



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

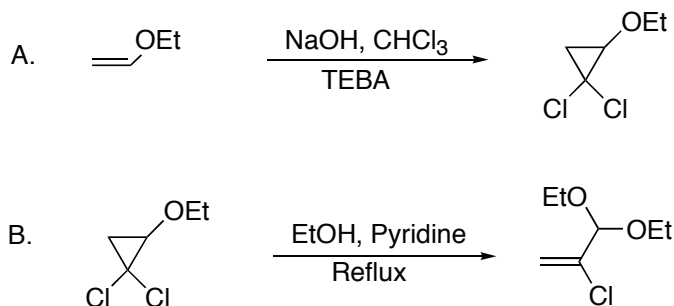
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*September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

**SYNTHESIS OF 2-CHLOROACROLEIN DIETHYL ACETAL**  
**(2-Chloroprop-2-enal, diethyl acetal)**



Submitted by Ole H. Kvernenes and Leiv K. Sydnes.<sup>1</sup>

Checked by David M. Arnold and Peter Wipf.<sup>2</sup>

### 1. Procedure

*A. 1,1-Dichloro-2-ethoxycyclopropane.* A 250-mL, three-necked, round-bottomed flask equipped with a septum, a 3.8 cm Teflon-coated magnetic stir bar and a condenser connected to a drying tube containing Drierite<sup>®</sup> is charged with ethyl vinyl ether (9.55 mL, 7.20 g, 0.10 mol) (Note 1), chloroform (31.9 mL, 47.8 g, 0.40 mol) (Note 2), and benzyltriethylammonium chloride (TEBA) (0.100 g, 0.44 mmol) (Note 3) and placed in an ice bath (Note 4). After the reaction flask is cooled for 10 min, the mixture is stirred vigorously (Note 5) and 24 g of a 50% aqueous solution of sodium hydroxide (NaOH) (12.0 g, 0.30 mol in 12 mL of H<sub>2</sub>O) (Note 6) is added dropwise via a syringe in 10 min (Note 7). The reaction mixture is stirred vigorously at bath temperature (approximately 0 °C) for 2 h and at room temperature for 22 h. The reaction mixture is then cooled in an ice bath and quenched by injecting 6 M hydrochloric acid (30 mL) dropwise over a 10 min period (Note 8). The hydrolysate is transferred to a 500-mL separatory funnel, and the flask is rinsed with water (2 x 20 mL) and dichloromethane (30 mL), which is also added to the funnel. After addition of more water (60 mL) to the funnel, the mixture is shaken and the organic layer is separated from the aqueous layer. The aqueous layer is extracted with dichloromethane (3 x 60 mL) (Note 9). The combined organic extracts are dried with approximately 2 g of anhydrous magnesium sulfate (MgSO<sub>4</sub>) (Note 10), vacuum filtered, and concentrated under reduced pressure on a rotary evaporator (25 °C at 70 mmHg) to afford a pale yellow residue. This residue is transferred to a 50-mL round bottom flask using

approximately 2 mL of dichloromethane (Note 11). The dichloromethane is removed at 30–35 °C (oil bath temperature) at 50 mmHg, and the product is distilled at 65–70 °C (oil bath temperature) at 30 mmHg to give 12.94 g (84%) (Note 12) of 1,1-dichloro-2-ethoxycyclopropane (Note 13) as a colorless liquid, bp 55 °C/30 mmHg.

*B. 2-Chloro-3,3-diethoxyprop-1-ene* (Note 14). A 250-mL, single-necked, round-bottomed flask equipped with a 3.8 cm Teflon-coated magnetic stir bar and a condenser connected to a Drierite<sup>®</sup> drying tube is charged with absolute ethanol (50 mL) (Note 15), pyridine (7.33 mL, 7.20 g, 0.09 mol) (Note 16) and 1,1-dichloro-2-ethoxycyclopropane (10.86 g, 0.070 mol) (Note 17). The resulting mixture is stirred at a moderate speed at reflux for 48 h in an oil bath at 95 °C (bath temperature), and is then allowed to cool to room temperature before being concentrated under reduced pressure on a rotary evaporator (40 °C at 70 mmHg vacuum) until the volume is approximately 20 mL (Note 18). The residue is transferred to a 250-mL separatory funnel, and the flask is rinsed with water (2 x 50 mL) and dichloromethane (60 mL), which are also added to the separatory funnel. The mixture is shaken, and the organic layer is separated from the aqueous layer. The aqueous phase is extracted with dichloromethane (2 x 50 mL), and the combined organic phases are washed with a 0.7 M aqueous solution (2 x 100 mL) of copper sulfate (CuSO<sub>4</sub>) (Note 19), and dried with approximately 2 g of anhydrous magnesium sulfate (Note 10). The organic phase is then vacuum filtered into a 500-mL round-bottomed flask through a plug of aluminum oxide (Note 20). Dichloromethane (15 mL) is added to the flask containing the MgSO<sub>4</sub> and after mixing the contents for approximately 1 min, the dichloromethane solution is filtered through the plug as well. The combined filtrates are then concentrated under reduced pressure on a rotary evaporator (25 °C at 70 mmHg) and transferred with approximately 2 mL of dichloromethane to a 50-mL round-bottomed flask for vacuum distillation (Notes 11, 21). The dichloromethane is removed at 21 °C and 30 mmHg. Following the removal of the dichloromethane, the apparatus is placed again under vacuum (30 mmHg) and the 25-mL receiving flask is submerged in an acetone/dry ice bath. The product is distilled with an oil bath temperature of 80–85 °C. Upon completion of the distillation, nitrogen gas is bled into the apparatus from the vacuum adaptor as the vacuum is released. The receiving flask is warmed to room temperature under a nitrogen atmosphere before being removed. The distillation yields 6.75 g (59 %) of a clear liquid, bp 70–71 °C/30 mmHg

(Note 22). The product, 2-chloro-3,3-diethoxyprop-1-ene (Note 23), is found by GC analysis to be 96.0–97.2% pure (Notes 24, 25, 26).

## 2. Notes

1. Ethyl vinyl ether of 99% purity was purchased from Aldrich Chemical Co. and used as obtained.

2. Chloroform, with a purity of better than 99%, was purchased from J. T. Baker (Mallinckrodt Baker) and used as obtained.

3. Checkers used TEBA, a phase-transfer catalyst, which was 98% pure, purchased from Acros Organics, and used as obtained. Submitters used 99% pure TEBA purchased from Aldrich Chemical Co.

4. The bath was a Pyrex dish (125 mm x 65 mm), to which were added about 300 mL of ice and 300 mL of cold water.

5. It is essential that the stirring is vigorous so that the organic and aqueous phases are thoroughly mixed. The submitters used a mechanical stirrer with a stirring speed of approximately 500 revolutions per min.

6. Sodium hydroxide, with a purity of 98.4%, was purchased from J. T. Baker and used as obtained. A 50% stock solution of sodium hydroxide was made by dissolving 20.0 g of sodium hydroxide in 20.0 g of water.

7. The submitters report that the sodium hydroxide solution can be added much faster without any consequences at the scale used here. At larger scales, however, it is important to add the solution slowly to avoid excessive heating. When the reaction was carried out on a 2-mole scale, the addition of 240 g of 50% aqueous sodium hydroxide required 30 min.

8. The hydrochloric acid was prepared by dilution of concentrated (36-38%, 1.19 g/mL, 12 M) hydrochloric acid of Baker-analyzed quality purchased from J. T. Baker (Mallinckrodt Baker). Rapid addition of the hydrochloric acid solution at room temperature generated a lot of heat and discoloration (yellowing) of the reaction mixture was noted.

9. Dichloromethane with a purity of 99.5% was purchased from EMD Chemicals Inc. and used as obtained.

10. Checkers used anhydrous magnesium sulfate that was purchased from EMD Chemicals Inc. and used as obtained. Submitters used dehydrated but not completely anhydrous magnesium sulfate from several suppliers.

11. Checkers carried out the distillation with a 50-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a short path

distillation head fitted with a 25-mL receiving flask. Submitters used standard equipment consisting of a 100-mL pear-shaped flask with a magnetic stirrer, a connecting adapter with thermometer, a Liebig condenser, a vacuum adapter, and a 25-mL receiving flask, all with 14/23 joint(s).

12. The reaction was also run at a 50% scale and yielded 5.64 g of product. The yield range is 73–84%. The submitters report that the reaction has been reproduced up to a 2-mole scale following the procedure described here. At such a large scale, the yield is considerably better, usually in the 82–96% range, provided proper care is taken to avoid excessive heating of the reaction mixture (see Notes 7 and 8). When the reaction is carried out on a larger scale, the amount of product remaining in the distillation flask, the distillation head and the condenser is relatively smaller.

13. The product exhibits the following spectroscopic properties:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.29 (t, 3 H,  $J = 7.0$  Hz), 1.53 (dd, 1 H,  $J = 8.5$ , 5.1 Hz), 1.66 (t, 1 H,  $J = 8.5$  Hz), 3.54 (dd, 1 H,  $J = 8.1$ , 5.1 Hz), 3.68–3.89 (m, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 14.9, 27.9, 58.6, 63.1, 67.3; IR (neat) 3095 (w), 2980 (s), 2931 (m), 2875 (m), 1481 (w), 1444 (w), 1425 (m), 1398 (m), 1374 (m), 1345 (m), 1300 (w), 1235 (m), 1179 (m), 1115 (m), 1065 (s), 1019 (m), 977 (w), 905 (m), 890 (w), 800 (m), 766 (s)  $\text{cm}^{-1}$ ; EI-MS  $m/z$  158 ( $[\text{M}+4]^+$ , 0.1), 156 ( $[\text{M}+2]^+$ , 0.5), 154 ( $\text{M}^+$ , 0.8), 119 (54), 109 (17), 97 (34), 91 (100), 84 (9), 73 (8), 61 (62), 55 (8). The purity of the product was >99% based on GC analysis (assuming identical response factors) using a HP 6890 Series GC system (100% dimethylpolysiloxane coated column (30 m x 320  $\mu\text{m}$  x 0.25  $\mu\text{m}$ ); column flow rate 1 mL/min; 70  $^\circ\text{C}$  - start; temperature increased at 15  $^\circ\text{C}/\text{min}$  until 240  $^\circ\text{C}$ ; temperature kept at 240  $^\circ\text{C}$  for 5 min; temperature increased at 25  $^\circ\text{C}/\text{min}$  until 300  $^\circ\text{C}$ ; retention time: 3.975 min.

14. The procedure for this step is a modification of that described by Skattebøl.<sup>3</sup>

15. Checkers used absolute ethanol containing at least 99.95% ethanol without further purification as purchased from Pharmco Products Inc. Submitters used at least 99.98% pure absolute ethanol without further purification as purchased from Arcus, Norway.

16. Anhydrous pyridine, with a purity of 99.8%, was purchased from Aldrich Chemical Co. and was used without further purification. Submitters report that at least 1 equiv of pyridine has to be used; usually 1.3 equiv are used. If less than 1 equiv is used, ethanol addition to the product takes place, furnishing 2-chloro-1,1,3-triethoxypropane.

17. The order of addition does not affect the reaction yield.
18. When the volume is approximately 20 mL, the liquid turns turbid upon cooling. A slight yellowing of the solution was noted.
19. Checkers used copper sulfate pentahydrate, with a purity of >99%, purchased from Fisher Scientific to prepare the aqueous copper sulfate solution by dissolving 35.0 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 200 mL of water. Submitters used copper sulfate pentahydrate, with a purity of 98 %, purchased from Acros Organics.
20. Checkers used activated basic aluminum oxide (150 mesh, 58 Å) purchased from Aldrich Chemical Co. Submitters used the Fluka Chromatography product 6300, neutral 120–125 mesh aluminum oxide. The filtration was carried out using a column with a diameter of 2.0 cm and a height of 10 cm containing a vacuum adaptor connected to a water aspirator; upon addition of 6.3 g of aluminum oxide the alumina plug was 2.0 cm high.
21. Distillation of the product has to be carried out with care to avoid loss of material due to the high volatility of this alkene.
22. The reaction was also reproduced on a 50% scale and yielded 2.86 g of product for a yield range of 50-59%.
23. The product exhibits the following spectroscopic properties:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.23 (t, 6 H,  $J = 7.0$  Hz), 3.47–3.68 (m, 4 H), 4.84 (s, 1 H), 5.45 (dd, 1 H,  $J = 1.2, 0.5$  Hz), 5.66 (t, 1 H,  $J = 1.2$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 15.1, 61.8, 100.7, 115.1, 138.2; IR (neat) 2978 (s), 2886 (s), 1635 (m), 1481 (w), 1445 (m), 1372 (m), 1336 (m), 1296 (w), 1206 (m), 1062 (s), 964 (m), 904 (m), 765 (w), 747 (w) 703 (w), 677 (w)  $\text{cm}^{-1}$ ; EI-MS  $m/z$  166 ( $[\text{M}+2]^+$ , 4), 164 ( $\text{M}^+$ , 13), 129 (10), 119 (84), 103 (60), 91 (100), 75 (14), 63 (9), 55 (8); HRMS  $m/z$  calculated for  $\text{C}_7\text{H}_{13}\text{O}_2\text{Cl}$  164.0604, found 164.0612. Analysis calcd. for  $\text{C}_7\text{H}_{13}\text{O}_2\text{Cl}$ : C, 51.07; H, 7.96; found C, 50.90; H, 7.88.
24. The purity of the product was 96.0–97.2% according to GC analyses. The GC analyses (assuming identical response factors) were performed with a HP 6890 Series GC system (100% dimethylpolysiloxane column (30 m x 320  $\mu\text{m}$  x 0.25  $\mu\text{m}$ ); column flow rate 1 mL/min; 70 °C - start; temperature increased at 15 °C/min until 240 °C; temperature kept at 240 °C for 5 min; temperature increased at 25 °C/min until 300 °C; retention time: 4.410 min.
25.  $^1\text{H}$  NMR and GC analyses determined that the product was contaminated with 2.8–4.0% of 1,1-dichloro-2-ethoxycyclopropane.



Subsequent distillations did not improve the purity of the product above 97.2%.

26. An aliquot of the product mixture was resubjected to the reaction conditions, heated at reflux for an additional 24 h and worked up according to the outlined procedure. A GC analysis performed under identical conditions as above showed this product to be >99% pure.

### Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with “Prudent Practices in the Laboratory”; National Academy Press; Washington, DC, 1995.

### 3. Discussion

2-Haloacrolein diethyl acetals are densely functionalized compounds with a considerable potential in organic synthesis. This potential has been partly realized with 2-bromoacrolein diethyl acetal, which has proven to be useful for attachment of the 1-(diethoxymethyl)ethenyl group to a variety of substrates in multistep syntheses.<sup>4-15</sup> The chloro analogue, however, has barely been used,<sup>16</sup> probably due to its tedious synthesis.

Both 2-chloroacrolein diethyl acetal and 2-bromoacrolein diethyl acetal can be prepared from acrolein,<sup>9,17,18</sup> but the syntheses are hampered by the ease of polymerization of this unsaturated aldehyde.<sup>19</sup> Thus, the starting material should be thoroughly purified to facilitate product formation,<sup>20</sup> and an elaborate work-up procedure must be applied to obtain a pure product.<sup>9</sup> Furthermore, it is a disadvantage that hazardous chlorine gas and bromine liquid are used as reagents.

An alternative synthesis of 2-chloroacrolein diethyl acetal, involving ring opening of 1,1-dichloro-2-ethoxycyclopropane, has been reported by Skattebøl.<sup>3</sup> The cyclopropane is prepared from ethyl vinyl ether following the Doering-Hoffman procedure (CHCl<sub>3</sub>, *t*-BuOK, pentane, low temperature), which is rather laborious and requires absolutely dry conditions.<sup>21</sup> An alternative synthesis of the cyclopropane, using CCl<sub>4</sub>, CH<sub>2</sub>Br<sub>2</sub>, 50% aqueous NaOH, and tetrabutylammonium hydrogensulfate, has also been published,<sup>22</sup> but the method is rather unattractive due to the use of toxic CCl<sub>4</sub>.<sup>23</sup> A third procedure involves vinyl ether, chloroform and

magnesium,<sup>24</sup> but this synthesis is conceivably difficult to run on a large scale.

Inspired by Skattebøl's synthesis, we have worked out a new and simpler procedure for the preparation of the title compound. 1,1-Dichloro-2-ethoxycyclopropane is synthesized from ethyl vinyl ether by using Makosza's method with chloroform instead of CCl<sub>4</sub>.<sup>25</sup> This method has been used to prepare other 2-alkoxy-1,1-dichlorocyclopropanes,<sup>25-27</sup> albeit in lower yields than obtained in this case. The purification of the cyclopropane is straightforward, and it is rewarding that the yield is improved when the reaction is performed on larger scales.<sup>28</sup> The ring opening of the cyclopropane has also been modified compared to Skattebøl's method. Pyridine, added to remove the hydrogen chloride formed during the ring opening, is removed effectively by washing with a solution of copper(II) sulfate, which forms water-soluble complexes with pyridine.<sup>29</sup> Subsequent filtration through an aluminum-oxide pad was also introduced to remove any pyridine-copper complex remaining in the combined organic phases.

The yield of 2-chloroacrolein diethyl acetal in the second step is lower than what has been reported in the literature.<sup>3</sup> This is probably because we have performed the distillation in such a way that contamination of the corresponding acetylenic acetal, 1,1-diethoxy-2-propyne, was avoided.

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2. Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA.
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

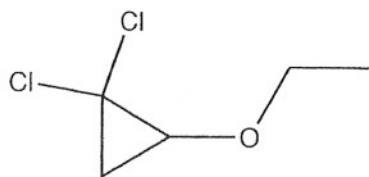
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1,1-Dichloro-2-ethoxycyclopropane; cyclopropane, 1,1-dichloro-2-ethoxy-; (7363-99-7)

Copper sulfate pentahydrate; Sulfuric acid copper(2+) salt (1:1), pentahydrate; (7758-99-8)

ppm

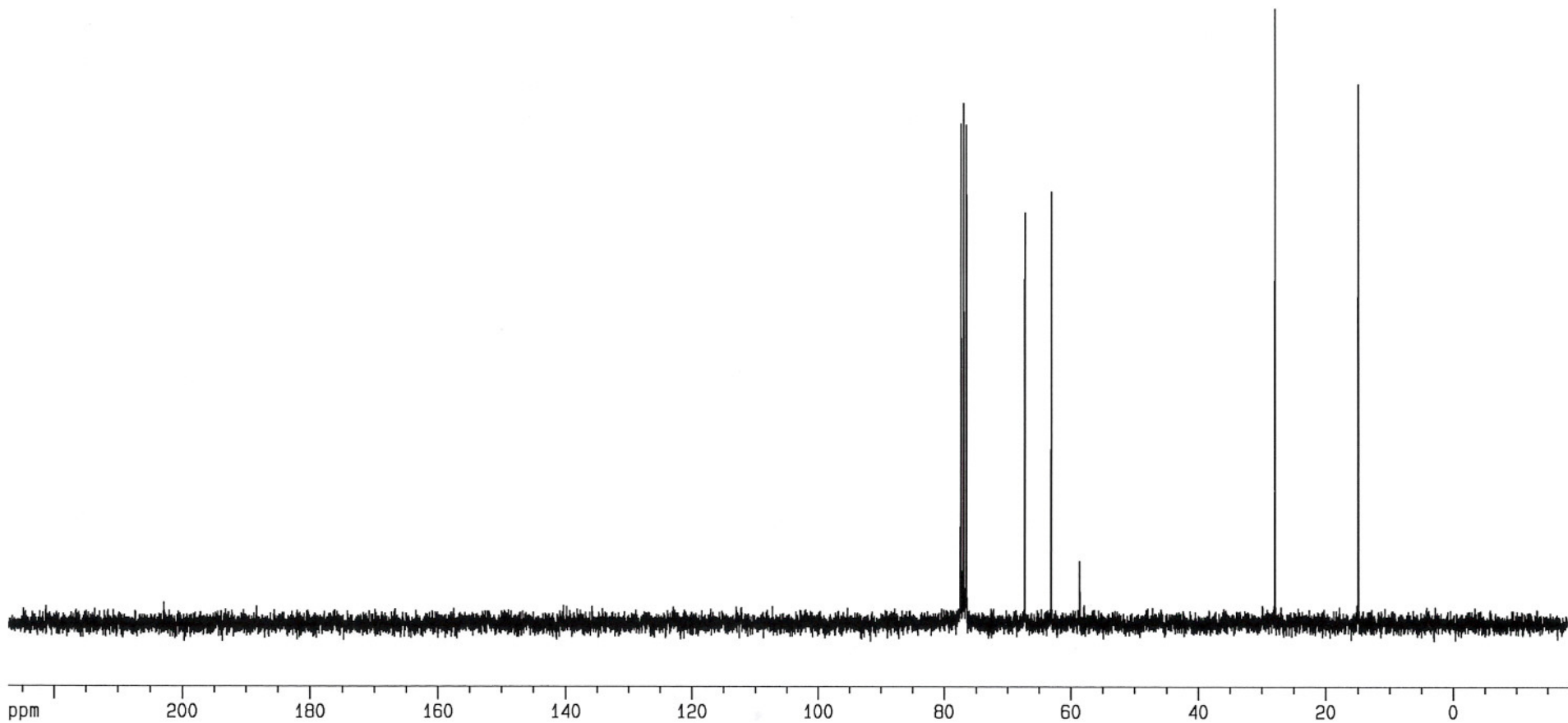


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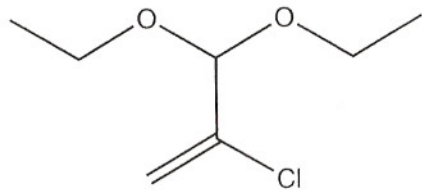
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ppm



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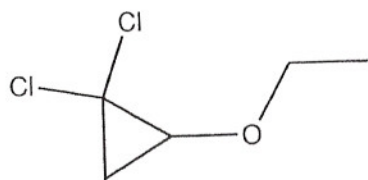
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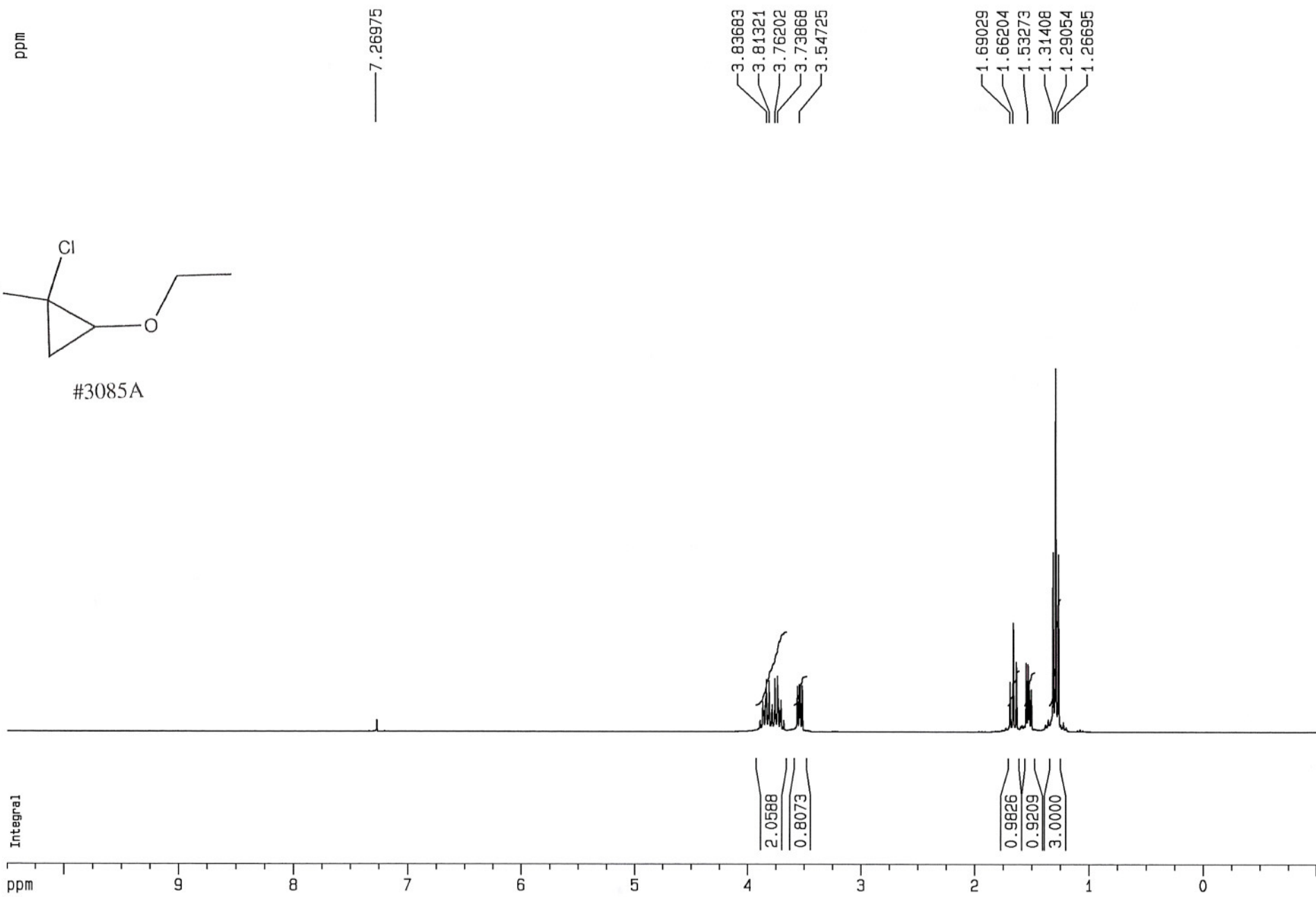
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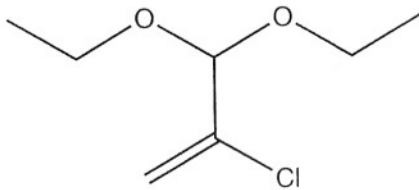




#3085A



ppm



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Integral

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6.0170

ppm

9

8

7

6

5

4

3

2

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