene [15] (10a) nor the trifluoroacetamide (13a) could be cyclized to give 1,2-dihydro-4-methylquinoline (12a) or the amide (15a), respectively. Similarly, 3-chloro-1-phenylthiobut-2-ene (16a) failed, under a variety of conditions, to give the thiochromen (18a).

TABLE 6

Preparation of 1-aryloxy, 1-arylthio-, and 1-anilino-3-chlorobut-2-enes

Compound	% Yield	B.p. (°C) [Torr]
(7a)	78	90 [1.4]
(7b)	76	119—120 [1.5]
(7c)	31	
(7c′)	*a*	
(10a) [b]	65	91 [0.5]
(16a) [c]	84	84 [0.75]

[a] The *cis*- and *trans*-isomers were separated by crystallization from benzene–petroleum; (7c) had m.p. 89—91 °C and (7c′) was an oil at room temperature; the ratio of (7c) to (7c′) was *ca.* 1 : 2. [b] Reaction time 4 h; lit. b.p. 147—149 °C at 17 Torr. [c] Reaction time 12 h.

EXPERIMENTAL

N.m.r. spectra were determined for solutions in CCl_4 solution (containing *ca.* 1% Me_4Si as internal standard) with a Varian T-60 spectrometer. I.r. spectra were determined for neat samples with a Perkin-Elmer 237 spectrometer. U.v. data were determined for solutions in 95% ethanol with a Beckman DB-G grating spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Petroleum refers to the fraction of b.p. 30—60 °C.

Spectral and analytical data for all new compounds are available as Supplementary Publication No. SUP 21561 (16 pp., 1 microfiche).* Specimen spectral data only are included here.

General Procedure for Preparation of Aromatic Ethers [(1a—g) *and* (7a—c)] *and Sulphides* [(5a—e) *and* (16a)].—A mixture of the phenol or benzenethiol (1.0 mol), the chloro-olefin (0.9 mol), and anhydrous potassium carbonate (1.2 mol) in reagent grade acetone (400 ml) was heated under reflux with stirring for 15 h (unless otherwise specified), cooled, and filtered, and the inorganic residue was dissolved in water and extracted with ether (2 × 100 ml).

* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

[15] J. J. D'Amico, C. C. Tung, and L. A. Walker, *J. Amer. Chem. Soc.*, 1959, **81**, 5957.
[16] W. K. Anderson, E. J. LaVoie, and P. G. Whitkop, *J. Org. Chem.*, 1974, **39**, 881.

The filtrate was concentrated *in vacuo* and the residue dissolved in ether (350 ml). The combined ethereal solutions were washed with 5% sodium hydroxide solution then water, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was either distilled under vacuum, or crystallized from benzene–petroleum after removal of all starting chloro-olefin by distillation.

General Procedure for Preparation of 2-(2-*Chloroprop*-2-*enyl*)*phenols* (2a—g) *and* 2-*Methylbenzo*[b]*thiophens* (6a—e).—A solution of either the aryl 2-chloro-2-propenyl ether or thioether (5 g) in *NN*-diethylaniline (or, for the formation of the phenolic compounds, *p*-di-isopropylbenzene) (25 ml) was heated at reflux under nitrogen; unless otherwise specified, reaction times for (2a—g) and (6a—e) were 48 and 24 h, respectively. 2-(2-Chloroprop-2-enyl)-phenols and 2-methylbenzo[*b*]thiophens were isolated by dilution of the cooled mixture with ether (100 ml), and extraction of the *NN*-diethylaniline with 10% hydrochloric acid (3 × 50 ml). The ethereal solution was dried (Na_2CO_3) and concentrated *in vacuo*. In an alternative procedure the phenols were extracted from the solvent with aqueous 25% potassium hydroxide. The aqueous phase was washed with ether (2 × 50 ml), neutralized with 10% hydrochloric acid, and extracted with ether. The ethereal solution was dried (Na_2SO_4) and concentrated *in vacuo*. The residue obtained from either procedure was distilled under vacuum in the presence of anhydrous potassium carbonate.

General Procedure for the Preparation of 2-*Methylbenzo*[b]-*furans* (4a—e).—(*a*) The appropriate 2-(2-chloroprop-2-enyl)phenol (2a—e) (3 g) was stirred in concentrated hydrochloric acid (15 ml) at 86—89 °C. The cooled two-phase mixture was diluted with water (50 ml), neutralized with aqueous 5% potassium hydroxide, and extracted with ether (3 × 50 ml). The ethereal solution was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was distilled under vacuum in the presence of anhydrous potassium carbonate.

(*b*) A solution of either (2f or g) (5 g) in trifluoroacetic acid (25 ml) was stirred at room temperature for 24 h, then diluted with ether (200 ml). The ethereal solution was washed with water (2 × 200 ml) and aqueous 5% potassium hydroxide (4 × 100 ml), dried (Na_2SO_4), and concentrated *in vacuo*, and the residue was distilled in the presence of anhydrous potassium carbonate [for (4f)] or chromatographed on silica with hexane as eluant [for (4g)].

Selected Spectral Data.—2-Chloroprop-2-enyl phenyl ether (1a) had $\nu_{max.}$ 1 639m, 1 079m, 1 049s, 1 024w, 964w, 889s, 843w, 821w, 778w, 752s, 717m, and 684s cm^{-1}; $\lambda_{max.}$ 223 (ε 5 350), 267 (1 020), 272 (1 410), and 279 nm (1 200); δ 4.56 (2 H, t, $J_{1,3}$ 1 Hz), 5.44 (1 H, q, $J_{3,3}$ 1.5 Hz), 2.59 (1 H, q), and 6.79—7.45 (5 H, m). 2-(2-Chloroprop-2-enyl)phenol (2a) had $\nu_{max.}$ 3 559s, 1 639m, 1 111s, 926w, 892m, 813s, 784w, 746w, 735w, and 670w cm^{-1}; $\lambda_{max.}$ 222 (ε 5 630) and 278 nm (2 560); δ 3.68 (2 H, s), 4.97 (1 H, OH), 5.12 (1 H, d, $J_{3',3'}$ 1.5 Hz), 5.29 (1 H, d), and 6.68—7.35 (4 H, m). 2-Methylbenzo[*b*]furan (4a) had $\nu_{max.}$ 1 613m, 1 592m, 1 104w, 1 035w, 1 008w, 964w, 940s, 925w, 877w, 817m, 792m, 750s, and 738s cm^{-1}; $\lambda_{max.}$ 217 (ε 9 270), 246 (11 200), 276 (3 150), and 282 nm (3 560); δ 2.41 (3 H, d, *J* 1 Hz), 3.75 (3 H, s), 6.24 (1 H, q), and 6.64—7.34 (3 H, m). 2-*Chloro*-3-p-*tolylthiopropene* (5b) had $\nu_{max.}$ 1 639m, 1 629m, 887s, 804s, 739w, and 680m cm^{-1}; $\lambda_{max.}$ 228 (ε 5 190) and 253 nm (4 620); δ 2.34 (3 H, s), 3.60 (2 H, s), 5.26—5.34 (2 H, m), and 7.06—7.43 (4 H, m).

2,6-Dimethylbenzo[*b*]thiophen (6b) had $\nu_{max.}$ 952w, 890s, 837s, 772s, 728m, 680w, and 667m cm^{-1}; $\lambda_{max.}$ 236 (ε 16 000), 260 (9 750), 292 (2 370), 296sh (1 990), and 302 nm (2 740); δ 2.43 (3 H, s), 2.57 (3 H, d, *J* 1 Hz), 6.88 (1 H, m), and 7.00—7.70 (3 H, m).

3-*Chloro*-1-*phenoxybut*-2-*ene* (7a) had $\nu_{max.}$ 1 678m, 1 082w, 1 035s, 1 015m, 996m, 885w, 778w, 755s, and 690s cm^{-1}; $\lambda_{max.}$ 226 (ε 3 010), 270 (1 620), and 278 nm (1 380); δ 2.12 (3 H, d, $J_{4,2}$ 1 Hz), 4.47 (minor isomer, pair of m, $J_{1,2}$ 7 Hz) and 4.62 (major isomer, pair of m, $J_{1,2}$ 6 Hz) (2 H), 5.56—5.99 (1 H, m), and 6.66—7.34 (5 H, m).

3-Anilino-2-chloropropene (4 h reaction time; 57% yield) had b.p. 78 °C at 0.7 Torr (lit.,[15] 130—131 °C at 15 Torr); $\nu_{max.}$ 3 413m, 1 639m, 1 095m, 1 074w, 997w, 898m, 751s, and 692s cm^{-1}; $\lambda_{max.}$ 209 (ε 5 260), 245 (11 500), and 294 nm (1 860); δ 3.77br (s, NH), 5.23 (1 H, m), 5.30 (1 H, m), and 6.37—7.27 (5 H, m). *N*-(2-Chloroprop-2-enyl)-*N*-phenylacetamide, synthesized by the procedure of Newman[17] in 80% yield, had m.p. 38.5—39.5 °C; $\nu_{max.}$ 1 698s, 1 078w, 1 041w, 1 009m, 901w, 781w, 758w, 699s, and 680m cm^{-1}; δ 4.56 (2 H, s), 5.15—5.33 (2 H, m), and 7.37 (5 H). 4-Methyl-2*H*-chromen (9a) (5 day reaction time; 64% yield) had b.p. 115 °C at 65 Torr (lit.,[18] 109—110° at 17 Torr.); $\nu_{max.}$ 1 653w, 1 081m, 1 070w, 1 050w, 1 029w, 1 003m, 935w, 907w, 813m, 795m, and 755s cm^{-1}; $\lambda_{max.}$ 223 (ε 9 320), 262 (2 840), and 306 nm (2 190); δ 1.94 (3 H, q, $J_{Me,2} = J_{Me,3} = 2$ Hz), 4.58 (2 H, pair of q, $J_{2,3}$ 4 Hz), 5.33—5.53 (1 H, m), and 6.57—7.20 (4 H, m). 1-Anilino-3-chlorobut-2-ene (10a) had $\nu_{max.}$ 3 413m, 1 667w, 870w, 813w, 751s, and 693s, cm^{-1}; $\lambda_{max.}$ 210 (ε 4 890), 247 (10 100), and 294 nm (1 830); δ 2.03 (3 H, m), 3.52 (NH), 3.64 (minor isomer, pair of m with D_2O, $J_{1,2}$ 7 Hz) and 3.83 (major isomer, $J_{1,2}$ 6 Hz) (2 H), 5.40—5.87 (1 H, m), and 6.37—7.27 (5 H, m). The *N*-trifluoroacetyl derivative (13a) of (10a) synthesized by the procedure of Newman[17] in 96% yield, had $\nu_{max.}$ 1 727s, 1 078w, 1 040w, 1 020w, 775m, 759m, and 699s cm^{-1}; δ 1.90 (minor isomer, m) and 2.07—2.17 (major isomer), 4.53 (pair of m, $J_{1,2}$ 7 Hz, major isomer) and 4.26 (single m of minor isomer) (2 H), 5.51—5.84 (1 H, triplet of m), and 7.11—7.54 (5 H, m). 3-*Chloro*-1-*phenylthiobut*-2-*ene* (16a) had $\nu_{max.}$ 1 639m, 1 087m, 1 025m, 876w, 826w, 766s, and 690s cm^{-1}; $\lambda_{max.}$ 224 (ε 4 260) and 254 nm (4 010); δ 1.82 (minor isomer, m) and 2.02—2.05 (major isomer, m) (3 H), 3.39 (minor isomer, pair of m, $J_{1,2}$ 7 Hz) and 3.58 (major isomer, pair of m, $J_{1,2}$ 8 Hz) (2 H), 5.37—5.70 (1 H, m), and 7.05—7.37 (5 H, m).

We thank the National Cancer Institute, National Institutes of Health, for financial support.

[4/2492 *Received*, 29*th November*, 1974]

[17] H. Newman, *J. Org. Chem.*, 1965, **30**, 1287.
[18] F. Baranton, G. Fontaine, and P. Maitte, *Bull. Soc. chim. France*, 1968, 4203.