

three-necked flask equipped with an addition funnel charged with 312 mg (4.45 mmol) of distilled⁵ crotonaldehyde (3) and 3.0 mL of anhydrous tetrahydrofuran. After the flask was cooled to 0 °C in an ice water bath, the crotonaldehyde was slowly added dropwise over 3 min. The mixture was subsequently stirred at 0 °C for 20 min before the reaction was quenched by addition of 5 mL of saturated aqueous ammonium chloride. The product was isolated in the usual manner by extraction with ether. Chromatography of the crude product mixture (1.10 g) on Florisil (50 mL, elution with hexane–15% ether), followed by evaporative distillation, afforded 692 mg (55%) of allylic alcohol 4: bp 130–145 °C (bath temperature) (0.07 mm); ν_{max} (film) 3420 (OH), 1675 (C=C), 1205, 1138, 1125, 1075, 1030, 970, 908, 870, 810 cm^{-1} ; NMR $\delta_{\text{Me}_4\text{Si}}$ (CCl_4) 5.52 (m, 2 vinyl H's), 4.55 (br s, 1 H, OCHO), 3.1–4.2 (complex, 5 H, CH_2O and CHO), 2.27 (s, OH), 1.1–2.2 (complex, 23 H). Anal. Calcd for $\text{C}_{17}\text{H}_{32}\text{O}_3$: C, 71.78; H, 11.34. Found: C, 71.55; H, 11.53.

(*E*)-12-(Tetrahydropyran-2-yloxy)-1,3-dodecadiene (5). To a solution of 278 mg (0.98 mmol) of allylic alcohol 4 and triethylamine (0.50 mL, 3.6 mmol) in 2.0 mL of 1,2-dichloroethane was added, in small portions over a period of several minutes, 576 mg (2.46 mmol) of 2,4-dinitrobenzenesulfonyl chloride.³ This solution was subsequently heated under gentle reflux at 80–85 °C (bath temperature) for 2 h. Dilution of this mixture at room temperature with 30 mL of 1 M aqueous sodium hydroxide solution followed by extraction with ether afforded 303 mg of crude diene 5, contaminated with a substantial amount of aromatic impurities. Chromatography on 15 mL of silica gel or Florisil (elution with hexane–2% ether) afforded 96 mg (37%) of diene 5 which previously had been prepared⁷ by a Grignard coupling reaction.

(*E*)-9,11-Dodecadien-1-ol (6). Tetrahydropyranyl ether 5 (95 mg) was dissolved in 2.0 mL of methanol containing 0.10 mL of water and 3 mg of *p*-toluenesulfonic acid monohydrate. This mixture was subsequently heated at 40–45 °C (bath temperature) for 3 h, after which the product was isolated in quantitative yield by extraction with ether. VPC analysis (oven temperature, 192 °C; flow 15 mL/min; retention time, 5.5 min) indicated that dieneol 6 was >99% pure. The IR and NMR spectral properties of the product were virtually identical with those previously reported^{7,9} for this same alcohol (6). Subsequent analysis, using a method devised by Nesbitt and co-workers,^{8,9} indicated that dieneol 6 was stereochemically homogeneous.

Registry No. 1, 50816-19-8; 2, 50816-20-1; 3, 123-73-9; 4, 71342-05-7; 5, 70863-83-1; 6, 55110-79-7; 7, 50767-78-7; 1,8-octanediol, 629-41-4; 2,3-dihydropyran, 110-87-2.

Cyclodehydration Reactions Using Molten Sodium Tetrachloroaluminate¹

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Intramolecular acylation of aryl-(alkyl)-carboxylic acids has been effected most commonly through the use of poly(phosphoric acid) (PPA).² We have found that these reactions often proceed in better yields and provide purer products, using fused sodium tetrachloroaluminate as the reagent and solvent for the cyclizations.

The use of molten salts as media for organic reactions is well established,³ however, they have seen infrequent use in synthetic organic chemistry. Molten tetrachloroaluminates provide several advantages as organic reaction media: the reagents are inexpensive and readily available; the medium is highly selective in its reactions; and workup procedures are unusually simple and convenient. A surprisingly large number of functional groups are completely stable to the reaction conditions. For instance, the following compounds are recovered intact after treatment at 300 °C for 25 min: diphenyl ether, diphenylamine, dibenzofuran, dibenzothiophene, carbazole, acridine, phenanthridine, coumarin, and caffeine.

Table I outlines representative cyclodehydrations which are easily accomplished, using molten sodium tetrachloroaluminate. The procedures involve mixing measured quantities of NaCl and AlCl_3 , heating them until they fuse (at about 155 °C), adding the substrates, and stirring the mixture for the appropriate contact time. After cooling the solution and hydrolysis of the salt, a simple extraction with methylene chloride normally affords products of purity similar to those available commercially.

Experimental Section⁴

General Procedure. A 1-L, round-bottom, three-neck flask was fitted with a heating mantle, mechanical stirrer, thermocouple well, and nitrogen inlet. AlCl_3 (50 g; 0.38 mol) (Mallinckrodt AR) and 25 g (0.43 mol) of NaCl (Baker Reagent) were added, and the mixture was stirred and heated until it had melted and its temperature had stabilized at the desired point. The starting material (about 10 g) was added, with constant stirring throughout the addition and contact period. After the appropriate contact time had elapsed, the molten mixture was poured into a 2-L beaker, which was tilted and rotated to allow the mixture to solidify as a thin layer on its sides and bottom. Decomposition of the salt with warm water (200 mL) was followed by extraction with distilled methylene chloride. Evaporation of the methylene chloride afforded the products, normally of sufficient purity (>97%) for use without further purification.⁵

1-Indanone (1). Reaction of 3-phenylpropanoic acid for 5 min at 170 °C afforded a 96% yield of 1-indanone, spectroscopically

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



(2) (a) F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958); (b) E. J. Eisenbraun et al., *J. Org. Chem.*, **36**, 2480 (1971); (c) G. Metz, *Synthesis*, 612, 614 (1972); (d) H. R. Snyder and F. X. Werber, "Organic Synthesis", Collect. Vol. III, Wiley, New York, 1955, p 798.

(3) (a) Review: H. L. Jones and R. A. Osteryoung in "Advances in Molten Salt Chemistry", Vol. 3, Plenum Press, New York, 1975, pp 121–176; (b) D. B. Bruce, A. J. S. Sorrie, and R. H. Thomson, *J. Chem. Soc.*, 2403 (1953); (c) G. Baddeley and R. Williamson, *J. Chem. Soc.*, 4647 (1957).

(4) Melting points are uncorrected. Identification and purity of all products were confirmed by spectroscopic comparison with authentic samples.

(5) The authors would like to thank Linda Stell, Kleber Hadsell, and Kurt Short for verification of procedures and yields.

Table I. Sodium Tetrachloroaluminate Promoted Cyclodehydrations

reactant	product	contact time, min	yield, %	PPA yield, % ^a
3-phenylpropanoic acid		5	96	87
4-phenylbutanoic acid		20	96	89
2-phenylbenzoic acid		20	100	99
2-phenoxybenzoic acid		20	99	97

^a G. Metz, *Synthesis*, 612, 614 (1972).

identical with an authentic sample, with a melting point of 39–40 °C (lit. mp 40–42 °C).

1-Tetralone (2). Reaction of 4-phenylbutanoic acid for 20 min at 180–200 °C afforded a 96% yield of 1-tetralone, spectroscopically identical with an authentic sample.

9-Fluorenone (3). Reaction of *o*-phenylbenzoic acid for 20 min at 180–190 °C afforded a quantitative yield of 9-fluorenone, spectroscopically identical with an authentic sample, with a melting point of 81–82 °C (lit. mp 84 °C).

Xanthone (4). Reaction of *o*-phenoxybenzoic acid for 25 min at 200 °C afforded a 99% yield of xanthone, spectroscopically identical with an authentic sample, with a melting point of 172–174 °C (lit. mp 174 °C).

Registry No. 1, 83-33-0; 2, 529-34-0; 3, 486-25-9; 4, 90-47-1; 3-phenylpropanoic acid, 501-52-0; 4-phenylbutanoic acid, 1821-12-1; 2-phenylbenzoic acid, 947-84-2; 2-phenoxybenzoic acid, 2243-42-7; sodium tetrachloroaluminate, 7784-16-9.

A New, Simple Synthesis of Tropone

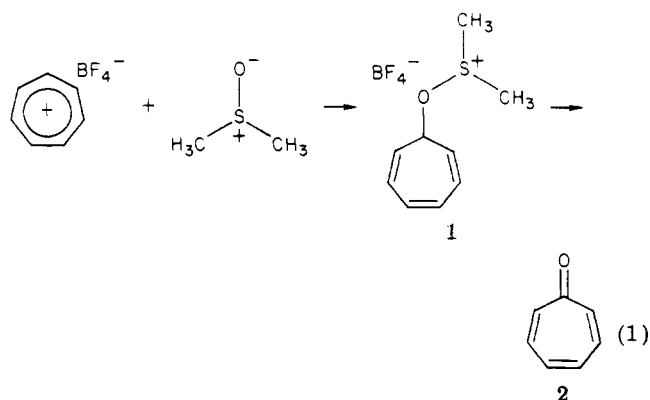
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Attempts to prepare tropone (2) by various literature methods¹⁻³ have met with only limited success in our hands: low yields and/or messy reaction conditions led us to consider an alternate route to tropone. The common intermediate of the Moffatt oxidation,⁴ the Corey–Kim oxidation,⁵ and the Swern oxidation,⁶ among others, appears to be an effective species for the generation of the carbonyl group. An analogous intermediate, 1, should be produced simply on mixing a tropylium salt with dimethyl sulfoxide (Me₂SO). Addition of triethylamine (TEA) should give tropone (eq 1).

At room temperature this sequence produced no product. At 55 °C, however, substantial amounts of



tropone were obtained. Surprisingly, a control reaction carried out without adding TEA proved to be just as good as those with TEA. The progress of the reaction was followed by NMR (in Me₂SO-*d*₆). Over the course of 4 h at 55 °C, the singlet of the tropylium salt was slowly converted to the complex pattern of a substituted cycloheptatriene. No tropone was observed, either with or without TEA, until the addition of water and chloroform, at which point the broad singlet of tropone (δ 7.05) replaced all the other peaks. Although the conditions have not been optimized, yields of 50% are routine. Our best yield to date is 58%.

Experimental Section

Tropone (2). A solution of 3.0 g (0.0168 mol) of tropylium fluoborate^{7,8} was dissolved in 15 mL of Me₂SO⁹ and heated overnight at 55 °C. The dark brown solution was cooled to room temperature and saturated aqueous sodium bicarbonate solution was added (with considerable gas evolution) until the mixture was basic to pH paper.¹⁰ The aqueous mixture was extracted several times with chloroform and the combined organic layers were washed with water and stripped of solvent. Chromatography of the residue on silica gel, using ethyl acetate as eluant, afforded 1.03 g (58%) of tropone as a pale yellow oil, identical in all respects with tropone prepared by literature methods.¹⁻³

On a sufficiently large scale, or on combination of several small-scale reactions, the chromatography could be replaced by a distillation. The major impurity was Me₂SO (bp 37 °C (3 mm)); tropone distilled at 60 °C (3 mm).

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Registry No. 2, 539-80-0; tropylium fluoborate, 27081-10-3; Me₂SO, 67-68-5.

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- (3) K. M. Harmon, A. B. Harmon, T. T. Coburn, and J. M. Fisk, *J. Org. Chem.*, 33, 2567 (1968).
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- (5) E. J. Corey and C. U. Kim, *J. Am. Chem. Soc.*, 94, 7586 (1972); *J. Org. Chem.*, 38, 1233 (1973).
- (6) S. L. Huang, K. Omura, and D. Swern, *J. Org. Chem.*, 41, 3329 (1976); K. Omura, A. K. Sharma, and D. Swern, *ibid.*, 41, 957 (1976).
- (7) Tropylium fluoborate was prepared by the method of Conrow.⁸ We have found that increasing the volume of solvent from 800 to 1200 mL and allowing the first step of the reaction to proceed overnight under nitrogen increases the yield and especially the ease of the reaction.
- (8) K. Conrow, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N. Y., 1973, p 1138.
- (9) Me₂SO was obtained from Eastman and used as received.
- (10) Some heat is necessary at this point. Generally the heat of neutralization is sufficient; however, reheating the mixture to 55 °C for 1 h does not hurt and may help. We thank Dr. David Ledlie of Bates College for this suggestion.

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