Synthesis of 7-Norbornadienyl Trifluoroacetate

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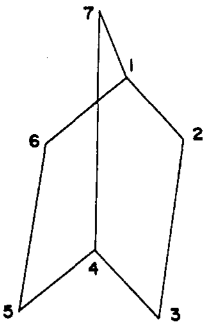
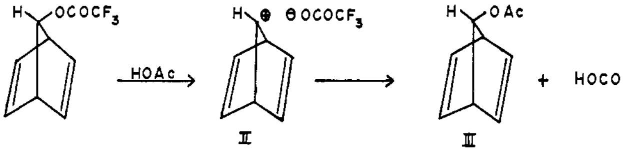
Synthesis of 7-norbornadienyl trifluoroacetate by reaction of 7-*tert*-butoxynorbornadiene with trifluoroacetic acid or trifluoroacetic anhydride is reported. Some physical properties including nmr and ir absorption for this compound have been measured.

For quite some time 7-substituted norbornyl, 2-norbornenyl, and 2,5-norbornadienyl derivatives have received wide attention because of the fund of information the studies and investigations concerning them have provided. They have been of particular interest because of the fixed stereochemistry of the unique ring system (I) which allows unusual interactions of functional groups. The carbonium ion generated from these substances, as a transient intermediate, has stimulated many investigations to determine its stability as related to nonclassical electron delocalization.



I

7-Norbornadienyl trifluoroacetate (II) was synthesized because it theoretically would provide an easily generated carbonium ion. The expected ease of removal of the trifluoroacetate leaving group made this material most favorable for investigation. In addition, the trifluoroacetate is relatively stable and easy to work with at normal room temperature.



We wish to report that II was synthesized using both trifluoroacetic acid or anhydride and 7-*tert*-butoxynorbornadiene (III). The preparation of this material is not unique to this paper. It has been prepared and identified by Winstein and Ordronneau (*5*). They did very little work concerning reactivity and basic physical data. Thus, this paper provides some information concerning the physical properties of 7-norbornadienyl trifluoroacetate.

EXPERIMENTAL

7-*tert*-Butoxynorbornadiene. III was prepared by the method of Story (*2*, *3*). The authors wish to advise all others of the possibility of an explosive hazard in working up the reaction mixture. To ensure that the reaction had gone to completion, a sample was qualitatively tested as follows. Several drops of the reaction mixture were put into a test tube containing approximately 3 ml of a near-saturated solution of potassium iodide in 0.1*N* sulfuric acid. The sample was heated and any color change observed. The appearance of a deep yellow color indicated that perbenzoate was still present.

7-Norbornadienyl Trifluoroacetate from Trifluoroacetic Anhydride. To a stirred refluxing mixture of 35.5 grams (0.184 mole) of trifluoroacetic anhydride and 2 ml of trifluoroacetic acid in 40 ml of benzene, was added a solution of 10 grams (0.061 mole) of freshly distilled III in 15 ml of benzene. This was done under a dry nitrogen atmosphere over a period of 1 hr. After addition was complete, stirring and refluxing were continued for an additional hour. The reaction mixture changed from a colorless solution to yellow-brown. Infrared analysis of the reaction mixture indicated that no 7-*tert*-butoxynorbornadiene remained after this time. Careful removal of benzene at reduced pressure and distillation of the crude product yielded 3.2 grams (21.6%) of II (bp = 50–60°C 19 mm; 84–85°C 66 mm) (*5*). This material could be recognized by its characteristic sweet-smelling raspberry-like odor. d_4^{20} = 1.18 g/ml, $n^{25}{}_D$ = 1.4080, literature 1.4095 (*5*). Ir (neat) 2980 (C—H), 1750 (C=O), 1335 (C—F), 1245 (ester), 1150, 725. *Anal.* Calcd for $C_9H_7O_2F_3$: C, 52.9; H, 3.43; F, 27.9. Found: C, 52.5; H, 3.62; F, 26.6.

7-Norbornadienyl Trifluoroacetate from Trifluoroacetic Acid. To a stirred refluxing mixture of 20.9 grams(0.188 mole) of trifluoroacetic acid in 40 ml of benzene, was added a solution of 10 grams (0.061 mole) of freshly distilled III in 10 ml of benzene. This was done under a dry nitrogen atmosphere over a period of 1 hr. After addition was complete, stirring and refluxing were continued for an additional 45 min. The reaction mixture changed from a clear solution to deep purple. Infrared analysis of the reaction mixture indicated that no ether remained. Careful removal of benzene at reduced pressure and distillation of the crude product yielded 2.9 grams (24%) of product.

Preparation of 7-Norbornadienyl Acetate. To a stirred refluxing quantity of 17.7 grams (0.294 mole) of glacial acetic acid, under a nitrogen atmosphere, were added 6 grams (0.029 mole) of II over a period of 1/2 hr. After addition was complete, stirring and refluxing were continued for an additional 15 min. Careful removal of acetic acid and distillation of the crude product at reduced pressure yielded 1.4 grams (31%) of the acetate. Bp = 64–65°C 9 mm. Ir (neat) 3000 (C—H), 1735 (C=O), 1245 (ester), 1043, 735.

RESULTS AND DISCUSSION

II was prepared using both trifluoroacetic acid or anhydride in approximately the same yields. In Table I are shown nmr absorption data for II along with that for III, 7-norbornadienyl acetate, and the 7-chloride for comparison. The spectrum of II together with the elementary analysis is consistent with the assigned structure. The τ values for II all occur at low-fields relative to III and the 7-acetate, and, in fact are fairly close to those reported for the 7-chloride. The low-field τ values are

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Table I. Nmr Absorption Data for Some 7-Norbornadienyl Derivatives[a]

Type of protons	II	III (*2*)	7-Acetate (*3*)	7-Chloride (*4*)
Olefinic	3.30 (3) 3.45 (3)	3.56 (m) 3.70 (m)	3.56 (3) 3.72 (m)	3.2 (3) 3.4 (3)
Bridgehead	6.35 (6)	6.77 (m)	6.46 (6)	6.3 (6)
Bridge	5.40 (s)	6.38 (s)	5.55 (s)	5.8 (s)
tert-Butoxy		8.94		
Methyl			8.14 (s)	

[a] All values of τ in ppm relative to tetramethylsilane at 10.00. CCl_4 was the solvent except for the 7-chloride which was run in liquid SO_2 (*4*); m = unresolved multiplet; s = singlet; 3 equals triplet, etc.

consistent with the strong electron withdrawing effect of the trifluoroacetoxy group. Table II, "Comparison with Other Normal-Octane," has been deposited with the ACS Microfilm Depository Service.

It seems likely that the reaction of III with either trifluoroacetic acid (IV) or the anhydride with added IV proceeds through the norbornadienyl carbonium ion to produce II. Likewise formation of the 7-acetate from II probably proceeds through the same intermediate with the more nucleophilic acetic acid attacking preferentially to produce product. A carbonyl addition mechanism would also lead to the same product (*1*). The latter mechanism would require the formation of 7-norbornadienol and mixed anhydride. This is considered unlikely since the dienol would be a much poorer leaving group than the attacking acetic acid.

ACKNOWLEDGMENT

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RECEIVED for review December 14, 1970. Accepted April 28, 1971. Table II will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Reprint Department, ACS Books and Journals Division, 1155 16th St., N.W., Washington, D.C. 20036. Refer to author, title of article, volume, and page number. Remit by check or money order $3.00 for photocopy or $2.00 for microfiche.

Alkyl 2-Picolyl Ketones and Derivatives

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Nine alkyl 2-picolyl ketones were prepared by the interaction of 2-picolyllithium and the requisite methyl ester. Physical properties were determined, and hydantoin and picrate derivatives of these ketones were prepared.

Recently, we had need of some alkyl 2-picolyl ketones. A careful perusal of the literature revealed that most of the required ketones had been prepared, but physical properties as well as derivatives were very sparse or lacking completely. Therefore, as the ketones were prepared, some of their physical constants were determined and derivatives prepared.

The ketones were prepared by the method of Goldberg et al. (*3*) in which 2-picolyllithium was interacted with the requisite methyl ester. Typical carbonyl derivatives—i.e., oximes, semicarbazones, and 2,4-dinitrophenylhydrazones—proved to be very difficult to prepare from these ketones. Thus, hydantoin derivatives, which could be prepared with relative ease, were chosen and prepared by the method of Henze and Speer (*4*).

Table I lists the yields of the alkyl 2-picolyl ketones as well as some of their physical constants. Table II lists the data on the hydantoin and picrate derivatives.

EXPERIMENTAL

Reactants were obtained commercially and used without further purification. Elemental analyses were performed by Huffman Microanalytical Laboratories, Wheatridge, Colo. Melting points were determined on a Thomas-Hoover melting point apparatus and were corrected. Density determinations were determined using a pycnometer which held 1.5291 grams of water at 4.0°C (*5*). The following examples illustrate the synthesis of the alkyl 2-picolyl ketones and the 5-alkyl-5-(2-pyridyl)hydantoins.

1-(2-Pyridyl)-3-methyl-2-pentanone. 2-Picolyllithium was prepared by the addition of 93.1 grams (1.0 mole) of 2-picoline to 84 grams (1.0 mole) of phenyllithium (from bromobenzene and lithium wire) in 1.0 liter of anhydrous ether. The addition was completed over a 30-min period and the mixture refluxed for an additional 30 min. To the rapidly stirred solution of 2-picolyllithium was added 51 grams (0.5 mole) of methyl 2-methylbutyrate dissolved in 100 ml of anhydrous ether over a 30-min period so that the ether re-

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