(CCl_4): multiple peaks from 0.70 to 1.08 (side-chain methyl groups) and from 1.08 to 1.88 (methylene groups), singlet at 1.22 (ring methyl groups), and singlet at 2.66 (ring methylene group) p.p.m.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.2; H, 12.1. Found: C, 79.3; H, 12.0.

2-Butyl-2-ethyl-3-(5-hexenyl)cyclobutanone (21a) and 3,3′-Tetramethylenebis[2-butyl-2-ethylcyclobutanone] (21b).—A mixture of 30 g. (0.27 mole) of 1,7-octadiene and 76 g. (0.6 mole) of butylethylketene was heated at 180° for 6 hr. Distillation of this solution through a 12-in. packed column afforded 5 g. of unchanged 1,7-octadiene, 30.5 g. (47%) of **21a**, b.p. 121° (1.6 mm.), $n^{20}\mathrm{D}$ 1.4628, and 17.6 g. (18%) of **21b**, b.p. 178° (0.2 mm.).

21a had infrared absorptions (smear) at 5.67 and 6.11 μ; n.m.r. spectrum (neat): multiplet at 0.94 (methyl groups), broad multiplets from 1.10 to 2.30 (methylene groups), ring methylene group consisting of two chemically different protons, the first as a pair of doublets at 2.58 (J = 17.1 and 6.9 c.p.s.) and the second as a pair of doublets at 3.05 (J = 17.1 and 9.0 c.p.s.), and complex multiplets at 5.04 and 5.83 (vinyl group) p.p.m.

Anal. Calcd. for $C_{16}H_{28}O$: C, 81.3; H, 11.9. Found: C, 81.4; H, 11.8.

21b had infrared absorption (smear) at 5.67 μ; n.m.r. spectrum (neat): triplet at 0.92 (methyl groups), multiplet at 1.45 multiplet at 1.45 (methylene groups), broad peak at 2.10 (methylidyne protons), and two equivalent ring methylene each consisting of two chemically different protons, the first as pair of doublets at 2.59 (J = 17.1 and 7.0 c.p.s.), and the second as a pair of doublets at 3.04 (J = 17.1 and 8.9 c.p.s.) p.p.m.

Anal. Calcd. for $C_{24}H_{42}O_2$: C, 79.5; H, 11.7. Found: C, 79.6; H, 11.7.

8-Butyl-8-ethylbicyclo[4.2.0]octan-7-one (22a).—A mixture of 63 g. (0.5 mole) of butylethylketene and 164 g. (2.0 moles) of cyclohexene was heated at 180° for 12 hr. Distillation of the reaction solution through a 12-in. packed column gave 132 g. of unchanged cyclohexene and 71 g. of a material boiling at 90–93° (0.75 mm.). Analysis by g.l.p.c. showed this distillate to be a mixture containing 31% of butylethylketene dimer and 69% of **22a**. Pure **22a** was separated by g.l.p.c.: infrared absorption (smear) at 5.65 μ.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.8; H, 11.5. Found: C, 80.7; H, 11.5.

10-Butyl-10-ethylbicyclo[6.2.0]decan-9-one (22b).—A mixture of 34.0 g. (0.27 mole) of butylethylketene and 57.0 g. (0.52 mole) of cyclooctene was heated in an autoclave at 180° for 8 hr. Analysis by g.l.p.c. indicated the high-boiling portion of the reaction mixture to be 30% butylethylketene dimer and 70% new product **22b**. Distillation through a 12-in. packed column gave 37 g. of unchanged cyclooctene and 35.8 g. (57%) of **22b**, b.p. 113–115° (0.9 mm.), $n^{20}\mathrm{D}$ 1.4854.

Anal. Calcd. for $C_{16}H_{28}O$: C, 81.3; H, 11.9. Found: C, 81.2; H, 11.9.

10-Butyl-10-ethylbicyclo[6.2.0]dec-4-en-9-one (23a) and 6,11-Dibutyl-6,11-diethyltricyclo[8.2.0^{4,7}]dodecane-5,12-dione (23b).—A mixture of 68.0 g. (0.54 mole) of butylethylketene and 29.3 g. (0.27 mole) of 1,5-cyclooctadiene was heated in an autoclave at 180° for 8 hr. Distillation of the resulting solution through a 12-in. packed column gave 7 g. of unchanged 1,5-cyclooctadiene, 27.8 g. (44%) of **23a**, b.p. 103–105° (0.4 mm.), $n^{20}\mathrm{D}$ 1.4918, and 22.0 g. (23%) of **23b**, b.p. 198–199° (0.75 mm.), $n^{20}\mathrm{D}$ 1.4958.

23a had infrared absorptions (smear) at 5.69 and 6.1 μ; n.m.r. spectrum (neat): multiplet at 0.92 (methyl groups) and complex broad peaks from 1.10 to 2.50 (methylene groups), broad multiplet at 3.20 (>CHC(=O)–, and multiplet at 5.72 (olefinic protons) p.p.m.

Anal. Calcd. for $C_{16}H_{26}O$: C, 82.0; H, 11.2. Found: C, 81.7; H, 11.2.

23b had infrared absorption (smear) at 5.67 μ.

Anal. Calcd. for $C_{24}H_{40}O_2$: C, 79.9; H, 11.2. Found: C, 79.4; H, 11.1.

Alkylation of N,N-Dialkylarylamines with Tropylium Fluoroborate

J. J. LOOKER

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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Alkylation of aromatic rings, activated by dialkylamino groups, occurred when tropylium fluoroborate was the alkylating agent. The products obtained were isomeric mixtures of dialkylaminoarylcycloheptatrienes resulting from double bond shifts in the seven-membered ring. Some of these isomers were isolated and their structures were established. The thermal isomerization of some 7-substituted 1,3,5-cycloheptatrienes was examined by n.m.r. spectroscopy. Oxidation of the substituted cycloheptatrienes to the corresponding tropylium salts occurred with triphenylmethyl fluoroborate, giving deep blue, stable compounds.

The presence of the hydroxyl[1] or methoxyl[2] group on an aromatic ring allows electrophilic substitution by the tropylium ion, but benzene is not attacked.[2] Electrophilic substitution occurs with other cations (methylbenzo-1,3-dithiolium,[3] flavylium,[4] and phenyl-1,2-dithiolium[5]) when a dialkylamino group is present. These results suggested that the presence of a dialkylamino group on an aromatic ring would permit electrophilic substitution by the tropylium ion. Hydride abstraction from such substituted cycloheptatrienes might be expected to give resonance-stabilized colored cations. This suggestion has recently been verified by Jutz and Voithenleitner,[6] who found that N,N-dimethylaniline was alkylated in the *para* position by methyl tropyl ether and that the product was readily converted to a stable tropylium salt. This paper describes our findings when tropylium fluoroborate was the alkylating agent.

1-Dimethylaminonaphthalene (**1a**) was alkylated when treated with tropylium fluoroborate in acetonitrile at room temperature. The product (83%) has the correct elemental composition ($C_{19}H_{19}N$), but the n.m.r. spectrum has two groups of peaks in the τ 7 to 8 region (allylic seven-membered ring protons), indicating that it is a mixture of isomers differing in the position of substitution on the seven-membered ring. One isomer was isolated as the amine salt (23%) and found to be identical with the product obtained from 4-lithio-1-dimethylaminonaphthalene (**1d**) and tropylium fluoroborate. Thus, the seven-membered ring is attached to the 4 position of the naphthalene ring.

The n.m.r. spectrum of this amine established its structure as 3-(1-dimethylamino-4 naphthyl)-1,3,5-cy-

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[1] T. Nozoe and K. Kitahara, *Chem. Ind.* (London), 1192 (1962).

[2] D. Bryce-Smith and N. Perkins, *J. Chem. Soc.*, 5295 (1962).

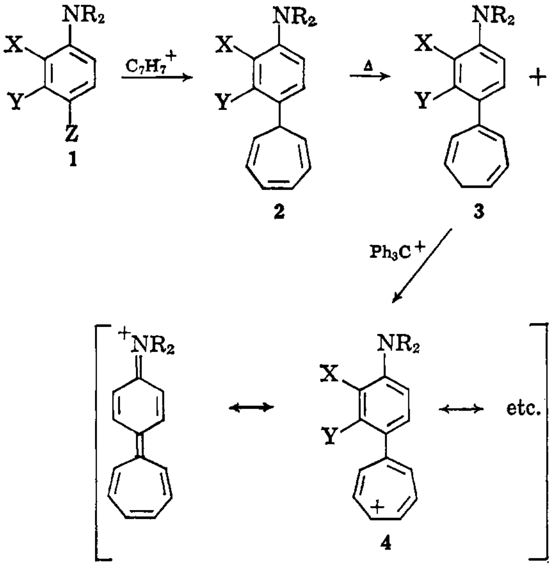
[3] L. Soder and R. Wizinger, *Helv. Chim. Acta*, **42**, 1779 (1959).

[4] R. Shriner and J. Shotton, *J. Am. Chem. Soc.*, **74**, 3622 (1952).

[5] E. Klingsberg, A. Schreiber, and N. VanMeurs, *ibid.*, **84**, 2941 (1962).

[6] C. Jutz and F. Voithenleitner, *Chem. Ber.*, **97**, 29 (1964).

cloheptatriene (**3a**). It has two allylic protons (τ 7.52, triplet) in the seven-membered ring, and one proton for the group of peaks representing the hydrogens on carbon 4 and carbon 3 of the seven-membered ring (τ 3.31, doublet). These bands could only arise from the 3 isomer. The remainder of the spectrum is in agreement with structure **3a**.



a, X = Y = benzo; R = Me; Z = H
b, X = Y = Z = H; R = Me
c, X = Z = H; Y = Me; R = Et
d, X = Y = benzo; R = Me; Z = Li
e, X = Y = H; R = Me; Z = Li

When tropylium fluoroborate was allowed to react with N,N-dimethylaniline (**1b**) under the same conditions, tropylation occurred, giving a mixture of isomers (80%). One of these, **3b**, was isolated (18%) and found to be identical with the product obtained from the condensation of 4-lithio-N,N-dimethylaniline (**1e**) with tropylium fluoroborate. Thus, the tropylium ion attacked the 4 position of N,N-dimethylaniline. Upon catalytic hydrogenation, this amine consumed 3 equiv. of hydrogen and gave 4-cycloheptyl-N,N-dimethylaniline.

The n.m.r. spectrum of amine **3b** has two allylic ring protons (τ 7.75, triplet), indicating that it is either a 2- or a 3-substituted cycloheptatriene. The overlap of vinyl and aromatic proton bands prevented complete determination of the structure by n.m.r., but the observation that 7-phenyl-1,3,5-cycloheptatriene is easily converted to the 3 isomer, which is not so readily transformed into the 2 isomer,[7] suggests that the compound obtained has structure **3b**. Formation of the naphthyl compound **3a** under the same conditions also supports this conclusion.

N,N-Diethyl-*m*-toluidine (**1c**) was alkylated in a similar manner and gave a mixture of isomers (84%) having the correct elemental composition ($C_{18}H_{23}N$). The n.m.r. spectrum indicated the presence of a 1-substituted cycloheptatriene (τ 7.48, doublet) and a 2- or 3-substituted cycloheptatriene (τ 7.72, triplet). The 7 isomer, **2e**, whose preparation will be described later, has a triplet in the n.m.r. spectrum at τ 7.19 and is not present in this mixture.

Formation of these mixtures, in contrast to the high-yield preparation of 7-(4-dimethylaminophenyl)-1,3,5-cycloheptatriene from methyl tropyl ether and N,N-dimethylaniline,[6] might be due to the method of isolation. The present products were obtained by distillation above 100°; the 7 isomer was obtained by crystallization. Thermal isomerization of 7-phenyl-[7] and 7-deuterio-1,3,5-cycloheptatriene[8] has been studied and shown to involve a 1,5 hydride shift. The result is formation of the various substitution isomers.

In order to determine whether thermal rearrangement was responsible, 7-(4-dimethylaminophenyl)-1,3,5-cycloheptatriene (**2b**) was prepared by crystallization of the product from the condensation of **1b** with 4-lithio-N,N-dimethylaniline and heated at reflux in toluene. The course of the isomerization was followed by n.m.r. spectroscopy. The spectrum of the 7 isomer, **2b**, has a triplet at τ 7.62 which represents one allylic ring proton. The area of this group decreased with time and a new triplet appeared at τ 7.75 (3 isomer **3b**). After 22 hr., the spectrum was identical with that of the 3 isomer.

7-(1-Dimethylamino-4-naphthyl)-1,3,5-cycloheptatriene (**2a**) was prepared by using the method of Jutz and Voithenleitner[6] and isolated as the hydrochloride salt in order to prevent isomerization. The n.m.r. spectrum showed it to be the 7 isomer (τ 6.65, triplet, one proton). This amine is a viscous liquid which did not crystallize. Heating amine **2a** in toluene for 20 hr. caused isomerization and led to a mixture of three compounds. The n.m.r. spectrum showed the presence of compound **2a** (τ 6.65, triplet), the 3 isomer **3a** (τ 7.52, triplet), and a third isomer (τ 7.68, doublet) which is probably the 1 isomer. The latter two groups of peaks began to appear simultaneously after 2 hr.

The 7 isomer **2c** was obtained from N,N-diethyl-*m*-toluidine and methyl tropyl ether and was a liquid. Its structure was established by the presence of a triplet in the n.m.r. spectrum representing one hydrogen at τ 7.19 (allylic seven-membered ring proton). Thermal isomerization of amine **2c** in refluxing toluene was followed by n.m.r. spectroscopy and gave a mixture of two isomers. The spectrum was identical with that of the mixture obtained by treatment of **1c** with the tropylium ion followed by distillation. Separation of the isomers by recrystallization of the hydrochloride salt of the mixture was unsuccessful.

The crude reaction mixtures obtained by tropylation of **1a**, **b**, and **c** were examined by n.m.r. before distillation and found to contain only the 7 isomers **2a**, **b**, and **c**. Thus, it is established that the 7 isomer is formed initially and is isomerized to the observed product under isolation conditions.

The ultraviolet spectra of 4-cycloheptyl-N,N-dimethylaniline, 7-(4-dimethylaminophenyl)-1,3,5-cycloheptatriene (**2b**), and 3-(4-dimethylaminophenyl)-1,3,5-cycloheptatriene (**3b**) also support the assigned structures. The cycloheptyl compound has $\lambda_{\max}^{\mathrm{EtOH}}$ 252 mμ (log ϵ 4.17) and 302 mμ (log ϵ 3.27), which is nearly identical with the peaks of 4-N,N-trimethylaniline,[9] $\lambda_{\max}^{\mathrm{EtOH}}$ 253 mμ (log ϵ 4.10) and 307 mμ (log ϵ 3.25). The spectrum of 7-(4-dimethylaminophenyl)-1,3,5-

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[7] A. terBorg and H. Kloosterziel, *Rec. trav. chim.*, **82**, 717 (1963).

[8] A. terBorg and H. Kloosterziel, *ibid.*, **82**, 741 (1963).

[9] P. Grammaticakes, *Bull. soc. chim. France*, **18**, 220 (1951).

cycloheptatriene (**2b**) has $\lambda_{\max}^{\text{EtOH}}$ 256 mμ (log ϵ 4.45) and a shoulder at 300 mμ (log ϵ 3.76), which approximates the spectrum obtained by the addition of the spectrum of N,N-dimethylaniline,[10] $\lambda_{\max}^{\text{EtOH}}$ 251 mμ (log ϵ 4.14) and 299 mμ (log ϵ 3.32), to that of 1,3,5-cycloheptatriene,[11] $\lambda_{\max}^{\text{isooctane}}$ 266 mμ (log ϵ 3.62). Conjugation of the two rings of the 3 isomer is indicated by its absorption at a longer wave length than the 7 isomer; $\lambda_{\max}^{\text{EtOH}}$ 255 mμ (log ϵ 4.05) and 318 mμ (log ϵ 4.21). Similarly, 3-(1-dimethylamino-4-naphthyl)-1,3,5-cycloheptatriene (**3a**) absorbs at a longer wave length, $\lambda_{\max}^{\text{EtOH}}$ 323 mμ (log ϵ 4.03), than the 7 isomer **2a**, $\lambda_{\max}^{\text{EtOH}}$ 313 mμ (log ϵ 2.98). Conjugation is further indicated by the increase in extinction coefficient.

Hydride abstraction from amine **3a** occurred when it was allowed to react with triphenylmethyl fluoroborate. The stable blue salt **4a** was obtained which has ultraviolet absorption (EtOH) at 333 mμ (log ϵ 3.22) and visible absorption at 628 mμ (log ϵ 3.36). This salt was decolorized by base, and the reaction was reversed with acid.

Carbonium ion **4a** is attacked by sodium methoxide and forms an amorphous solid in good yield. Treatment of this material with fluoroboric acid regenerated the starting material. The infrared spectrum of the amorphous material shows hydroxyl absorption at 3500 cm.$^{-1}$; the n.m.r. spectrum suggests that it may be a mixture of methyl ethers, but is not definitive. The material could not be purified.

Hydride abstraction from 3-(4-dimethylaminophenyl)-1,3,5-cycloheptatriene (**3b**) was also effected with triphenylmethyl fluoroborate. The stable salt **4b** obtained absorbed in the visible region (EtOH) at 570 mμ (log ϵ 3.38) and in the ultraviolet region at 306 mμ (log ϵ 4.08). Solutions of the salt were deep blue. On treatment with base, the blue color was discharged. Acidification of this solution regenerated the blue material.

The substituted tropylium ion **4c** could not be obtained in this manner from the mixture of isomers, although blue solutions formed.

Abstraction of hydride ion from the 7 isomer **2b** has been demonstrated.[6] Treatment of either 7 isomer **2a** or **2c** with triphenylmethyl fluoroborate gave no blue color, indicating that the substituted tropylium ion did not form. This failure may be due to steric effects.

Experimental Section

Melting points and boiling points are uncorrected. The n.m.r. spectra were measured in deuteriochloroform with a Varian A-60 instrument. Ultraviolet and visible spectra were measured in ethanol.

Alkylation of 1-Dimethylaminonaphthalene with Tropylium Fluoroborate.—A solution of 18 g. (0.10 mole) of tropylium fluoroborate[12] in 200 ml. of acetonitrile was added dropwise to a solution of 34 g. (0.20 mole) of 1-dimethylaminonaphthalene in 100 ml. of acetonitrile. After the mixture had stood overnight, the solvent was removed and the residue was treated with excess dilute sodium hydroxide. The organic material was taken up in methylene chloride, washed with water, dried, and distilled to give 21.7 g. (83%) of oil, b.p. 144–152° (0.06 mm.).

Anal. Calcd. for $C_{19}H_{19}N$: C, 87.4; H, 7.3; N, 5.3. Found: C, 87.8; H, 7.6; N, 5.3.

Isomer **3a** was isolated by stirring 2.6 g. (0.010 mole) of the mixture in 50 ml. of ethanol for 5 min. with 3 ml. of 40% aqueous fluoroboric acid, removing the solvent, and recrystallizing the solid from ethanol, m.p. 197–199°. The amine was liberated with aqueous sodium bicarbonate and extracted into ether to give 0.6 g. (23%) of product.

Condensation of 4-Lithio-1-dimethylaminonaphthalene with Tropylium Fluoroborate.—A mixture of 9.0 g. (0.036 mole) of 4-bromo-1-dimethylaminonaphthalene,[13] 0.50 g. (0.0072 g.-atom) of lithium, and 150 ml. of ether was heated at reflux under nitrogen for 2 hr. The solid was removed by filtration through glass wool, and 6.4 g. (0.036 mole) of tropylium fluoroborate was added to the filtrate in small portions. After it had been stirred for 1 hr., the mixture was decomposed with water, and the ether layer was washed with water, dried, and concentrated. Distillation gave 3.5 g. (37%) of liquid, b.p. 148–154° (0.08 mm.). The infrared spectrum and the gas chromatographic retention time were identical with those of amine **3a** obtained from 1-dimethylaminonaphthalene and tropylium fluoroborate. The fluoroboric acid salt was prepared, recrystallized from ethanol to constant melting point, and found not to depress the melting point of the corresponding salt of **3a**.

Alkylation of N,N-Dimethylaniline with Tropylium Fluoroborate.—A solution of 9.0 g. (0.050 mole) of tropylium fluoroborate in 70 ml. of acetonitrile and a solution of 18 g. (0.15 mole) of N,N-dimethylaniline in 50 ml. of acetonitrile were allowed to react as described for 1-dimethylaminonaphthalene. Distillation of the residue gave 8.4 g. (80%) of yellow oil, b.p. 136–138° (0.15 mm.). Yields varied from 80 to 91%. The oil solidified on standing and melted at 38–48°. Several recrystallizations of this material from methanol gave 1.5 g. (18%) of **3b**, m.p. 64–65°.

Anal. Calcd. for $C_{15}H_{17}N$: C, 85.3; H, 8.1; N, 6.6. Found: C, 85.5; H, 7.7; N, 6.4.

The residue from recrystallization of **3b** was redistilled to give a material melting at 36–37°.

Anal.. Calcd. for $C_{15}H_{17}N$: C, 85.3; H, 8.1; N, 6.6. Found: C, 85.25; H, 8.1; N, 6.6.

The n.m.r. spectrum of this solid has a triplet at τ 7.75 and a doublet at τ 7.35, indicating a mixture of isomers. The remainder of the spectrum is almost identical with that of the 64° material.

Treatment of 4-Dimethylaminophenyllithium with Tropylium fluoroborate.—The lithium reagent[4] from 14.7 g. (0.0736 mole) of 4-bromo-N,N-dimethylaniline, 1.04 g. (0.150 g.-atom) of lithium, and 200 ml. of ether was filtered through glass wool under nitrogen and treated with solid tropylium fluoroborate (12.5 g., 0.070 mole), following the procedure for the reaction with 4-lithio-1-dimethylaminonaphthalene. Fractional distillation of the yellow residue gave 7.0 g. (47%), b.p. 112–114° (0.1 mm.), m.p. 58–60°, which did not depress the melting point of the solid obtained by treating N,N-dimethylaniline with tropylium fluoroborate.

4-Cycloheptyl-N,N-dimethylaniline.—A solution of 3.16 g. (0.0150 mole) of amine **3b** in 195 ml. of dioxane was reduced with hydrogen over 1 g. of 10% palladium on charcoal and consumed the calculated amount of hydrogen for three double bonds in 25 min. at 57 p.s.i. Distillation of the residue left after removal of the catalyst and solvent gave 1.7 g. (52%) of 4-cycloheptyl-N,N-dimethylaniline, b.p. 120° (0.4 mm.), $n^{25}\text{D}$ 1.5520.

Anal. Calcd. for $C_{15}H_{23}N$: C, 83.0; H, 10.6; N, 6.4. Found: C, 83.3; H, 10.3; N, 6.0.

Alkylation of N,N-Diethyl-*m*-toluidine with Tropylium Fluoroborate.—The procedure for alkylation of 1-dimethylaminonaphthalene was repeated with a solution of 9.0 g. (0.050 mole) of tropylium fluoroborate in 125 ml. of acetonitrile and 32 g. (0.20 mole) of N,N-diethyl-*m*-toluidine in 100 ml. of acetonitrile. Distillation of the product gave 10.6 g. (84%) of liquid, b.p. 150–152° (0.13 mm.). Gas chromatography on a silicone oil column showed one component. The n.m.r. spectrum indicated that two isomers were present.

Anal. Calcd. for $C_{18}H_{23}N$: C, 85.3; H, 9.2; N, 5.5. Found: C, 85.5; H, 9.0; N, 5.6.

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(10) A. E. Gellam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," 2nd. Ed., Edward Arnold, Ltd., London, 1957, p. 140.

(11) W. Doering and L. Knox, *J. Am. Chem. Soc.*, **75**, 297 (1953).

(12) K. Conrow, *Org. Syn.*, **43**, 101 (1963).

(13) H. R. Snyder and F. Wynan, *J. Am. Chem. Soc.*, **70**, 234 (1948).

The liquid could not be converted to a solid salt with fluoroboric acid in methanol. All attempts to effect hydride abstraction with triphenylmethyl fluoroborate in methylene chloride were unsuccessful, although the expected blue color was observed.

7-(4-Dimethylaminophenyl)-1,3,5-cycloheptatriene (2b).—The lithium reagent[4] was prepared from 16 g. (0.080 mole) of 4-bromo-N,N-dimethylaniline, 1.2 g. (0.18 g.-atom) of lithium wire, and 300 ml. of ether, cooled in an ice bath, and stirred while a solution of 11.2 g. (0.092 mole) of 7-methoxy-1,3,5-cycloheptatriene in 50 ml. of ether was added to it. Cooling and stirring were continued for 1 hr. Excess water was added and the organic layer was separated, washed with cold water, dried, and concentrated below 20°. A solid was obtained when the residue was taken up in ethanol and cooled. It was recrystallized from ethanol at −10°. After three recrystallizations, 2.85 g. (17%) of amine **2b** was obtained which had m.p. 49–51° (lit.[6] m.p. 49°).

Anal. Calcd. for $C_{15}H_{17}N$: C, 85.3; H, 8.1; N, 6.6. Found: C, 85.3; H, 8.4; N, 6.9.

Thermal Isomerization of 7-(4-Dimethylaminophenyl)-1,3,5-cycloheptatriene (2b) to 3-(4-Dimethylaminophenyl)-1,3,5-cycloheptatriene (3b).—A solution of 1.5 g. of **2b** (m.p. 49–51°) in 15 ml. of toluene was heated at reflux. At intervals of 2, 4, and 21 hr., samples were removed and analyzed by n.m.r. spectroscopy. The spectrum of the 2-hr. sample showed allylic ring proton bands for the 3 isomer **3b** (τ 7.75, triplet) in addition to those for the 7 isomer **2b** (τ 7.26, triplet). The areas of these bands indicated approximately equal amounts of each isomer after 4 hr. The spectrum was identical with that of **3b** after 21 hr. Recrystallization of this material from methanol gave a solid melting at 64–65°.

7-(1-Dimethylamino-4-naphthyl)-1,3,5-cycloheptatriene (2a).—The procedure of Jutz and Voithenleitner[6] for the preparation of 7-(4-dimethylaminophenyl)-1,3,5-cycloheptatriene was used with 1-dimethylaminonaphthalene (0.040 mole) and gave 10.0 g. (96%) of the amine as an oil. It was dissolved in ether, and hydrogen chloride gas was passed into the solution for 10 min. The precipitate, 10.0 g. (84%), melted at 186–187° dec. and was not further purified by recrystallization from benzene. The amine, liberated with dilute base, was a viscous oil.

Anal. Calcd. for $C_{19}H_{19}N$: C, 87.4; H, 7.3; N, 5.3. Found: C, 87.8; H, 7.3; N, 5.5.

7-(3-Methyl-N,N-diethylaminophenyl)-1,3,5-cycloheptatriene (2c).—The procedure for the preparation of **2a** was used with N,N-diethyl-*m*-toluidine (0.040 mole) and gave 10.0 g. (99%) of oil which was converted to the hydrochloride salt, m.p. 199–200° dec. This solid dissolved in ether when excess hydrogen chloride gas was added. Amine **2c** was obtained as an oil from the hydrochloride salt upon treatment with base.

Anal. Calcd. for $C_{18}H_{23}N$: C, 85.3; H, 9.2; N, 5.5. Found: C, 85.5; H, 9.6; N, 5.3.

1-Dimethylamino-4-naphthyltropylium Fluoroborate (4a).—A 4.3-g. (0.0165-mole) sample of amine **1a** was taken up in 50 ml. of methylene chloride, and a solution of 9.6 g. (0.029 mole) of triphenylmethyl fluoroborate[14] in 100 ml. of methylene chloride was added in portions, with swirling. A dark blue oil separated and the methylene chloride solution was decanted. The oil crystallized when it was heated with 150 ml. of methanol and gave 1.6 g. of solid. An additional 1.0 g. was obtained by concentration of the methanol solution. The yield was 2.6 g. (46%) of solid which decomposed at 180°. An analytical sample was prepared by recrystallization from methanol.

Anal. Calcd. for $C_{19}H_{18}BF_4N$: C, 65.6; H, 5.2; N, 4.0. Found: C, 65.2; H, 5.1; N, 4.1.

Treatment of 1-Dimethylamino-4-naphthyltropylium Fluoroborate with Sodium Methoxide.—A solution of excess sodium methoxide in methanol was added to a suspension of 1.0 g. (0.0029 mole) of 1-dimethylamino-4-naphthyltropylium fluoroborate (**4a**) in 20 ml. of methanol. When the blue color disappeared, the mixture was filtered, concentrated, treated with water, extracted with ether, and dried. The solvent was removed, leaving a noncrystalline solid (0.72 g., 90%). The infrared spectrum showed the presence of a hydroxyl group (3500 cm.$^{-1}$).

When the solid (0.72 g.) was taken up in 15 ml. of 1,2-dimethoxyethane and treated with 1 ml. of 40% fluoroboric acid, a purple color developed. The solid that separated was collected, washed with ether, and air dried to give 0.76 g. (84%) of 1-dimethylamino-4-naphthyltropylium fluoroborate, which was identified by comparison of its infrared spectrum with that of authentic material.

4-Dimethylaminophenyltropylium Fluoroborate (4b).—A solution of 4.0 g. (0.019 mole) of amine **3b** in 25 ml. of methylene chloride was treated with a solution of 8.2 g. (0.025 mole) of triphenylmethyl fluoroborate[14] in 100 ml. of methylene chloride. A deep blue color developed and a blue oil separated. After the mixture had been swirled for 10 min., the solvent was decanted and the oil was dried to a dark powder (1.6 g., 35%), which did did not melt below 300°. An analytical sample was prepared by recrystallization from methanol.

Anal. Calcd. for $C_{15}H_{16}BF_4N$: C, 60.6; H, 5.4; N, 4.7. Found: C, 60.2; H, 5.0; N, 4.6.

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Reactions of Thiyl Radicals with 4-Vinylcyclohexene

J. Reid Shelton and Antony E. Champ[1]

Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106

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Thiyl radicals generated by photolysis of either diphenyl disulfide or dibenzyl disulfide in 4-vinylcyclohexene add to a vinylic double bond in preference to abstraction of α-hydrogen. The resulting carbon free radical then abstracts an α-hydrogen leading to an adduct and a new radical which is the source of dehydro dimers and substitution products, or it reacts further to yield a higher molecular weight material. The characterization of the products from these and related reactions is discussed.

This study of the reactions of thiyl radicals with 4-vinylcyclohexene is part of a continuing study of the reactions of free radicals with olefins.

Preceding papers in this series[2-4] dealt with the reactions of alkoxy and alkyl peroxy radicals with the same compound. This olefin provides a useful combination of a vinyl plus a *cis* internal double bond together with five α-hydrogens, and thus affords opportunity for both addition and abstraction by the free radical.

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