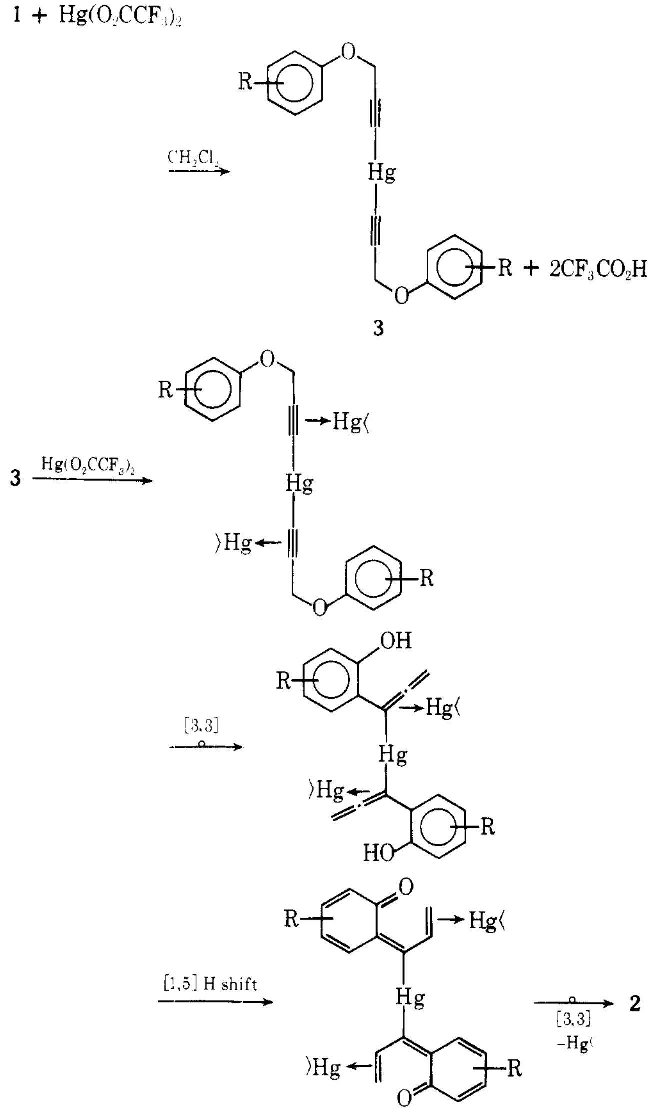
Scheme I



will be reported in due course as will the utility of **2** in organic synthesis.

Experimental Section

Melting points were determined on a Fischer–Johns melting point apparatus and are corrected. Spectral data was collected as follows: IR, Perkin-Elmer 435B (KBr); NMR, $CDCl_3$; Me_4Si reference (δ 0.00), Varian T-60; mass spectra, Hitachi Perkin-Elmer RMU-6E. The mass spectra were kindly provided by Dr. J. D. Willett of the University of Idaho, Moscow, Idaho. Microanalyses were performed under the supervision of Mr. Mike Gilles in the Michigan Technological University microanalytical laboratory.

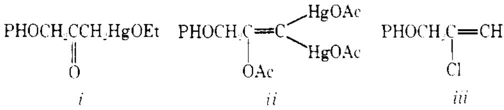
General Procedure for the Preparation of 2. Equimolar amounts of **1a** and mercuric trifluoroacetate were mixed, under N_2, in dichloromethane (5 mL/mmol) and stirred at room temperature for 2 h. The reaction was then quenched slowly (frothing) with excess alkaline (2 M NaOH) 2 M $NaBH_4$ solution. The mixture was filtered and the organic phase was washed with water. The dried ($MgSO_4$) organic layer was rotary evaporated to yield the products listed in Table I as colorless crystalline solids.

Acknowledgment. We wish to thank Dr. K. K. Balasubramanian for supplying spectral data for 4,4′-bis(6-methyl-2*H*-chromene). This research was supported by the Research Corp.

Registry No.—Phenyl 2-propynyl ether, 13610-02-1; *p*-tolyl 2-propynyl ether, 5651-90-1; *p*-anisyl 2-propynyl ether, 17061-86-8; *p*-chlorophenyl 2-propynyl ether, 19130-39-3; *o*-chlorophenyl 2-propynyl ether, 17061-92-6; 2,4-dichlorophenyl 2-propynyl ether, 17061-90-4; mercuric trifluoroacetate, 13257-51-7; 1-(4-chlorophenoxy)-2-propanone, 18859-35-3; 1-(2,4-dichlorophenoxy)-2-propanone, 17199-30-3.

References and Notes

(1) V. K. Pomeranz, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **56**, 2981 (1973).
(2) Part 2. *J. Org. Chem*, submitted for publication.
(3) R. Pearson, Ed., "Hard and Soft Acids and Bases", Dowden, Hutchinson, and Ross Publishing Co., Stroudsburg, Pa., 1973.
(4) H. C. Brown and M. H. Rei, *J. Am. Chem. Soc.*, **91**, 5646 (1969).
(5) H. C. Brown and H. J. Hammar, *J. Am. Chem. Soc.*, **89**, 1522 (1967).
(6) R. Hug, Gy. Fráter, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **54**, 306 (1971).
(7) The reaction of **1** with other mercuric salts has been described. Compounds such as **3** have been observed only under alkaline conditions with HgI_2 and $Hg(CN)_2$ (see also ref 9). Under neutral conditions **1** reacts with mercuric oxide (in aqueous ethanol) to give i and with mercuric acetate to give ii. Under acidic conditions mercuric chloride and **1** yield iii: A. Filippova, et al., *Dokl. Vses. Konf. Khim. Atsetilena, 4th*, **2**, 206 (1972).



(8) The mass spectra of alkyl and aryl bis(ethynyl)mercury compounds are dominated by C–Hg bond fission and Hg extrusion, cf. N. A. Bell and S. W. Brewer, *J. Chem. Soc., Perkin Trans. 2*, 717 (1974).
(9) J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926); the reported melting point of bis(3-phenoxyprop-1-ynyl)mercury is 120.5–121 °C.
(10) K. S. Bokarev and N. N. Melnikov, *Chem. Abstr.*, **49**, 14678 (1955).
(11) R. M. Roberts and M. B. Abdel-Baset, *J. Org. Chem.*, **41**, 1698 (1976).
(12) Mercuric ion catalysis of a [3,3] sigmatropic rearrangement via a σ complex has been reported: L. E. Overman and C. B. Campbell, *J. Org. Chem.*, **41**, 3338 (1976).
(13) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials", McGraw-Hill, New York, N.Y., 1968.
(14) This paper is dedicated to the memory of Professor H. Schmid.

Photocyclodimerization of Bicyclo[6.3.0]undec-1(8)-en-9-one. Synthesis of Highly Congested Pentacyclopropellanones

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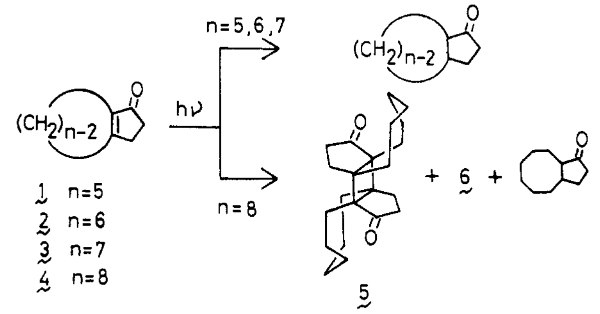
There has been considerable interest recently in pentacyclopropellanes wherein two propellane units share a common cyclobutane ring from theoretical and synthetic viewpoints.[1] Within this class of highly strained compounds, those constituted of large carbocyclic rings fused to the cyclobutane ring are expected to show unusual chemical and physical properties as a consequence of significantly repulsive nonbonded interaction of hydrogens between two kinds of carbocyclic rings facing each other. In this connection, we present here the synthesis of highly congested pentacyclopropellanes as a part of studies on the synthesis of sterically crowded polycyclic propellanes.[2]

For the purpose of building up such pentacyclic skeleton, photocyclodimerization of bicyclic cyclopentenones **1**–**4** was



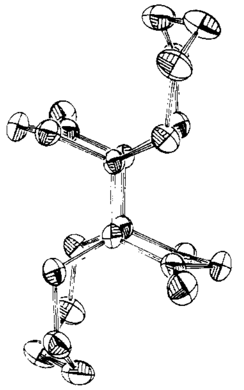


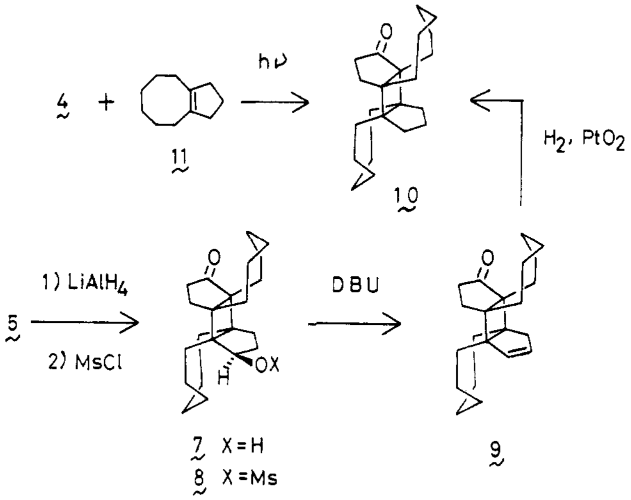
Figure 1. Molecular structure of **5**.

attempted, because we have already found that these enones are very reactive toward photocycloaddition to monocyclic olefins.[2] When a 0.5 M solution of enone **4** in ethyl ether was irradiated, crystalline cyclodimer (**5**) (mp 271–272 °C) was obtained in 42% yield ($\Phi = 0.041$) along with small amounts of its isomer (**6**) (5.3%, mp 253–254 °C) and bicyclo[6.3.0]undecan-9-one (9.6%). Absence of olefinic absorption in ^{1}H NMR, ^{13}C NMR, and IR spectra of **5** and **6** suggests that these are cyclodimers of **4**. Configuration around cyclobutane of the major cyclodimer **5** was established to be anti-head-to-tail by X-ray crystallographic study (Figure 1).[3] On the other hand, in the cases of enones **1–3**, consumption of enones was very slow and small amounts (15–19%) of the corresponding saturated ketones were obtained as the only product identified without any formation of cyclodimers.

It is significant that reactivity of bicyclic cyclopentenones toward photocyclodimerization is principally governed by the degree of flexibility of alicyclic rings fused to the double bond of cyclopentenone.[4] We have already found on the basis of the spectroscopic data of **1–4** that flexibility of the fused alicyclic rings has no significant effect on the nature of their excited triplet states,[2b] which are the reactive species for photocyclodimerization.[5] Consequently, the observed distinction in reactivity between **1–3** and **4** is interpreted in terms of the steric effects of alicyclic rings fused to the double bond of cyclopentenone in 1,4-diradical intermediates derived from one-bond formation between excited and ground state enones as well as the case of photocycloaddition of **1–4** to cyclohexene.[2b] Namely, in the cases of **1–3**, having cyclopentene, cyclohexene, and cycloheptene ring, respectively, second bond formation by radical coupling in the 1,4-diradical intermediates is markedly depressed owing to large nonbonded interaction of hydrogens facing each other between alicyclic ring methylenes. On the other hand, such nonbonded interaction in the case of **4** is smaller than those in the above cases because of large flexibility of cyclooctene ring, and, therefore, second bond formation occurs readily to afford the cyclodimers effectively. But in the cases of higher bicyclic cyclopentenones, containing more flexible rings than cyclooctene such as cyclononene and cyclodecene, intramolecular hydrogen abstraction took place exclusively and, as a result, cyclodimer was not formed.[6]

Pentacyclopropellanone (**10**) was, moreover, synthesized by cross photocycloaddition of enone **4** to bicyclo[6.3.0]undec-1(8)-ene (**11**). Irradiation of **4** with twofold excess of **11** in ethyl ether gave **10** in 65% yield ($\Phi = 0.085$) as a sole cycloadduct. Configuration around cyclobutane of **10** was confirmed by its identity with the compound prepared by the stepwise reduction of **5** as shown in Scheme I. Treatment of **5** with a large excess of lithium aluminum hydride gave monoalcohol (**7**) in 94% yield.[7] **7** was treated with methanesulfonyl chloride in pyridine to afford methane sulfonate (**8**) in 95% yield, which was heated with 1,8-diazabicyclo[5.4.0]undec-7-ene in dimethyl sulfoxide to give olefin (**9**) in 17% yield. Hydrogenation of **9** over platinum dioxide catalyst afforded **10** in 94% yield. High reactivity of **4** toward cross cycloaddition to **11** is similarly interpreted in terms of large flexibility of cyclooctene ring in **4** and **11**.

Scheme I



Unlike a variety of tetracyclopropellanones reported previously,[2] the present highly congested compounds, **5** and **10**, and their derivatives might be expected to show unusual chemical and physical properties owing to the nonbonded interaction of hydrogens between rings facing each other. Work on this subject is now being undertaken.

Experimental Section[8]

Irradiation of Enones 1, 2, and 3 in Ether. Enones **1**,[9] **2**,[10] and **3**[11] in ether (0.4–0.5 M) were irradiated for 30–100 h. During irradiation no precipitate was formed and the color of the solution gradually turned brown. After removal of the ether, the brown residue was distilled under reduced pressure and the distillate was analyzed by GLC to show the presence of unreacted enones (conversion ~30%) and the corresponding saturated ketones (15–19% yields).

Irradiation of Enone 4 in Ether. Enone **4** (9.6 g, 58.5 mmol) in 100 mL of ether was irradiated for 150 h. During irradiation white precipitate formed was collected at appropriate intervals to afford 3.1 g of a mixture of dimer **5** and **6**. The ether was removed from the filtrate and the residue was distilled under reduced pressure. GLC analysis of the distillate showed the presence of **4** (conversion 65%) and bicyclo[6.3.0]undecan-9-one (9.6%). Cyclodimers **5** and **6** were isolated by chromatography on silica gel and elution with benzene first gave 2.6 g (42%) of **5** and then 0.32 g (5.3%) of **6**. **5**: mp 271–272 °C from dioxane; IR (KBr) 1700 cm^{-1}; MS *m/e* 165 ($M^+/2 + 1$); ^{1}H NMR ($CDCl_3$) δ 0.65–2.65 (m); ^{13}C NMR ($CDCl_3$) δ 21.90 (t), 24.95, 25.21, 26.12, 30.54 (t), 39.31 (t), 49.25 (s), 59.58 (s), 222.34 (s);[12] UV ($CHCl_3$) λ_{max} 304 nm (ϵ 72.7). Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.83. Found: C, 80.55; H, 10.10. The structure of **5** was determined by the X-ray analysis. **6**: mp 253–254 °C from THF; IR (KBr) 1710 cm^{-1}; MS *m/e* 165 ($M^+/2 + 1$); ^{1}H NMR ($CDCl_3$) δ 0.60–2.60 (m); ^{13}C NMR ($CDCl_3$) δ 22.55, 24.30, 24.62, 24.95, 25.73, 26.05, 31.38 (t), 39.24 (t), 49.83 (s), 56.40 (s), 219.74 (s); UV ($CHCl_3$) λ_{max} 320 nm (ϵ 154). Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.83. Found: C, 80.19; H, 9.88.

Pentacyclopropellanone (10). (a) By Photocycloaddition of Enone 4 to Olefin 11. Enone **4** (0.820 g, 5.00 mmol) and 1.50 g (10.0 mmol) of olefin **11** in 10 mL of ether was irradiated for 25 h. The white solid formed was filtered (0.667 g) and the filtrate was concentrated and chromatographed on silica gel. Elution with petroleum ether afforded unreacted **11**, petroleum ether–benzene (1:1) additional **10** (0.17 g, total yield 65%), petroleum ether–benzene (1:4) bicyclo[6.3.0]undecan-9-one (0.029 g, 4.2%), and benzene–ether (9:1) unreacted **4** (0.144 g, conversion; 82.4%). An analytical sample of **10** was obtained by recrystallization from THF–methanol: mp 223–225 °C; IR (KBr) 1700 cm^{-1}; MS *m/e* 314 (M^+), 165, 150; ^{1}H NMR ($CDCl_3$) δ 0.60–2.75 (m); UV ($CHCl_3$) λ_{max} 304 nm (ϵ 49.8). Anal. Calcd for $C_{22}H_{34}O$: C, 84.01; H, 10.90. Found: C, 83.81; H, 11.02.

(b) By Reduction of 5. **5** (0.656 g, 2.00 mmol) in 100 mL of THF was added dropwise to a suspension of 0.76 g (20 mmol) of $LiAlH_4$ in

100 mL of THF, and the reaction mixture was refluxed for 20 h. The excess hydride was decomposed by water and the organic layer was washed with dilute hydrochloric acid and saturated sodium chloride solution and then dried (Na_2SO_4). Evaporation of the solvent gave 0.62 g (94%) of white solid which was recrystallized from THF–methanol to give **7**: mp 237–238 °C; IR (KBr) 3550, 1700, 1075 cm^{-1}; MS *m/e* 330 (M^+), 165, 149; ^1H NMR (pyridine-d_5) δ 0.70–2.80 (m, 32 H), 4.72 (q, 1 H), 6.05 (broad s, 1 H). Anal. Calcd for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37. Found: C, 79.89; H, 10.40.

To a solution of 0.360 g (1.09 mmol) of **7** in 20 mL of pyridine was added dropwise 0.57 g (5.0 mmol) of methanesulfonyl chloride and the solution was stirred at room temperature for 20 h. The solution was diluted with 150 mL of water and extracted with THF. The organic layer was washed with saturated sodium chloride solution and dried (Na_2SO_4). Evaporation of the solvent and trituration with ether gave 0.42 g (95%) of pale yellow solid which was recrystallized from THF–petroleum ether to give **8**: mp 155–156 °C with decomposition; IR (KBr) 1700, 1320, 1160 cm^{-1}. Anal. Calcd for $C_{23}H_{36}O_4S$: C, 67.61; H, 8.88; S, 7.85. Found: C, 67.23; H, 9.01; S, 7.85.

To a solution of 0.427 g (1.05 mmol) of **8** in 40 mL of dimethyl sulfoxide was added dropwise 0.38 g (2.5 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene and the solution was heated with stirring at 100–110 °C for 45 h. The solution was diluted with 200 mL of water and extracted with THF. The organic layer was washed with dilute hydrochloric acid and saturated sodium chloride solution and then dried (Na_2SO_4). Evaporation of the solvent gave brown residue, which was chromatographed on silica gel. Elution with petroleum ether–benzene (1:1) gave 0.052 g (17%) of **9**: mp 191–193 °C from THF–methanol; IR (KBr) 3030, 1700, 720 cm^{-1}; MS *m/e* 165 ($M^+ - C_{11}H_{17}$); ^1H NMR ($CDCl_3$) δ 0.80–2.60 (m, 30 H), 5.50–5.80 (m, 2 H); UV ($CHCl_3$) λ_{max} 304 nm (ϵ 43.6). Anal. Calcd for $C_{22}H_{32}O$: C, 84.56; H, 10.32. Found: C, 84.34; H, 10.51.

9 (0.102 g, 0.33 mmol) in 80 mL of acetic acid was hydrogenated with PtO_2 in the presence of hydrogen under atmospheric pressure. The catalyst was filtered off and the filtrate was diluted with 150 mL of water and extracted with chloroform. The organic layer was washed with dilute sodium carbonate solution and water. Evaporation of the solvent gave 0.098 g (94%) of white solid which was recrystallized from THF–methanol to give **10**. This material was identical with the sample synthesized by cross photocycloaddition of **4** to **11** (IR and melting point).

Bicyclo[6.3.0]undec-1(8)-ene (11). Olefin **11** was prepared according to the method of Ohloff et al.,[13] namely hydrogenation of enone **4** with Raney nickel in the presence of hydrogen at atmospheric pressure in 1% methanolic sodium hydroxide gave a mixture of saturated alcohols (90%), which was dehydroxylated with *p*-toluenesulfonic acid in boiling toluene to afford a mixture of olefins (78%). This mixture contains ~5% of undesired bicyclo[6.3.0]undec-1(2)-ene. Purification of **11** was carried out through hydroboration–oxidation (60%) according to the procedure of Benkeser et al.[14] GLC and NMR analysis showed **11** thus prepared was >99% pure. **11**: bp 88–90 °C (15 mmHg); IR (neat) 2900, 1440 cm^{-1}; MS *m/e* 150 (M^+); ^1H NMR (CCl_4) δ 1.30–2.45 (m). Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.55; H, 12.03.

Registry No.—**1**, 10515-92-1; **2**, 22118-00-9; **3**, 769-32-4; **4**, 38262-50-9; **5**, 66921-98-0; **6**, 67009-06-7; **7**, 66922-00-7; **8**, 66922-01-8; **9**, 66921-99-1; **10**, 66922-02-9; **11**, 25107-10-2; bicyclo[6.3.0]undecan-9-one, 40696-12-6; bicyclo[6.3.0]undec-1(2)-ene, 66922-03-0.

References and Notes

(1) Although some pentacyclopropellanes consisting of small carbocyclic rings,[1a,b] heterocyclic rings,[1c–e] and aromatic rings[1f] have so far been known, most of them appear to be unsuitable for a model of a congested compound: (a) K. B. Wiberg and M. E. Jason, *J. Am. Chem. Soc.*, **98,** 3393 (1976); (b) R. Greenhouse, W. T. Borden, K. Hirotsu, and J. Clardy, *ibid.*, **99,** 1664 (1977); (c) I. Lantos and D. Ginsburg, *Tetrahedron,* **28,** 2507 (1972); (d) T. Hiyama, S. Fujita, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **45,** 2797 (1972); (e) G. Ahlgren and B. Akermark, *Tetrahedron Lett.*, 987 (1974); (f) N. L. Goldman and R. A. Ruden, *ibid.*, 3951 (1968).

(2) (a) Y. Tobe, H. Omura, A. Kunai, K. Kimura, and Y. Odaira, *Bull. Chem. Soc. Jpn.*, **50,** 319 (1977); (b) Y. Tobe, A. Doi, A. Kunai, K. Kimura, and Y. Odaira, *J. Org. Chem.*, **42,** 2523 (1977).

(3) H. Matsuura, S. Koshibe, Y. Kai, N. Yasuoka, and N. Kasai, unpublished results. We are grateful to Professor N. Kasai and his co-workers for the X-ray analysis of **5**. As for configuration around cyclobutane of **6**, X-ray work is in progress. At present, we assume that **6** may be anti-head-to-head dimer by analogy with photocyclodimers of cyclopentenone. P. E. Eaton, *J. Am. Chem. Soc.*, **84,** 2344 (1962).

(4) Similar ring size effect of alicyclic rings fused to the double bond of vinylene carbonates was reported by Nozaki et al.[1d]

(5) In general, photocyclodimerization of α,β-unsaturated ketones takes place from a triplet state. D. J. Trecker in "Organic Photochemistry", Vol. 2, O. L. Chapman, Ed., Marcel Dekker, New York, N.Y., 1969, p 71.

(6) Intramolecular hydrogen abstraction by β carbon of α,β-unsaturated ketones is recently investigated by S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Am. Chem. Soc.,* **94,** 7797 (1972); A. B. Smith, III, and W. C. Agosta, *ibid.,* **95,** 1961 (1973). Details of our results will be reported shortly.

(7) The stereochemistry of the hydroxy group was assigned to be endo based on the α-hydroxy proton coupling constant (q, $J = 7$ Hz), according to the well-established stereochemical assignments of the bicyclo[3.2.0]heptan-2-ol system: S. C. Lewis and G. H. Whitham, *J. Chem. Soc. C,* 274 (1967); P. G. Gassman and J. M. Pascone, *J. Am. Chem. Soc.,* **95,** 7801 (1973).

(8) Melting points were measured in a sealed tube and are uncorrected. Infrared spectra were recorded using a JASCO IR-G spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained in JEOL JNM-PS-100 and JEOL JNM-FX60S spectrometers, respectively, using Me_4Si as an internal standard. Mass spectra were measured with a Hitachi RMU-6E spectrometer. UV spectra were recorded on a Hitachi 356 spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph. Irradiation was carried out using a 500-W high-pressure mercury lamp through a Pyrex filter under nitrogen at room temperature.

(9) S. B. Kulkarni and S. Dev, *Tetrahedron,* **24,** 553 (1968).

(10) S. Dev, *J. Indian Chem. Soc.,* **34,** 169 (1957).

(11) Pl. A. Plattner and G. Büchi, *Helv. Chim. Acta,* **29,** 1608 (1946).

(12) ^{13}C NMR of **5** shows nine signals because two pairs of the methylene carbon have nearly the same shifts most likely at 25.21 and 26.12 ppm which have almost twice the intensity of the other methylene signals.

(13) G. Ohloff, J. Becker, and K. H. Schulte-Elte, *Helv. Chim. Acta;* **50,** 705 (1967).

(14) E. M. Kaiser and R. A. Benkeser, "Organic Synthesis", Vol. 50, Wiley, New York, N.Y., 1970, p 88.

A Facile Synthesis of (3-Methoxyisoquinol-7-yl)acetic Acids

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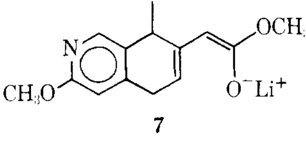
Received April 12, 1978

Our work on the total synthesis of 2-azasteroids necessitated the development of a synthesis of 7-aza-6-methoxy-1-tetralone (**1**).[1] While this compound has been successfully utilized for the preparation of 2-azaestrone derivatives, its potential as a precursor for the preparation of other biologically interesting molecules was apparent. We would now like to report on the use of this material for the facile preparation of (3-methoxyisoquinol-7-yl)acetic acids.[2] Previous syntheses of the carbocyclic analogues of this system have employed the Wilgerodt–Kindler reaction[3] on the appropriately substituted 2-acylnaphthalene,[2] or high temperature catalytic dehydrogenation of the dihydro derivatives produced from tetralones.[4] In contrast to the rather severe conditions of these methods, the approach described herein proceeds under mild conditions and provides a method of general utility for the synthesis of a variety of systems related to **6**.

Treatment of the azatetralone **1** with glyoxylic acid monohydrate in aqueous alcoholic hydroxide solution[5] afforded the unsaturated acid **2**.[6] Following esterification to the methyl ester, sodium borohydride reduction of the ketone **3** provided the conjugated hydroxyester **4**. This ester **4** could then be conveniently converted to the isoquinoline system (**6**) by deconjugation with 2 equiv of lithium diisopropylamide (LDA)[7] and subsequent dehydration of the allylic alcohol **5** with acetic acid at room temperature. It was originally thought that the intermediate **7** generated from LDA treatment might be susceptible to side-chain alkylation during the isomerization process and provided **8** in essentially a single-pot process from



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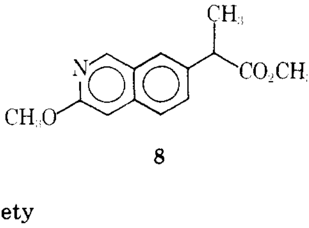

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