was added 2.0 mL of 2.0 M $H_2SO_4$.[17] The mixture was vigorously stirred and a small aliquot of the organic layer was subjected to GC analysis. Equilibrium was reached after 700 min and the equilibrium mixture consisted of 2,7,7-trimethylnorbornene, (3.0%) α-fenchene (81.5%), 2,7,7-trimethyl-*exo*-2-norbornanol (10.7%), and the endo alcohol (4.8%). The exo alcohol could not be studied in this fashion due to rapid dehydration. However, the equilibration of a mixture of 40.0 mg of the exo alcohol and 21.7 mg of the endo alcohol by the same procedure led to an equilibrium mixture of 2,7,7-trimethylnorbornene (2.1%), α-fenchene (61.8%), the exo alcohol (26.4%), and the endo alcohol (9.7%).

**Kinetics Measurements.** The rates of solvolysis of the *p*-nitrobenzoates in 80% acetone were determined by the titrimetric method.[27] The sealed ampule technique was employed for measuring the rates at higher temperatures. The data are summarized in Table I.

**Acknowledgment.** We are deeply indebted to Professor Paul von R. Schleyer for relinquishing his own plans for a closely related problem. He generously supplied us with a sample of 6,6-dimethyl-2-norboranone, which facilitated the initial experiments. We also thank the National Science Foundation (Grant GP 6492X) for their financial support.

# Solvomercuration-Demercuration. 12. The Solvomercuration-Demercuration of Olefins in Alcohol Solvents with Mercuric Trifluoroacetate—An Ether Synthesis of Wide Generality

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*Received October 16, 1984*

Studies on the solvomercuration–demercuration (SM–DM) of olefins in methyl, ethyl, isopropyl, and *tert*-butyl alcohols with mercuric trifluoroacetate have been extended. 1-Dodecene undergoes the SM–DM sequence with typical results for a monosubstituted olefin. Cyclopentene similarly exhibited behavior characteristic of a 1,2-disubstituted olefin in methanol, ethanol, and 2-propanol, giving high yields, >90% of the corresponding ethers. However, in *tert*-butyl alcohol, the yields of ether were lower than normal and decreased somewhat with time. 2-Methyl-1-butene gives >90% yields of the Markovnikov methyl ether. On the other hand, the yields of ethyl, isopropyl, and *tert*-butyl ethers are lower and decrease with time. Major improvements in yields, however, are possible by lowering the reaction temperature from room temperature to 0 °C. Cyclooctene, surprisingly, behaves more like a tri-, tetra-, or isosubstituted olefin than a 1,2-disubstituted olefin. The yields of cyclooctyl methyl ether are >90% and do not decrease with time. However, yields of the ethyl, isopropyl, and *tert*-butyl ethers are lower and drop with time. Again, lowering the reaction temperature from room temperature to 0 °C markedly improves the yields of the cyclooctyl ethers. These results, coupled with those of a previous study, clearly reveal the exceptional superiority of mercuric trifluoroacetate for the SM–DM of olefins in alcohol solvents.

The results of the previous paper[1] revealed mercuric trifluoroacetate to be a remarkably effective reagent for the etherification of olefins using the solvomercuration–demercuration (SM–DM) sequence in alcohols. Consequently, we felt it desirable to expand on the SM–DM of olefins with this mercuric salt.[2] 1-Dodecene, cyclopentene, 2-methyl-1-butene, and cyclooctene were chosen for examination. We also examined scaling up representative reactions to a preparative scale.

## Results and Discussion

1-Dodecene is converted in near quantitative yield to the corresponding methyl, ethyl, and isopropyl Markovnikov ethers. Trace amounts of 2-dodecanol accompany the formation of the isopropyl ether. The *tert*-butyl ethers are synthesized in somewhat lower but nevertheless good yields.

The results are essentially identical with those of 1-hexene. However, one important difference was noted. Initially, in methanol, low and irreproducable yields of the 2° ether (ca. 75–85%) were obtained. An investigation revealed the problem to be in the demercuration step. Apparently the oxymercurials produced from 1-dodecene are somewhat insoluble in the reaction media following the addition of aqueous sodium hydroxide (see Experimental Section). By rapidly stirring the reactions for ca. 2 min

**Table I. Solvomercuration–Demercuration of 1-Dodecene[a]**

| ROH | R | time, min | % products[b] $n$-$C_{10}H_{21}$CH(OR)$CH_3$ | % products[b] $n$-$C_{10}H_{21}$CH(OH)$CH_3$ |
|---|---|---|---|---|
| methanol | Me | 5, 60 | 91 | 0 |
| ethanol | Et | 5, 60 | 94 | 0 |
| 2-propanol | *i*-Pr | 5, 60 | 100 | trace |
| 2-methyl-2-propanol | *t*-Bu | 5 | 76 | 21 |
| | | 80, 180 | 87 | 10 |

[a] Reaction at room temperature, 22–23 °C. [b] Quantitative VPC analysis.

**Table II. Solvomercuration–Demercuration of Cyclopentene[a]**

| ROH | R | time, min | % products[b]  | % products[b]  |
|---|---|---|---|---|
| methanol | Me | 5, 60 | 94 | 0 |
| ethanol | Et | 5, 60 | 93 | 0 |
| 2-propanol | *i*-Pr | 5, 60 | 100 | trace |
| 2-methyl-2-propanol[d] | *t*-Bu | 5 | 79 | *c* |
| | | 60 | 72 | *c* |
| | | 165 | 67 | *c* |

[a] Reaction at room temperature, 22–23 °C. [b] Quantitative VPC analysis. [c] Cyclopentanol present but not analyzed quantitatively as it was partially lost during workup. [d] Trace amounts of one other product.

(1) Brown, H. C.; Kurek, J. T.; Rei, M-H.; Thompson, K. L. *J. Org. Chem.* **1984**, *49*, 2551.

(2) A preliminary communication was published earlier: Brown, H. C.; Rei, M.-H. *J. Am. Chem. Soc.* **1969**, *91*, 5646.

0022-3263/85/1950-1171$01.50/0 

**Table III. Solvomercuration–Demercuration of 2-Methyl-1-butene with Mercuric Trifluoroacetate**

| ROH | temp,[b] °C | time, min | % products[a] $CH_3CH_2C(OR)CH_3$ | % products[a] $CH_3CH_2C(OH)CH_3$ |
|---|---|---|---|---|
| methanol | rt | 5 | 89 | trace |
| | | 60 | 45 | trace |
| | 0 | 5, 30 | 90 | trace |
| ethanol | rt | 5 | 82 | trace |
| | | 60 | 43 | trace |
| | 0 | 5, 60 | 82 | trace |
| 2-propanol | rt | 5 | 39 | trace |
| | | 60 | 1 | trace |
| | 0 | 5 | 80 | trace |
| | | 60 | 72 | trace |
| 2-methyl-2-propanol | rt | 10 | 0 | 0 |

[a] Quantitative VPC analysis. [b] rt = room temperature, ca. 22–23 °C.

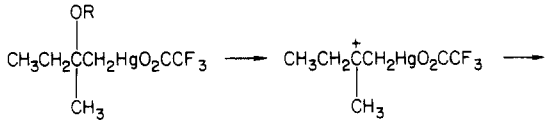
following this addition and by carrying out the alkaline sodium borohydride demercuration with rapid stirring, excellent and reproducible results are obtained (Table I).

Cyclopentene gives similarly excellent results in methanol, ethanol, and 2-propanol. However, in *tert*-butyl alcohol the yields of ether are low and decrease with time (Table II).

This decomposition is most readily attributable to the eclipsing interactions present in the envelope skeleton of the cyclopentyl ring.

2-Methyl-1-butene undergoes the SM–DM reaction sequence with results very similar to those of 2-methyl-2-butene and tetramethylethylene (Table III). At room temperature, the alkoxy mercurials are unstable to the reaction conditions. However, at 0 °C, major improvements are obtained in methanol, ethanol, and 2-propanol.

The major pathway for decomposition of the alkoxy mercurials again appears to be the formation of the Denigès complex (eq 1). No products attributable to the



Denigès complex (1)

solvolysis of the mercury group, i.e., the vinyl ether or the diether, are present in significant amounts.

Cyclooctene exhibits behavior very similar to tri-, tetra-, and isosubstituted olefins (Table IV). While the methoxy mercurial is stable to the reaction conditions, the ethoxy, isopropoxy and *tert*-butoxy derivatives are not. Moreover, their decomposition is accompanied by the formation of the yellow Denigès complex. VPC analysis of the product mixture revealed that in addition to the cyclooctyl ethers and cyclooctanol trace amounts of other compounds are formed, which we could not identify. Consequently, solvolysis of the mercury group is of little or no importance in the decomposition of these mercurials under these reaction conditions.

The rate and extent of the decomposition of the mercurials appear to be proportional to the size of the alkoxy group. This behavior is readily attributable to the transannular interactions engendered in the cyclooctyl skeleton. To the best of our knowledge, this is the first example of a 1,2-disubstituted olefin which undergoes the solvomercuration chemistry characteristic of tri-, tetra-, and isosubstituted olefins.

A number of representative oxymercuration–demercuration reactions leading to ethers were scaled up, with isolation of the products. No difficulties were encountered.

## Summary

The results described in the previous and present studies clearly reveal the remarkable synthetic utility of mercuric trifluoroacetate. The solvomercurations are remarkably rapid, often being complete within 5 min at room temperature. No difficulties were encountered in scaling up. The isolated yields are quite good (Table V).

## Experimental Section

The materials, solvomercuration–demercuration procedures, and VPC analyses are as described in the previous paper.[1]

Infrared spectra were recorded on neat samples on a Perkin-Elmer Model 137 spectrophotometer (calibrated to polystyrene). $^1H$ NMR spectra were recorded in carbon tetrachloride (ca. 10% v/v), relative to tetramethylsilane on a Varian Model T-60 spectrometer.

**Representative Solvomercuration–Demercuration Procedures on a Preparative Scale. Cyclohexyl Methyl Ether.** A 250-mL, round-bottom flask equipped with a magnetic stirring bar and a water condenser was charged with mercuric trifluoroacetate (22.00 g, 51.6 mmol) and anhydrous methanol (52 mL). To the stirred suspension was added cyclohexene (4.34 g, 51.6 mmol). After stirring for 15 min, 3 M NaOH (52 mL) was added (reaction vessel immersed in an ice–water bath) with vigorous stirring. After 2 min, 0.5 M $NaBH_4$ in 3 M NaOH (52 mL) was added. After 15 min (Hg coagulation in 2 min), the mixture was extracted with *n*-pentane (75 mL). The organics were washed with water (3 × 60 mL) and dried ($MgSO_4$). The solvent was

**Table IV. Solvomercuration–Demercuration of Cyclooctene with Mercuric Trifluoroacetate**

| ROH | temp,[d] °C | time, min | % products[a]  | % products[a]  | % products[a]  |
|---|---|---|---|---|---|
| methanol | rt | 5, 60 | 93 | 0 | 0 |
| ethanol | rt | 5 | 95 | 0 | 0 |
| | | 60 | 85 | trace | 0 |
| | 0 | 5 | 77 | 0 | |
| | | 60 | 96 | 0 | |
| 2-propanol[b] | rt | 5 | 73 | trace | 28 |
| | | 60 | 58 | trace | 34 |
| | 0 | 5 | 24 | 0 | 75 |
| | | 60, 120 | 80 | trace | 22 |
| 2-methyl-2-propanol[c] | rt | 5 | 12 | 7 | 68 |
| | | 60 | 6 | 10 | 68 |

[a] Quantitative VPC analysis. [b] Trace amounts of one other compound were observed. [c] Trace amounts of three other compounds were observed. [d] rt = room temperature.

**Table V. Solvomercuration–Demercuration of Olefins with Mercuric Trifluoroacetate**

| olefin | ether, R'OR | % yields for R'[a-c] methoxy | ethoxy | isopropoxy | *tert*-butoxy |
|---|---|---|---|---|---|
| 1-hexene | 2-*n*-hexyl | 90 | 97 | 94 (82) | 82 (84) |
| 1-dodecene | 2-*n*-dodecyl | 91 (73) | 94 (80) | 100 (93) | 87 [80 min] |
| styrene | α-phenethyl | 96 (79) | 100 | 93 [60 min] | 87 (85) |
| *tert*-butylethylene | pinacolyl | 86 (62) | 83 (75) | 67 [60 min] | 34 [1440 min] |
| cyclohexene | cyclohexyl | 92 (78) | 100 (85) | 95 (84) | 89 (82) |
| cyclopentene | cyclopentyl | 94 | 93 | 100 (77) | 79 |
| cyclooctene | cyclooctyl | 93 | 95 | 80 [60 min][d] | 12 |
| norbornene | *exo*-norbornyl | 91 | 73 | 47 [1440 min] | 84 [1440 min] (80) |
| 2-methyl-2-butene | *tert*-amyl | 89[d] | 88[d] | 50[d] | 0 |
| 2-methyl-1-butene | *tert*-amyl | 90[d] | 82[d] | 80[d] | 0 |
| tetramethylethylene | thexyl | 82[d] | 59[d] | 26[d] | 0 |

[a] Yields by quantitative VPC analysis. Isolated yields in parentheses. [b] Reaction time 5 min, except where otherwise indicated (minutes in brackets). Reaction at room temperature, 22–23 °C, except where otherwise indicated. [c] Only yields of Markovnikov ethers are listed. [d] Reaction temperature is 0 °C.

removed by distillation through a Vigreux column and the residue was distilled, employing a heat gun (foaming) to yield 4.60 g (78%) of product, bp 65 °C (120 mm); VPC analysis indicated a purity of >99%; NMR ($CCl_4$) δ 3.23, 3.05 (s, m, shift determined with Eu(fod)$_3$, 4 H), 0.95–2.12 (m, 10 H); IR (neat) cm$^{-1}$ 1370, 1111, 1093.

**Cyclohexyl Ethyl Ether.** A 300-mL, three-necked, round-bottomed flask, equipped with a magnetic stirring bar and a water condenser was charged with mercuric trifluoroacetate (17.95 g, 42.1 mmol) and ethanol (42 mL). To the stirred suspension was added cyclohexene (3.53 g, 42.0 mmol). After 6 min of stirring, 3 M NaOH (42 mL) was added with vigorous stirring (reaction vessel immersed in an ice–water bath). After 2 min, 0.5 M $NaBH_4$ in 3 M NaOH (42 mL) was added. The reaction mixture was extracted 15 min later with *n*-pentane (50 mL) (Hg coagulation after 5 min). The organics were washed with water (3 × 50 mL) and dried ($MgSO_4$). The solvent was distilled off through a Vigreux column and the residue was distilled, employing a heat gun (foaming) to yield 4.61 g (85%) of product, bp 47 °C (22 mm); VPC analysis indicated a purity of 100%; $^1$H NMR ($CCl_4$) δ 3.40, 3.17 (q, 7 Hz, overlapping m, shift determined by Eu(fod)$_3$, 3 H), 0.85–2.33, 1.13 (m, t, 7 Hz, 13 H); IR (neat) cm$^{-1}$ 1379, 1368 (sh), 1109.

**Cyclohexyl Isopropyl Ether.** A 250-mL, round-bottomed flask equipped with a magnetic stirring bar and a water condenser was charged with mercuric trifluoroacetate (16.8 g, 39.4 mmol) and anhydrous 2-propanol (39 mL). To the stirred suspension was added cyclohexene (3.32 g, 39.4 mmol). After 10 min of stirring, 3 M NaOH (39 mL) was added with vigorous stirring (reaction vessel immersed in an ice–water bath). After 2 min, 0.5 M $NaBH_4$ in 3 M NaOH (39 mL) was added. After 30 min of stirring (no Hg coagulation), the mixture was extracted with *n*-pentane (70 mL). The organics were washed with water (5 × 60 mL) and dried ($MgSO_4$). The solvent was removed by short-path distillation and the residue was distilled, employing a heat gun to give 4.70 g (84%) of product: bp 87 °C (77 mm); $^1$H NMR ($CCl_4$) δ 3.65, 3.25 (septet, 7 Hz, m, 2 H), 1.08, 0.95, 2.15 (d, 7 Hz, m, 16 H); IR (neat) cm$^{-1}$ 1387, 1134, 1087.

***tert*-Butyl Cyclohexyl Ether.** A 200-mL, round-bottomed flask equipped with a magnetic stirring bar and a water condenser was charged with mercuric trifluoroacetate (10.66 g, 25.0 mmol) and *tert*-butyl alcohol (25 mL). To the stirred suspension was added cyclohexene (2.05 g, 25.0 mmol). After stirring for 12 min, 3 M NaOH (25 mL) was added with vigorous stirring (reaction vessel immersed in an ice–water bath). After 2 min of stirring, 0.5 M $NaBH_4$ in 3 M NaOH (25 mL) was added. After 30 min (no Hg coagulation), the mixture was extracted with *n*-hexane (50 mL). The organics were washed with water (15 × 60 mL) and dried ($MgSO_4$). The solvent was removed by distillation through a Vigreux column and the residue was distilled by employing a heat gun to give 3.22 g of product (82%): bp 77 °C (31 mm); VPC analysis indicated the purity to be >99%; $^1$H NMR ($CCl_4$) δ 3.25 (m, 1 H), 1.00–1.95 (m), 1.15 (s, *t*-Bu), 19 H total; IR (neat) cm$^{-1}$ 1397, 1368, 1202, 1079.

**Spectral Properties of the Remaining Ethers. 2-*n*-Dodecyl methyl ether:** $^1$H NMR ($CCl_4$) δ 3.23 (s, m, 4 H), 0.67–1.62 (m, 20 H); IR (neat) cm$^{-1}$ 1377, 1105.

**2-*n*-Dodecyl ethyl ether:** $^1$H NMR ($CCl_4$) δ 3.37 (m, 3 H), 0.90–1.67 (m, ca. 25 H); IR (neat) cm$^{-1}$ 1379, 1127.

**2-*n*-Dodecyl isopropyl ether:** $^1$H NMR ($CCl_4$) δ 3.60 (septet, 6 Hz, m, 2 H), 0.83–1.53 (m, 30 H); IR (neat) cm$^{-1}$ 1372, 1127.

***tert*-Butyl 2-*n*-dodecyl ether:** $^1$H NMR ($CCl_4$) δ 3.50 (m, 1 H), 0.67–1.53, 1.12 (m, s, ca. 33 H); IR (neat) cm$^{-1}$ 1389, 1362, 1205, 1139, 1125.

**Cyclooctyl methyl ether:** $^1$H NMR ($CCl_4$) δ 3.25, 3.18 (s, m, 4 H), 1.53 (m, 14 H); IR (neat) cm$^{-1}$ 1366, 1001.

**Cyclooctyl ethyl ether:** $^1$H NMR ($CCl_4$) δ 3.38, 3.24 (q, 7 Hz, m, 3 H), 1.55, 1.12 (m, t, 7 Hz, 17 H); IR (neat) cm$^{-1}$ 1370, 1124, 1093.

**Cyclooctyl isopropyl ether:** $^1$H NMR ($CCl_4$) δ 3.55 (septet, 6.0 Hz, m, 2 H), 1.55 (m, 14 H), 1.05 (d, 6.0 Hz, 6 H); IR (neat) cm$^{-1}$ 1377, 1364, 1159, 1135.

***tert*-Butyl cyclooctyl ether:** $^1$H NMR ($CCl_4$) δ 3.50 (m), 1.50 (m), 1.13 (s).

**Cyclopentyl methyl ether:** $^1$H NMR ($CCl_4$) δ 3.73 (m, 1 H), 3.20 (s, 3 H), 1.63 (m, 8 H); IR (neat) cm$^{-1}$ 1366, 1107.

**Cyclopentyl ethyl ether:** $^1$H NMR ($CCl_4$) δ 3.82 (m, 1 H), 3.35 (q, 7 Hz, 2 H), 1.58 (m, 8 H), 1.15 (t, 7 Hz, 3 H); IR (neat) cm$^{-1}$ 1370, 1135.

**Cyclopentyl isopropyl ether:** $^1$H NMR ($CCl_4$) δ 3.92, 3.52 (m, septet, 6 Hz, 2 H), 1.58 (m, 8 H), 1.07 (d, 6 Hz, 6 H); IR (neat) cm$^{-1}$ 1377, 1368, 1136.

***tert*-Butyl cyclopentyl ether:** $^1$H NMR ($CCl_4$) δ 3.97 (m, 1 H), 1.57 (m, 8 H), 1.13 (s, 9 H); IR (neat) cm$^{-1}$ 1389, 1362, 1208, 1094.

**Acknowledgment.** We are deeply indebted to the Corporate Research Laboratories of the Exxon Research and Engineering Company for a grant which made this investigation possible.

**Registry No.** $CH_3(CH_2)_9CH(OCH_3)CH_3$, 95363-55-6; $CH_3(CH_2)_9CH(OC_2H_5)CH_3$, 95363-56-7; $CH_3(CH_2)_9CH(OCH(CH_3)_2)CH_3$, 95363-57-8; $CH_3(CH_2)_9CH(OC(CH_3)_3)CH_3$, 95363-58-9; $CH_3CH_2C(OCH_3)(CH_3)_2$, 994-05-8; $CH_3CH_2C(OC_2H_5)(CH_3)_2$, 919-94-8; $CH_3CH_2C(OCH(CH_3)_2)(CH_3)_2$, 3249-46-5; $CH_3(CH_2)_3CH(CH_3)OCH_3$, 25246-71-3; $CH_3(CH_2)_3CH(CH_3)OC_2H_5$, 25246-72-4; $CH_3(CH_2)_3CH(CH_3)OCH(CH_3)_2$, 25246-73-5; $CH_3(CH_2)_3CH(CH_3)OC(CH_3)_3$, 25246-74-6; $C_6H_5CH(CH_3)OCH_3$, 4013-34-7; $C_6H_5CH(CH_3)OC_2H_5$, 3299-05-6; $C_6H_5CH(CH_3)OCH(CH_3)_2$, 65757-61-1; $CH_3CH(C_6H_5)OC(CH_3)_3$, 90367-83-2; $(CH_3)_3CCH(OCH_3)CH_3$, 25246-75-7; $(CH_3)_3CCH(OC_2H_5)CH_3$, 25246-76-8; $(CH_3)_3CCH(OCH(CH_3)_2)CH_3$, 25246-77-9; $(CH_3)_3CCH(OC(CH_3)_3)CH_3$, 25246-78-0; $CH_3CH_2C(CH_3)_2OCH_3$, 994-05-8; $CH_3CH_2C(CH_3)_2OC_2H_5$, 919-94-8; $CH_3CH_2C(CH_3)_2OCH(CH_3)_2$, 3249-46-5; $(CH_3)_2CHC(CH_3)_2OCH_3$, 26356-10-5; $(CH_3)_2CHC(CH_3)_2OC_2H_5$, 90367-80-9; $(CH_3)_2CHC(CH_3)_2OCH(CH_3)_2$, 90367-81-0; $CH_3(CH_2)_9CH(OH)CH_3$, 10203-28-8; cyclopentyl ethyl ether, 26306-40-1; cyclopentyl isopropyl ether, 90200-67-2; cyclopentyl *tert*-butyl ether, 95363-59-0; cyclooctyl ethyl ether, 95387-25-0; cyclooctyl isopropyl ether, 95363-60-3; cyclooctyl *tert*-butyl ether, 95363-61-4; cyclohexyl isopropyl ether, 1860-29-3; *exo*-2-methoxynorbornane, 10395-53-6; *exo*-2-ethoxybornane, 25273-25-0; *exo*-2-isopropoxynorbornane, 25273-26-1; *exo*-2-*tert*-butoxynorbornane, 25273-27-2; 2-propanol,

67-63-0; 2-methyl-1-butene, 563-46-2; cyclopentyl methyl ether, 5614-37-9; cyclooctyl methyl ether, 13213-32-6; cyclooctanol, 696-71-9; cyclooctene, 931-88-4; cyclohexyl methyl ether, 931-56-6; cyclohexyl ethyl ether, 932-92-3; *tert*-butyl cyclohexyl ether, 25246-83-7; mercuric trifluoroacetate, 13257-51-7; methanol, 67-56-1; ethanol, 64-17-5; *tert*-butyl alcohol, 75-65-0; 1-dodecene, 112-41-4; cyclopentene, 142-29-0; tetramethylethylene, 563-79-1; 1-hexene, 592-41-6; styrene, 100-42-5; *tert*-butylethylene, 558-37-2; cyclohexene, 110-83-8; norbornene, 498-66-8; 2-methyl-2-butene, 513-35-9.

# Condensation–Cyclization of Carbanions with Electron-Deficient Aromatics. Formation and Structure of Delocalized Anions Containing the Bicyclo[3.3.1]nonane Skeleton

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*Received July 30, 1984*

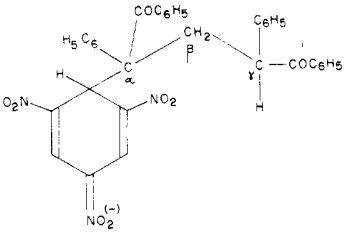
A series of new bicyclic anions containing the bicyclo[3.3.1]nonane skeleton have been prepared using *sym*-trinitrobenzene, ethyl 3,5-dinitrobenzoate, and picramide as the nitroaromatic moieties. Benzoylacetone, (*p*-nitrobenzoyl)acetone, (*m*-nitrobenzoyl)acetone, 1-(ethoxycarbonyl)-1-(X-benzyl)-2-propanone (X = H, *p*-$OCH_3$, *p*-$CH_3$, *p*-Cl, *p*-Br, *p*-$NO_2$ and *o*-$NO_2$), 1-(ethoxycarbonyl)-1-(2,3-dimethylbenzyl)-2-propanone, 1-(ethoxycarbonyl)-1-(1-naphthylmethyl)-2-propanone, and 1-(ethoxycarbonyl)-1-benzoyl-2-propanone have been utilized as the carbanion precursors. The condensation–cyclizations are initiated with triethylamine and piperidine. The cyclic adducts derived from (*p*-nitrobenzoyl)acetone and (*m*-nitrobenzoyl)acetone are identical due to loss of the nitrobenzoyl moiety. Similarly the adduct from the addendum 1-(ethoxycarbonyl)-1-benzoyl-2-propanone suffers cleavage of the benzoyl moiety. Observations on the steric effects caused by some substituents at the site of condensation and spectral characterizations of the bicyclics have been recorded.

A series of new bicyclic anions containing the bicyclo-[3.3.1]nonane skeleton has been prepared from TNB, 3,5-dinitrobenzonitrile, methyl 3,5-dinitrobenzoate, and carbanions derived from various ketones and keto esters such as acetone, acetylacetone, dicarbomethoxyacetone, and ethylacetoacetate, and a lactone ($\alpha$-acetylbutyrolactone) by Strauss et al.[2]

No crystalline adduct has been prepared from TNB, benzoylacetone (1-benzoyl-2-propanone), and $NEt_3$. Interesting results in the kinetics of formation of this complex reported in the subsequent paper necessitated the isolation of the adduct. In the preparation of this adduct, the method of Strauss and co-workers[2] yielded only a pasty mass. In the present paper, a new procedure has been adopted to get a crystalline adduct **1** (see Experimental Section).

Attempts to prepare bicyclic adducts from TNB, $NEt_3$, and the compounds (*p*-nitrobenzoyl)acetone [1-(*p*-nitrobenzoyl)-2-propanone] and (*m*-nitrobenzoyl)acetone [1-(*m*-nitrobenzoyl)-2-propanone] under the same experimental conditions as for the formation of the adduct from benzoylacetone resulted in failure. Surprisingly, an unexpected product **2** resulted from both, but under different experimental conditions (see Experimental Section). Elemental analysis and visible, IR, and NMR spectra support structure **2**. It is noteworthy that this adduct **2** could not be obtained from TNB, acetone, and $NEt_3$.

Strauss et al.[3] have observed that in the presence of diethylamine the 1:1 Meisenheimer adduct of TNB–acetone cyclizes more rapidly than TNB–1,1-diphenylacetone and TNB–1,1,3,3-tetraphenylacetone adducts. The steric problems in the latter cases should be more severe than in the former. The same authors have reported that Meisenheimer adduct **3** fails to cyclize due to (i) two bulky groups $C_6H_5$ and $COC_6H_5$ at $C_\gamma$ and (ii) hybridizational change of trigonal to tetrahedral at $C_\beta$. Previous

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studies in our laboratories[4] have established that $\alpha$-bromo and $\omega$-bromo acetoacetanilides do not form stable bicyclic adducts with TNB in the presence of $NEt_3$ due to the presence of a bulky bromine at the site of condensation. There have been only a few reports on steric effects at the $C_\gamma$ position. The growing interest in examining the favorable conformation and conditions for cyclization promoted us to isolate a series of new adducts [**4–16**, Table I] from electron deficient aromatics and compounds of the type $CH_3COCHYZ$, where Y and Z are different substituents. A study of the kinetics of formation of the reported adducts is under progress and will form the subject matter of a later publication. The melting points, visible absorption maxima, and NMR data of the isolated adducts are listed in Table II.

## Discussion

**Benzoylacetone Adducts.** In structure **2** the nitrobenzoyl moiety has cleaved off. This is probably due to

(1) To whom all inquiries should be addressed.
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(3) Strauss, M. J.; Schran, H.; Taylor, S. P. B., unpublished results.
(4) Gnanadoss, L. M.; Radha, N. *J. Org. Chem.* **1983**, *48*, 570.

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