collected until only a trace of colored residue remained. The sublimate was recrystalized from 10 mL of petroleum ether, bp 37–55 °C; chilling of the solution in dry ice gave 0.98 g (81%) of colorless 3-methoxy-4-chloro-5-bromopyridine (8): mp 97–98 °C; NMR (CCl_4) δ 4.00 (s, 3, OCH_3), ~8.35 (evident only by integration, 2, C(2) and C(6) protons). Anal. Calcd for $C_6H_5BrClNO$: C, 32.39; H, 2.27; N, 6.30. Found: C, 32.42; H, 2.31; N, 6.36.

***N*,2-Dimethyl-3-methoxy-5-bromo-γ-pyridone (9).** A solution prepared by dissolving 1 g of bromomaltol methyl ether and 20 mL of 40% aqueous methylamine in 25 mL of ethanol was refluxed for 3 h. The solvent was evaporated by flash evaporation. The residue was dissolved in 10 mL of hot chloroform and shaken with 1 g of Norite A, the mixture was filtered, and the filtrate was evaporated in vacuo. The tarry residue was extracted with 5-mL portions of hot toluene twice, the combined extracts were refrigerated, and product was collected. The solid then was recrystallized repeatedly from 5–10 mL of benzene to give 0.8 g (77%) of the colorless pyridone: mp 172–173 °C. Anal. Calcd. for $C_6H_{10}BrNO_2$: C, 41.38; H, 4.34; Br, 34.43; N, 6.03. Found: C, 41.54; H, 4.35; Br, 34.20; N, 6.30.

Acknowledgment. This work was supported in part by a grant (AI-01703) from the National Institutes of Health, U.S. Public Health Service. The XL-100 NMR instrument used in this investigation was purchased with funds from NSF grant GP 10293. Both grants are gratefully acknowledged.

Registry No. 1, 118-71-8; 2, 71001-54-2; 3, 71001-55-3; 4, 71001-56-4; 5, 71001-57-5; 6, 71001-58-6; 7, 71001-59-7; 8, 71001-60-0; 9, 71001-61-1.

Alkyl Nitrate Nitration of Active Methylene Compounds. Nitration of Alicyclic Ketimines[1]

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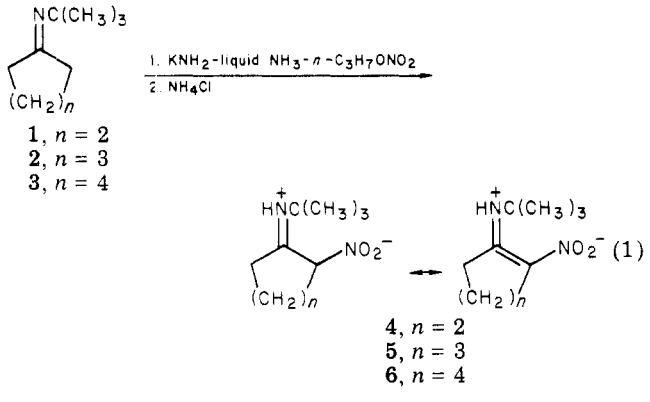
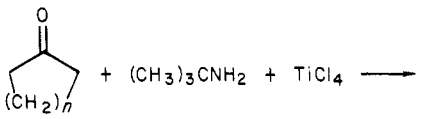
Received April 2, 1979

In continuation[2] of our studies of the alkyl nitrate nitration, we now report on its application to the preparation of 1-nitro-2-(*tert*-butylamino)cycloalkenes **4–6** directly from the corresponding alicyclic *tert*-butyl imines **1–3** (eq 1).



(1)

Compounds **1–3** were obtained in about 50% yield by an adaptation of the method by Weingarten et al.[3] (eq 2). The presence of the tautomeric enamine structure was



1-3 + $(CH_3)_3CNH_3^+ \cdot Cl^-$ + TiO_2 (2)

indicated only in *N*-cyclohexylidene-*tert*-butylamine (**2**). The NMR spectrum of **2** showed a triplet at 5.60 ppm (0.12 proton) due to the vinyl proton and two singlets for the *tert*-butyl group at 1.30 and 1.24 ppm (total of nine protons), indicating respectively the imine and enamine forms. A signal at 4.21 ppm for the vinyl proton was also reported for *N*-cyclohexylidene-*n*-butylamine.[4]

The nitration reaction in eq 1 was carried out in the potassium amide–liquid ammonia system employing conditions which were found to be optimum in the nitration of aldimines.[5] The molar ratio of imine to base to nitrating agent employed was 1:2:1.5, and ammonium chloride was used in the acidification step. Nitration of **1-3** gave 1-nitro-2-(*tert*-butylamino)cyclopentene (**4**), 1-nitro-2-(*tert*-butylamino)cyclohexene (**5**), and 1-nitro-2-(*tert*-butylamino)cycloheptene (**6**) in yields of 35, 44, and 50%, respectively. Only mononitration products were detected in these nitrations.

The formation of compound **4** is of interest in view of the fact that attempts to prepare 2-nitrocyclopentanone by the alkyl nitrate nitration of cyclopentanone were unsuccessful. Mainly, dipotassium 2-ketocyclopentane-1,3-dinitronate, the aldol condensation product, 2-(1-hydroxycyclopentyl)cyclopentanone, and amyl 5-nitropentanoate, arising from ring opening, were obtained.[6]

At ambient temperatures, **4** showed resistance to hydrolysis in 95% ethanolic hydrochloric acid. No changes in its UV spectrum were observed after 27 days. Compound **4** might be a useful synthetic intermediate as a substitute for 2-nitrocyclopentanone.

Spectra of Compounds 4–6. A study of the NMR spectra of compounds **4–6** indicated the presence of the dipolar structure. In $CDCl_3$ the presence of the iminium proton in compounds **4–6** was indicated at 10.17, 12.00, and 12.20 ppm, respectively. Addition of $(CD_3)_2SO$ to $CDCl_3$ solutions of compounds **4–6** did not affect the positions of these peaks. The iminium proton in pyridinium bromide has been reported to fall at 12.57 ppm.[7]

The ring protons of **4–6** appeared as two multiplets at about 1.80 and 2.80 ppm. The latter was assigned to the methylene groups adjacent to the iminium and nitronate groups.

The IR spectra (CCl_4) of compounds **4–6** showed the C=N absorptions as very strong bands in the region of 1595–1615 cm^{-1}. The expected absorptions for the nitronate group appeared at 1215–1245 (asymmetric stretch) and at 1120–1180 cm^{-1} (symmetric stretch).[8]

Absorptions due to the NH group were absent. Similar observations have been reported for several aminonitro olefins containing a secondary amino group and were attributed to intramolecular hydrogen bonding.[9] Similar hydrogen bonding in the dipolar structure A might account for the absence of absorption characteristic of the iminium group in **4–6**. The observed broad absorption of the iminium proton in the NMR spectra of **4–6** (vide supra) is further indication of structure A.

(1) Alkyl Nitrate Nitration of Active Methylene Compounds. 16. For part 15 see: Feuer, H.; Blecker, L. R.; Jans, R. W., Jr.; Frost, J. W. *J. Heterocycl. Chem.* **1979**, *16*, 481–5.

(2) For previous publications see: (a) Feuer, H.; Van Buren, W. D.; Grutzner, J. B. *J. Org. Chem.* **1978**, *43*, 4676–8. (b) Feuer, H. *ACS Symp. Ser.* **1976**, *No. 22*, 160.

(3) Weingarten, H.; Chupp, J. P.; White, W. A. *J. Org. Chem.* **1967**, *32*, 3246–9.

(4) Nelson, D. A.; Worman, J. J. *Chem. Commun.* **1966**, 487–8.

(5) Fetell, A. I.; Feuer, H. *J. Org. Chem.* **1978**, *43*, 497–501.

(6) Feuer, H.; Pivawer, P. M. *J. Org. Chem.* **1966**, *31*, 3152–8.

(7) Kotowicz, G.; Shaefer, T.; Bock, E. *Can. J. Chem.* **1964**, *42*, 2541–8.

(8) Feuer, H.; Savides, C.; Rao, C. N. R. *Spectrochim. Acta* **1963**, *19*, 431–4.

(9) Freeman, J. P. Emmons, W. D. *J. Am. Chem. Soc.* **1956**, *78*, 3405–8.

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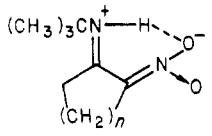
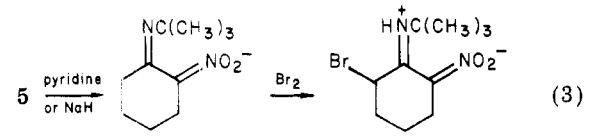


A

Structure A was also indicated in the UV spectra of **4–6** by an intense peak in the range 366–370 nm. Aminonitro olefins capable of hydrogen bonding have been reported to show maxima in this range, while those not capable of hydrogen bonding absorb at about 352 nm.[5,9]

The mass spectra of **4–6** exhibited molecular ions in about 50% relative abundance, which corresponded to the appropriate molecular formulas. Fragmentations were dominated by the loss of isobutene followed by the elimination of water from the resulting ion as evidenced by the corresponding metastable ions. The loss of water can be explained by the close proximity of the iminium proton to the nitro group, as shown in structure A.

Bromination of Compound 5. Bromination of **5** in the presence of pyridine did not occur as expected at the carbonitronate group.[10] Instead it took place at C-6 of **5** to give 1-nitro-2-(*tert*-butylamino)-3-bromocyclohexene (**7**) in 67% yield (eq 3). The dipolar structure of **7** was



8 7 (3)

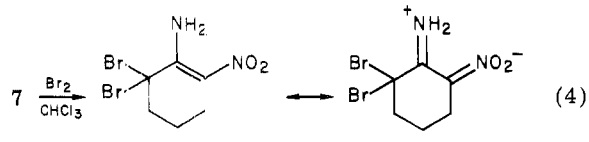
indicated by the similarity of its spectral data to those of **5**. The position of the bromine atom was clearly indicated in the NMR spectrum of **7** by a multiplet at 5.30 ppm due to the methine proton. This peak was absent in the NMR spectrum of **5**.

It is very likely that the bromination occurred via the anion **8** which was formed on treatment of **5** with pyridine or sodium hydride in THF (eq 3).

Sodium 2-(*tert*-butylamino)-2-cyclohexenenitronate (**9**) could not be obtained analytically pure; however, it was reconverted to **5** in 68% yield after acidification with glacial acetic acid.

The enamine structure of **9** was clearly indicated in its NMR spectrum, taken in $(CD_3)_2SO$, by a triplet at 4.34 ppm and a singlet at 8.10 ppm for the vinyl and amino protons, respectively. These peaks were absent when D_2O was used as a solvent because of a deuterium exchange reaction. In the solid-state IR spectrum (KBr) of **9** the presence of the NH group was clearly apparent at 3250 cm^{-1}.

Further bromination of **7** in chloroform solution gave, unexpectedly, 3,3-dibromo-2-amino-1-nitrocyclohexene (**10**) in a 53% crude yield (eq 4). Purification was difficult,



10 10a (4)

and pure **10** was obtained in only 10% yield. Its structure was indicated by its spectral data. In the NMR spectrum the *gem*-dibromo structure was indicated by the absence of the methine hydrogen present in **7**. The two amino protons appeared at 7.65 ppm.[5] In the IR spectrum two sharp peaks at 3470 and 3300 cm^{-1} confirmed the presence of the primary amino group.[11] The contribution of the dipolar structure **10a** was evident by an intense peak at 1623 cm^{-1} (C=N) and peaks at 1382 (asymmetric NO_2^-) and 1249 cm^{-1} (symmetric NO_2^-).

(10) Bromination of **5** in the absence of pyridine led to a mixture of products which was not characterized. The bulk (62% of the total weight) was an ether insoluble saltlike material which decomposed on standing in a desiccator.

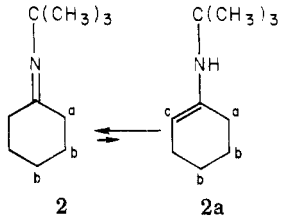
Experimental Section

Apparatus. Nitrations were performed in a 500-mL four-neck flask equipped with a mechanical stirrer, dry-ice condenser, thermometer, and pressure-equalizing addition funnel. The ammonia was passed through a sodium hydroxide tower prior to liquefaction. Solvents were removed on a Buchler flash evaporator.

IR spectra were taken with a Perkin-Elmer recording spectrophotometer, Models 221 and 421. NMR spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. UV spectra were obtained with a Cary 15 spectrophotometer. Mass spectra were recorded with a RMU-6 Hitachi mass spectrometer. Gas chromatographic analyses were performed on an Aerograph A-350B using a 10-ft SF 96 on Chromosorb W (A/W, dimethyldichlorosilane-treated) column.

***N*-Cyclohexylidene-*tert*-butylamine (2).** The following adaptation of the method of Weingarten et al.[3] is representative for the preparation of ketimines **1–3**.

To a stirred solution of 49.1 g (0.50 mol) of cyclohexanone in 300 mL of anhydrous ethyl ether under a nitrogen atmosphere was added 124.3 g (1.70 mol) of *tert*-butylamine. The reaction temperature was kept at −10 to 0 °C during the dropwise addition (70 min) of 51.2 g (0.27 mol) of titanium tetrachloride in 200 mL of pentane. The reaction mixture was then refluxed 3 h and stirred at room temperature overnight. The precipitate was filtered and thoroughly washed with ethyl ether. The combined filtrate and washings were dried ($MgSO_4$) and concentrated. The residue was distilled to afford 7.25 g of forerun and 42.95 g (56%) of **2**, bp



2 2a

83–85 °C (20 mmHg). Redistillation gave **2** of 99% purity (as determined by GC); bp 87–88 °C (20 mmHg); $n^{20}D$ 1.4704; IR (neat) 1667 (C=N) cm^{-1}; NMR ($CDCl_3$) δ 1.24 (s, ~0.5, CH_3 of **2a**), 1.30 (s, ~8.5, CH_3 of **3**), 1.70 (m, 6, H_b), 2.30 (m, 4, H_a), 4.60 (t, 0.12, H_c); mass spectrum (75 eV), *m/e* (rel intensity) 153 (34), 57 (100).

***N*-Cyclopentylidene-*tert*-butylamine (1).** The general procedure was followed except that the reaction mixture was kept at −55 to −40 °C for 6 h after the titanium tetrachloride dissolved in pentane was added. From 17.5 g (0.21 mol) of cyclopentanone, 51.2 g (0.70 mol) of *tert*-butylamine, 150 mL of anhydrous ethyl ether, and 20.9 g (0.11 mol) of titanium tetrachloride in 100 mL of pentane was obtained 12.89 g (46%) of *N*-cyclopentylidene-*tert*-butylamine of 97% purity (as determined by GC): bp 69–70 °C (20 mmHg); $n^{20}D$ 1.4650; IR ($CHCl_3$) 1676 (C=N) cm^{-1}; NMR ($CDCl_3$) δ 1.26 (s, 9, CH_3), 1.75 (m, 4, C_3H and C_4H), and 2.30 (m, 4, C_2H and C_5H).

***N*-Cycloheptylidene-*tert*-butylamine (3).** From 22.43 g (0.20 mol) of cycloheptanone, 51.2 g (0.70 mol) of *tert*-butylamine, 150 mL of anhydrous ethyl ether, and 20.54 g (0.11 mol) of titanium tetrachloride in 100 mL of pentane was obtained 14.95 g (45%) of ketimine: bp 87–89 °C (90% purity); bp 78–82 °C (9.0 mmHg). Redistillation gave *N*-cycloheptylidene-*tert*-butylamine of 99% purity (as determined by GC): bp 87–89 °C (11 mmHg); $n^{20}D$ 1.4741; IR (neat) 1650 (C=N) cm^{-1}; NMR ($CDCl_3$) δ 1.27 (s, 9, CH_3), 1.59 (m, 8, C_3H, C_4H, C_5H, and C_6H), 2.45 (m, 4, C_2H and C_7H).

(11) Nakanishi, K. "Infrared Absorption Spectroscopy"; Holden-Day: San Francisco, 1962.

1-Nitro-2-(*tert*-butylamino)cyclohexene (5). The following experiment is typical of the procedure employed in the preparation of 1-nitro-2-(*tert*-butylamino)cycloalkenes. A stirred suspension of potassium amide was prepared by adding 7.82 g (0.20 g-atom) of freshly cut potassium metal and a crystal of ferric nitrate decahydrate to 150 mL of liquid ammonia. After the suspension was cooled to -40 °C, 15.33 g (0.10 mol) of *N*-cyclohexylidene-*tert*-butylamine (**2**) was added in one portion. After the suspension was stirred for 30 min, the temperature was lowered to -60 °C and 15.76 g (0.15 mol) of *n*-propyl nitrate added (**Caution**: cooling must be maintained during the addition of the nitrating agent as long as the high exotherm persists) over a period of 3 min while the reaction temperature was kept below -40 °C. After the suspension was stirred for 30 min at -33 °C, 11.77 g (0.22 mol) of ammonium chloride was added at -45 °C.

The ammonia was replaced with absolute ether, the inorganic salts were filtered off, and the ether was removed in vacuo. Trituration of the residue with hexane gave 9.54 g of crude **5**. Recrystallization from hexane using decolorizing carbon gave 8.77 g (44%) of **5** (mp 120–122 °C). Further recrystallization gave analytically pure **5**: mp 122–123 °C; UV max (95% C_2H_5OH) 246 nm (sh). 370 (log ϵ 4.31); IR (CCl_4) 1602 (C=N), 1219 and 1122 cm^{-1} (NO_2^-); NMR ($CDCl_3$) δ 1.50 (s, 9, CH_3), 1.74 (m, 4, C_4H and C_5H), 2.70 (m, 4, C_3H and C_6H), 12.0 (br, 1, ^+NH); mass spectrum (70eV), *m/e* (rel intensity) 198 (59), 125 (100). Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.59; H, 9.15; N, 14.13. Found: C, 60.70; H, 8.91; N, 14.40.

1-Nitro-2-(*tert*-butylamino)cyclopentene (4). From 7.82 g (0.20 g-atom) of potassium, 13.9 g (0.10 mol) of *N*-cyclopentylidene-*tert*-butylamine, 15.75 g (0.15 mol) of *n*-propyl nitrate, and 12.77 g (0.24 mol) of ammonium chloride was obtained 6.40 g (35%) of **4**: mp 111–112 °C (hexane); UV max (95% C_2H_5OH) 241 nm (sh), 366 (log ϵ 4.39); IR (CCl_4) 1615 (C=N), 1205 and 1180 cm^{-1} (NO_2^-); NMR ($CDCl_3$) δ 1.44 (s, 9, CH_3), 1.98 (m, 2, C_4H), 2.84 (m, 4, C_3H and C_5H), 10.2 (br, 1, ^+NH); mass spectrum (75 eV), *m/e* (rel intensity) 184 (50), 57 (100). Anal. Calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.20. Found: C, 58.58; H, 8.71; N, 15.32.

1-Nitro-2-(*tert*-butylamino)cycloheptene (6). From 7.82 g (0.20 g-atom) of potassium, 16.7 g (0.10 mol) of *N*-cycloheptylidene-*tert*-butylamine, 15.75 g (0.15 mol) of *n*-propyl nitrate, and 12.30 g (0.23 mol) of ammonium chloride was obtained 10.72 g (50%) of **6**: mp 116–119 °C (hexane); UV max (95% C_2H_5OH) 245 nm (sh), 370 (log ϵ 4.19); IR (CCl_4) 1595 (C=N), 1212 and 1122 cm^{-1} (NO_2^-); NMR ($CDCl_3$) δ 1.48 (s, 9, CH_3), 1.72 (m, 6, C_4H, C_5H, and C_6H), 2.88 (m, 4, C_3H and C_7H), 12.2 (br, 1, ^+NH); mass spectrum (75 eV), *m/e* (rel intensity) 212 (55), 57 (100). Anal. Calcd for $C_{11}H_{20}N_2O_2$: C, 62.23; H, 9.50; N, 13.19. Found: C, 61.97; H, 9.33; N, 13.14.

1-Nitro-2-(*tert*-butylamino)-3-bromocyclohexene (7). (a) Using Compound 5. To a stirred solution of 5.94 g (0.030 mol) of **5** and 2.31 g (0.033 mol) of pyridine in 25 mL of chloroform was added dropwise, over a period of 25 min, 4.84 g (0.030 mol) of bromine dissolved in 25 mL of chloroform while the reaction temperature was kept at 3–5 °C. After continuing stirring for 30 min at ice bath temperature, the reaction mixture was washed with three 35-mL portions of water. The chloroform portion was dried ($MgSO_4$) and concentrated to give 9.53 g of solid residue. The residue was stirred successively in four 250-mL portions of ethyl ether, leaving 2.26 g of insoluble material which was pyridinium bromide.

Concentration of the combined ether extracts gave 7.00 g (84%) of crude **7**. Recrystallization gave 6.54 g (79%) of pure **7**: mp 131–135 °C dec (hexane); UV max (95% C_2H_5OH) 230 nm (log ϵ 3.66), 392 (4.21); IR (CCl_4) 1608 (C=N), 1215 and 1123 cm^{-1} (NO_2^-); NMR ($CDCl_3$) δ 1.54 (s, 9, CH_3), 2.06 (m, 4, C_4H and C_5H), 2.80 (m, 2, C_3H), 5.30 (m, 1, C_6H), 11.3 (br, 1, ^+NH); mass spectrum (75eV), *m/e* (rel intensity) 278 (7.6), 276 (7.6), 57 (100). Anal. Calcd for $C_{10}H_{17}BrN_2O_2$: C, 43.34; H, 6.18; N, 10.11; Br, 28.84. Found: C, 43.61; H, 6.33; N, 10.36; Br, 29.00.

(b) Using Sodium 2-(*tert*-Butylamino)-2-cyclohexenenitronate (9). To a suspension of 1.82 g (8.2 mmol) of **9** in 40 mL of chloroform kept at 3–5 °C was added dropwise over a period of 10 min 1.31 g (8.2 mmol) of bromine dissolved in 10 mL of chloroform. After being stirred an additional 5 min at ice-bath temperature, the mixture was filtered and the filtrate dried ($MgSO_4$). Removal of the solvent gave 1.06 g (47%) of **7**, mp 129–130.5 °C dec (hexane). A mixture melting point determination with **7** obtained in (a) gave no depression. Also the IR and NMR spectra were identical with those of **7**.

Sodium 2-(*tert*-Butylamino)-2-cyclohexenenitronate (9). To a solution of 3.96 g (0.020 mol) of **5** in 250 mL of dry THF was added 0.929 g of sodium hydride suspended in mineral oil (52% sodium hydride by weight, 0.021 mol). After the mixture was stirred at 25 °C for 5 h, 480 mL (~0.020 mol) of hydrogen was collected. The reaction mixture was filtered and the residue washed with ethyl ether to give 4.50 g of air-dried crude **9**: IR (KBr) 3250 (NH_2) 1612 (C=N, C=C), 1231 and 1146 cm^{-1} (NO_2^-); NMR [$(CD_3)_2SO$] δ 1.16 (s, 9, CH_3), 1.52 (m, 2, C_4H), 2.00 (m, 2, C_5H), 2.50 (m, C_6H; this peak overlapped the residual proton peak of the solvent, and its integration was not obtained), 4.34 (t, 1, C_3H), 8.10 (s, 1, NH).

Conversion of Salt 9 to Compound 5. Crude **9** (0.83 g, 3.8 mmol) was suspended in 250 mL of ethyl ether, and glacial acetic acid (0.22 g, 3.8 mmol) was added dropwise while the reaction temperature was kept at 3–5 °C and the reaction mixture was kept under nitrogen. The reaction was continued 3 h at room temperature, the mixture filtered, and the filtrate dried ($MgSO_4$) and concentrated to give 0.51 g (68%) of **5**, mp 121–122 °C. The spectra were identical with those of authentic **5**.

3,3-Dibromo-2-amino-1-nitrocyclohexene (10). To a stirred solution of 2.00 g (7.2 mmol) of **7** in 20 mL of chloroform kept at 3–5 °C was added dropwise over a period of 10 min 1.15 g (7.2 mmol) of bromine dissolved in 10 mL of chloroform. Stirring was continued for 30 min. Then the reaction mixture was concentrated and the residue triturated with hexane to give 2.18 g of yellow solid, mp 121–125 °C. The solid was taken up in ethyl ether, the mixture filtered, and the filtrate concentrated to give a solid residue. Trituration with hexane afforded 1.14 g (53%) of crude **10**. Two recrystallizations, the first from cyclohexane and the second from hexane, gave 0.22 g (10%) of analytically pure **10**: mp 122.5–123 °C; UV max (95% C_2H_5OH) 230 nm (log ϵ 3.64), 371 (4.13); IR (CCl_4) 3470 and 3300 (NH_2), 1623 (C=C, C=N), 1382 and 1249 cm^{-1} (NO_2^-); NMR ($CDCl_3$) δ 1.95 (m, 2, C_5H), 2.82 (m, 4, C_4H and C_6H), 7.65 (br, 2, NH_2); mass spectrum (15 eV), *m/e* (rel intensity) 302 (22), 300 (43), 298 (22), 221 (97), 219 (100). Anal. Calcd for $C_6H_8Br_2N_2O_2$: C, 24.03; H, 2.69; N, 9.34; Br, 53.28. Found: C, 24.00; H, 2.73; N, 9.09; Br, 53.60.

Acknowledgment. The support of this investigation by a grant from the IMC Chemical Group, Inc., is greatly appreciated.

Registry No. **1**, 25115-61-1; **2**, 37810-16-5; **3**, 71041-39-9; **4**, 71041-40-2; **5**, 71041-41-3; **6**, 71041-42-4; **7**, 71041-43-5; **9**, 71060-33-8; **10**, 71041-44-6; cyclohexanone, 108-94-1; *tert*-butylamine, 75-64-9; cycloheptanone, 502-42-1; cyclopentanone, 120-92-3; potassium amide, 17242-52-3.

A Convenient Preparation of β-Damascenone from Dimedone

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Received March 5, 1979

In contrast to synthetic studies of cyclocitryl homologues,[1] a different route from 3-ethoxy-6-[(*E*)-1-hydroxy-2-butenyl]-5,5-dimethyl-2-cyclohexen-1-one (**2a**),[2] prepared from the condensation of a kinetic enolate anion[3]

(1) Torii, S.; Uneyama, K.; Ichimura, H. *J. Org. Chem.* **1979**, *44*, 2229.
(2) The compound **2a** has been prepared from dimedone smoothly and used for the preparation of megastigma-4,6,8-trien-3-ones (**4**), a characteristic flavoring component of Burley tobacco: Torii, S.; Inokuchi, T.; Ogawa, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1233 and references cited therein.

0022-3263/79/1944-3412$01.00/0