amido-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (26 and 27) by comparison of the glc retention times of the product components with those of authentic samples of these acetoxy acetamides prepared in this laboratory[12] and by adding authentic samples to the unknown. Retention times were 35.4 min for 26 and 11.2 min for 27.

Hydrolysis of *anti*-9,10-Imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (2). A solution of *anti*-9,10-imino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (2, 10 mg, 0.05 mmol) in 10 ml of 5% aqueous sulfuric acid was refluxed for 1 hr, cooled, made alkaline (to pH 11) with 4 *N* aqueous sodium hydroxide, and extracted with ether. The ether solution was washed with water, dried, and evaporated. The solid remaining was dissolved in 0.5 ml of methanol and analyzed by glc using a 1.88 m × 0.32 cm 10% UC-W98 silicone rubber column (Hewlett-Packard, F & M Scientific Division), operating temperature 230°, helium carrier gas flow rate 50 ml/min. The product composition was determined to be 90% 9(a)-hydroxy- and 10% 9(e)-hydroxy-10(a)-amino-1,2,3,4,4a,9,10,10a-(*trans*-4a,10a)-octahydrophenanthrene (25 and 24) by comparison of the glc retention times of the product components with the retention times of authentic samples of these amino alcohols prepared in this laboratory[12] and adding authentic amino alcohols to the unknown samples. Retention times were 11.2 min for 25 and 12.2 min for 24.

Acknowledgments. Support for a portion of this research was provided from a Career Development Award (5-K4-GM-70,023) to W. L. N. from the National Institute of General Medical Sciences, which is gratefully acknowledged. Funds for partial support of the mass spectrometric facility, Department of Chemistry, were provided by the National Science Foundation.

Registry No. 1, 28352-29-6; 2, 42822-53-7; 4, 42822-54-8; 6, 28352-40-1; 7, 28387-39-5.

References and Notes

(1) (a) K. Kotera, M. Motomura, S. Miyazaki, T. Okada, and Y. Matsukawa, *Tetrahedron*, **24**, 1727 (1968); (b) K. Kotera, T. Okada, and S. Miyazaki, *ibid.*, **24**, 5677 (1968).
(2) N. B. Chapman and D. J. Triggle, *J. Chem. Soc.*, 1385 (1963).
(3) (a) N. J. Leonard, E. F. Kiefer, and L. E. Brady, *J. Org. Chem.*, **28**, 2850 (1963); (b) N. J. Leonard and K. Jann, *J. Amer. Chem. Soc.*, **84**, 4806 (1962).
(4) W. L. Nelson and D. D. Miller, *J. Org. Chem.*, **35**, 1185 (1970).
(5) The designations syn and anti indicate the geometry of the heterocyclic three-membered ring with respect to the hydrogen atom at C-10a.
(6) All materials are racemic, although only a single isomer is drawn.
(7) The central ring is arbitrarily assigned the half-chair conformation where the axial (a) and equatorial (e) substituents are, in fact, pseudoaxial and pseudoequatorial, respectively.
(8) K. Ponsold, *Chem. Ber.*, **97**, 3524 (1964).
(9) D. H. Buss, L. Hough, and C. A. Robinson, *J. Chem. Soc.*, 5295 (1963).
(10) R. D. Gutherie and D. Murphy, *J. Chem. Soc.*, 5288 (1963).
(11) R. J. Anderson, C. A. Henrick, and J. B. Siddall, *J. Org. Chem.*, **37**, 1266 (1972).
(12) W. L. Nelson and D. D. Miller, *J. Med. Chem.*, **13**, 807 (1970).
(13) (a) H. W. Heine, *Angew. Chem., Int. Ed. Engl.*, **1**, 528 (1962); (b) H. W. Heine and M. S. Kaplan, *J. Org. Chem.*, **32**, 3069 (1967), and references cited therein; (c) H. W. Heine, D. C. King, and L. A. Portland, *J. Org. Chem.*, **31**, 2622 (1966).
(14) P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, **30**, 3574 (1965).
(15) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

Some Reactions of Tetrahydrocarbazolechloroindolenine

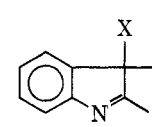
Richard J. Owellen

Department of Medicine, The Johns Hopkins University, Oncology Service, Baltimore City Hospitals, Baltimore, Maryland 21224

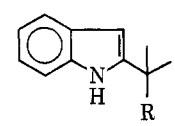
Received June 4, 1973

Tetrahydrocarbazolechloroindolenine (9), when allowed to react with NaOMe at −10°, gave 4a-methoxy-1,2,3,4-tetrahydrocarbazoleindolenine (10), while reaction with NaOH–MeOH under reflux gave 2-methoxyspiro[cyclopentane-1,3′-indolenine] (12). The relative proportion of 10 and 12 formed was dependent upon both base and temperature. When 10 was allowed to react with $LiAlH_4$, tetrahydrocarbazole was the product, while acid treatment gave bis[1,9-(1,2,3,4-tetrahydrocarbazole)] (11). $LiAlH_4$ reduction of 12 followed by Ac_2O–pyridine gave 1-acetoxyspiro[cyclopentane-1,3′-indoline] (14). Acid treatment of 12 gave spiro[cyclopentane-1,3′-indolin]-2′-one (13). 1-Methoxy-1,2,3,4-tetrahydrocarbazole (16) was prepared by NaOMe treatment of 1-pyridinium 1,2,3,4-tetrahydrocarbazole bromide (15).

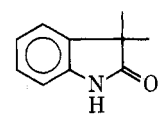
The reaction of indole derivatives with *tert*-butyl hypochlorite or sodium hypochlorite to yield chloroindolenines (1) is a well-known reaction.[1-3] Transformation of these highly reactive intermediates has yielded a variety of products depending on the conditions used. Buchi[4] found that the chloroindolenine of ibogaine, when treated with methanolic HCl, gave a methoxy derivative of structure 2, and reaction with potassium cyanide gave structure 3. The formation of oxindoles (4) has been reported by gentle acid treatment in aqueous media of the chloroindolenines of certain yohimbine alkaloids by Zinnes and Shavel.[5] Taylor and Finch[6] reported the formation of imido ethers of structure 5 by treating the chloroindolenines of various yohimbine alkaloids with methanolic base. Treatment of these imido ethers with aqueous acetic acid readily provided the corresponding oxindoles of structure 4. Recently, Gassman, *et al.*,[3] have reported a series of reactions on the chloroindolenine of 2,3-dimethylindole, where they found that treatment with silver ion and methanol gave direct substitution of the chlorine atom and formation of the 3-methoxyindolenine 6. They reported that



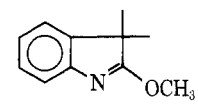
1, X = Cl
6, X = OCH_3



2, R = OCH_3
3, R = CN
7, R = OAc



4

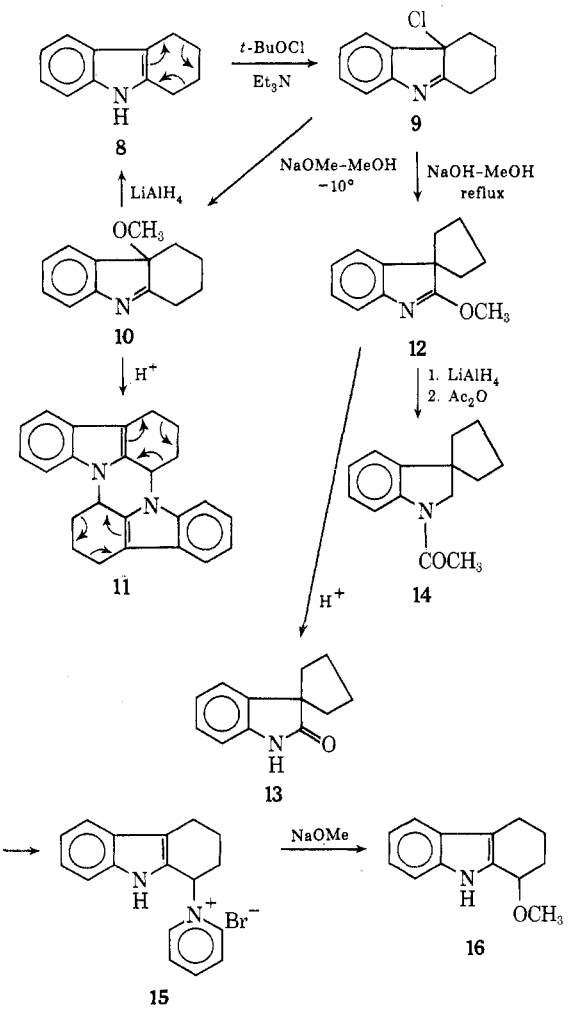


5

brief warming of a solution of the chloroindolenine caused rearrangement, evidenced by alteration of the ultraviolet and nmr spectra. When treated with NaOMe or $Th(OAc)_2$, the rearranged product gave derivatives of structure 2 and 7, respectively.

Because of our interest in certain aspects of tetrahydrocarbazole (THC, 8) chemistry, we decided to study some

reactions of its chloroindolenine, **9**. Generation of **9** at 0° was readily achieved using either *tert*-butyl hypochlorite or *N*-chlorobenzotriazole in the presence of triethylamine, as evidenced by disappearance of the 292- and 283-nm bands and emergence of an absorption maximum at 264 nm in the ultraviolet (CH_2Cl_2). The nmr spectrum of **9** showed a complex of aromatic protons at δ 6.8–7.6, a multiplet at δ 1.98–2.72, and another at δ 1.24–1.91 in approximately 4:4:4 ratio, the latter two groupings having the chemical shifts to be expected for four aliphatic protons, two protons α to a chlorine, and two protons α to a C=N bond. Isolation of this material in pure form was not possible, as it spontaneously and violently reacted when solvent was removed. A mass spectrum of this crude material gave *m/e* peaks compatible with THC (*m/e* 171, 143), carbazole (*m/e* 167), a chlorinated product (*m/e* 205, 207), and the dimer **11** (*m/e* 338, 310, 282). In contrast with the chloroindolenine of 2,3-dimethylindole,[3] the THC chloroindolenine **9** did not undergo rearrangement while in solution on warming, even at 70° for 1 hr, as shown by uv and nmr spectra identical with those obtained at 0°. Product formation (to be discussed later) after reaction of these solutions with NaOMe and NaOH–MeOH was also the same for both samples.



Treatment of THC chloroindolenine **9** with sodium methoxide at 0° gave **10** in 88% yield. This product had a uv absorption band 260 nm expected for an indolenine, which was unchanged in acid solution, and a C=N stretching band at 1650 cm^{-1} (indicating a strain in the five-membered ring) and did not show an NH stretching band (3425 cm^{-1} for THC). The nmr spectrum[13] established the remainder of the structure unequivocally, with a multiplet of four aromatic protons at δ 6.90–7.67, a singlet of three protons at δ 2.78 from the aliphatic methoxyl, and a very broad complex of eight aliphatic protons at δ 0.75–3.15. That the aliphatic proton signals were so widely spread out was in contrast to THC, where two broad signals occur at δ 1.77 and 2.55. When a model of **10** was made, it was seen that the six-membered ring was neither planar nor of the classical chair or boat conformation. Instead, the C-1 carbon must be coplanar with the nitrogen and the 9a carbon due to the double bond, while the C-4 carbon lies above the plane of the five-membered ring by approximately 54°. This imparts a spiral strained twist to the six-membered ring, making each proton around the ring nonequivalent to any other, and giving the complex nmr pattern seen. Strain in the five-membered ring, and consequently the six-membered ring as well, was already noted in the C=N stretching band. The mass spectrum of **10** had an intense M^+ ion at *m/e* 201, confirming the displacement of chlorine with a methoxyl group, and peaks which indicated loss of a methyl ($M^+ - 15$) and a methoxy ($M^+ - 31$) group.

Treatment of **10** with $LiAlH_4$ gave a 71% yield of THC (**8**) identical in the uv and mixture melting point with an authentic sample. Reduction can be rationalized as attack of an hydride ion on the nitrogen, followed by migration of the double bond to the indole position, and elimination of a methoxide anion.

When **10** was treated with dilute hydrochloric acid in aqueous methanol, a yield of 41% of crystalline product melting at 253–255° was formed. This dimer **11** has been reported with two different melting points (255 and 313° after resolidification[7] and 293–295°[8]). The mass spectrum of **11** had a molecular ion of *m/e* 338, and there were two ions at M − 28 and M − 56, as one might expect for this structure (see arrows in **11**), after comparing it with that of THC, where the major fragment is the M − 28 ion, the elements of ethylene having been lost from the saturated ring (see arrows in **8**). The uv spectrum was that of an indole, and the ir had no NH absorption band. An nmr of **11** was not possible because of its limited solubility in all solvents attempted.

When the chloroindolenine of THC (**9**) was treated with sodium hydroxide in methanol under reflux, a second product **12**, isomeric with **10**, was obtained in 82% yield. This compound was also an indolenine, as evidenced by the uv absorption at 255 nm, with no alteration in acid media. The ir had no NH band, but did have a C=N band at 1618 cm^{-1}. That this latter band is at a lower wavelength than in **10** is consistent with the less strained five-membered indolenine ring as shown in **12**. The molecular weight by mass spectral measurement was 201, and the spectrum was almost identical with that of **10**. The nmr spectrum[13] allowed firm assignment of the structure, since the eight protons of the spiro ring gave a singlet at δ 1.95, in contrast to the widely spread signal for the eight aliphatic protons in **10**. In addition, the methoxyl protons were much further downfield at δ 4.02, consistent with their proximity to the C=N bond.

When the spiro compound **12** was treated with aqueous methanolic HCl, it gave the oxindole **13** in 69% yield, previously reported by Witkop[9] and Moore.[10] All of the physical data were consistent with **13**, save the melting point of 95–96° (reported mp 113°). Preparation of **13** by Moore's method gave an ir, a melting point, and a mixture melting point identical with those of our products.

Treatment of **12** with $LiAlH_4$ gave a basic product which was difficult to characterize, and so it was derivatized with acetic anhydride in pyridine. This gave **14** in 65% overall yield. The uv spectrum of **14** was compatible with an *N*-acylindoline, with an absorbance at 252 nm.

Table I

Base	Reaction temp, °C	Ratio of 10/12
NaOMe	−10	4.00
	25	1.30
	65	0.90
NaOH	−10	1.92
	45	0.29
	65	0.17

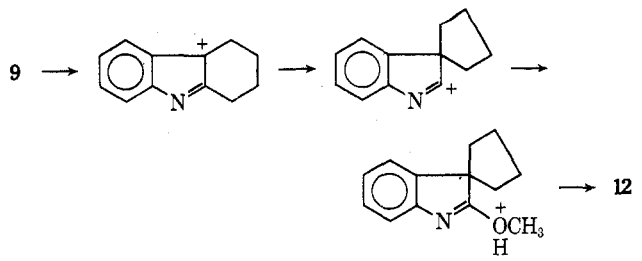
This structure was further supported by the ir with a band at 1660 cm^{-1} and disappearance of the NH absorbance, consistent with formation of an amide. The nmr had a singlet of two aliphatic protons α to the NAc at δ 3.82, a three-proton singlet at δ 2.22 from the *N*-acetyl group, and an eight-proton singlet from the spiro ring protons.

One product which might have been expected from reaction of **9** with either NaOMe or NaOH-MeOH is 1-methoxy-1,2,3,4-tetrahydrocarbazole (**16**). Since no product **16** was found, we decided to investigate the reaction of NaOMe with the known pyridinium salt **15**.[11] When the compound **15** was treated at room temperature with excess NaOMe, work-up gave a crystalline product in 52% yield, which had a molecular ion of *m/e* 201 and a pattern of fragmentation very similar to those of **10** and **12**, save that the intensity of the *m/e* 201 ion was much less and the *m/e* 186 fragment was shifted to *m/e* 185. The uv, in contrast to that of either **10** or **12**, is that of an indole, with peaks of almost equal intensity at 276, 283, and 291 nm. The ir had an indolic NH stretching band at 3300 cm^{-1}, and lacked a band in the 1600-cm^{-1} region. The nmr again provided confirmation of the structure,[13] with NH and methoxyl singlets at δ 8.13 and 3.38, respectively, a single proton at δ 4.48, α to the methoxyl group, a multiplet of two protons at C-4 at δ 2.67, and a multiplet of four protons from the C-2 and C-3 positions at δ 1.93. Especially important is the single proton at δ 4.48, adjacent to both a methoxyl and the indole system, and the two-proton multiplet at δ 2.67 on a carbon α to the indole ring. This locates the methoxyl at either C-1 or C-4, and, from the past behavior of **15**, we obviously prefer C-1.

That the two products **10** and **12** are obtainable from the chloroindolenine **9** is not surprising in view of prior studies with compounds of structure **1**. What was unusual and interesting was the dependence of product formation upon the conditions used. To further explore this phenomenon, we decided to study variations in both base and temperature upon the reaction. Since the two products **10** and **12** have sharp, easily integrated, and well-separated peaks in the nmr, we elected to run spectra on the crude reaction products without purification. Thus, each reaction mixture was run in the same manner as for **10** or **12** in the Experimental Section, save that the reaction temperature was varied. The chloroform extract of the crude reaction mixture was evaporated *in vacuo* to a viscous oil. This oil was then analyzed in the nmr in $CDCl_3$–TMS directly. The results are shown in Table I.

As the temperature was raised, both with NaOMe and NaOH, the spiro compound **12** increased in proportion to **10**. Also noticeable was the persistently higher proportion of **12** when NaOH was used, at each temperature. Rearrangement of **10** to **12** (or vice versa) under the reaction conditions used was ruled out when both products were recovered completely unchanged (nmr) after reflux in NaOMe–MeOH for several hours. Formation of **10** obviously follows from direct substitution at 4a, probably as an SN2 reaction. On the other hand, **12** is most probably formed *via* the C-4a carbonium ion, with subsequent Wagner–Meerwein rearrangement to the C-2 cation, and consequent reaction with methanol, as shown in Scheme I.

Scheme I



Since no **16** was formed in the reactions of the chloroindolenine **9**, even when the nmr of the crude reaction products was examined, we assume that generation of the C-1 carbonium ion, or similar C-1 activated species, did not occur under these conditions, in contrast with 2,3-dimethylindole.[3]

Experimental Section[12]

Tetrahydrocarbazolechloroindolenine (9). 1,2,3,4-Tetrahydrocarbazole (2.50 g) and triethylamine (1.60 ml) in benzene (45 ml) were stirred in an ice bath while *tert*-butyl hypochlorite (1.60 ml) (or an equivalent amount of *N*-chlorobenzotriazole) was added dropwise. The mixture was stirred for 30 min; then a portion was used directly for nmr determinations. For uv determination, the above reaction was repeated substituting methylene chloride as solvent in place of benzene: uv 235 nm (ϵ 13,700), 264 (3650); nmr δ 6.2–7.6 (multiplet, 4 H, aromatic), 1.98–2.72 (multiplet, 4 H, α aliphatic), 1.24–1.91 (multiplet, 4 H, β aliphatic).

4a-Methoxy-1,2,3,4-tetrahydrocarbazoleindolenine (10). Tetrahydrocarbazolechloroindolenine (**9**) from 2.00 g of THC in benzene solution was run rapidly into a stirred solution of sodium (1 g) in 35 ml of absolute methanol precooled to −10° in an ice–methanol bath. After 30 min of stirring at −10°, the mixture was evaporated *in vacuo*, 30 ml of ice water was added, and the solution was extracted four times with 25-ml portions of chloroform. The chloroform extract was dried over sodium sulfate and evaporated to a viscous oil (2.06 g, 88%). Crystallization from hexane gave large, colorless prisms: mp 47–51°; ir 3080, 1585, 1440, 1275, 1110, 1060, 760 cm^{-1}; nmr[13] δ 6.90–7.68 (4 H, aromatic), 2.78 (3 H, OCH_3), 0.75–3.15 (8 H, aliphatic); mass spectrum *m/e* 201, 186, 170, 168, 160, 158, 130; uv 228 nm (ϵ 12,300), 260 (4100), unchanged in HCl solution. *Anal.* Calcd for $C_{13}H_{15}NO$: C, 77.61; H, 7.46; N, 6.97. Found: C, 77.69; H, 7.45; N, 6.90.

Bis[1,9-(1,2,3,4-tetrahydrocarbazole)] (11). One gram of the 4a-methoxy compound **10** was heated under reflux in 25 ml of methanol and 1 ml of 1 *N* HCl in a nitrogen atmosphere. The solution was cooled and filtered to give 342 mg (41%) of white, powdery crystals: mp 253–255°; ir 1460, 1335, 1320, 1290, 1240, 1165, 735 cm^{-1}; mass spectrum *m/e* 338, 310, 282, 168, 141; uv 238 nm (ϵ 20,100), 285 (8200), 293 (sh, 7100). *Anal.* Calcd for $C_{24}H_{22}N_2$: C, 85.25; H, 6.51; N, 8.28. Found: C, 85.09; H, 6.52; N, 8.38.

2-Methoxyspiro[cyclopentane-1,3′-indolenine] (12). Tetrahydrocarbazolechloroindolenine (**9**), from 1.25 g of THC in benzene solution, was run rapidly into a stirred refluxing solution of NaOH (3 g) in methanol (35 ml), and the mixture was refluxed for 30 min. The solvent was evaporated *in vacuo*, ice water (30 ml) was added, and the mixture was extracted four times with chloroform (25 ml). The chloroform was dried with Na_2SO_4 and evaporated to a viscous oil (1.20 g, 82%), which crystallized on standing at −20°. Recrystallization from diethyl ether gave white prisms: mp 66–68; ir 1618, 1570, 1335, 1275, 1190, 1015, 1000, 750 cm^{-1}; nmr[13] δ 6.90–7.50 (4 H, aromatic), 4.02 (singlet, 3 H, OCH_3), 1.95 (singlet, 8 H, aliphatic spiro ring); mass spectrum *m/e* 201, 186, 170, 160, 158, 130; uv 225 nm (ϵ 7500), 255 (7200), unchanged in HCl solution. *Anal.* Calcd for $C_{13}H_{15}NO$: C, 77.61; H, 7.46; N, 6.97. Found: C, 77.49; H, 7.29; N, 6.95.

Spiro[cyclopentane-1,3′-indolin]-2′one (13). The spiro compound **8** (300 mg) in 30 ml of methanol–water (1:1) and 1 ml of concentrated HCl was heated under reflux in a nitrogen atmosphere for 1 hr. The solution was cooled and evaporated *in vacuo*, and 25 ml of benzene and dilute NH_4OH were added. The aqueous layer was reextracted four times with benzene. The benzene was pooled, dried over Na_2SO_4, and evaporated to yield a crystalline product (193 mg, 69%) which recrystallized from hexane to give pale pink needles melting at 95–96°: ir 3220, 3100, 1710, 1620, 1340, 1310, 1220, 810, 755, 640 cm^{-1}; nmr δ 9.40 (1 H, NH), 6.78–7.35 (4 H, aromatic), 2.03 (8 H, aliphatic spiro ring); mass spectrum *m/e* 187, 158, 146, 130, 117; uv 251 nm (ϵ 9100), 280 (1600).

1-Acetoxyspiro[cyclopentane-1,3'-indoline] (14). Two grams of the spiro indolenine compound 9 was treated with 2.0 g of $LiAlH_4$ in refluxing diethyl ether for 3 hr, then 0.5 ml of water, 0.5 ml of 15% NaOH, and 1.5 ml of water were added in succession. The ether phase was removed by filtration and to it 4.0 ml of pyridine and 2.0 ml of Ac_2O were added. After standing overnight at 10°, the solvent was evaporated to give 1.4 g (65%) of white crystals, which when recrystallized from hexane melted at 122-123.5: ir 1660, 1600, 1480, 1460, 1410, 755 cm^{-1}; nmr δ 6.92-7.32 (4 H, aromatic), 3.82 (singlet, 2 H, aliphatic), 2.22 (singlet 3 H, Ac), 1.83 (singlet, 8 H, aliphatic, spiro); mass spectrum *m/e* 215, 173, 130; uv 222 nm (ϵ 2000), 252 (8600), 280 (2300), 290 (1950). *Anal.* Calcd for $C_{14}H_{17}NO$: C, 78.14; H, 7.91; N, 6.51. Found: C, 78.85; H, 8.28; N, 6.22.

1-Methoxy-1,2,3,4-tetrahydrocarbazole (16). To 1,2,3,4-tetrahydrocarbazole (3.00 g) and pyridine (3.6 ml) in benzene (60 ml) was added at once *N*-bromosuccinimide (3.3 g) and dibenzoyl peroxide (1 mg), and the mixture was stirred overnight at room temperature. The clear benzene layer was decanted from the oily product which separated, and the oil was dissolved in methanol (20 ml) and run into excess sodium methoxide in methanol at room temperature. This mixture was stirred for 1 hr, then evaporated under vacuum, and the residue was dissolved in $CHCl_3$. The $CHCl_3$ layer was washed with water twice, dried over Na_2SO_4 and evaporated to an oil which crystallized on standing (1.85 g, 52% yield). Recrystallization from hexane gave pale yellow rosettes melting at 74-76°: ir 3300, 1390, 1335, 1065, 910, 740; nmr[13] δ 8.13 (singlet, 1 H, NH), 6.92-7.50 (multiplet, 4 H, aromatic), 4.48 (1 H, α to OCH_3 at C-1), 3.38 (singlet, 3 H, OCH_3), 2.67 (multiplet, 2 H, aliphatic at C-4), 1.93 (multiplet, 4 H, aliphatic at C-2,3); mass spectrum *m/e* 201, 185, 170, 168; uv 230 nm (ϵ 17,800), 276 (7650), 283 (8150), 291 (6700). *Anal.* Calcd for $C_{13}H_{15}NO$: C, 77.61; H, 7.46; N, 6.97. Found: C, 77.73; H, 7.53; N, 6.89.

Acknowledgments. We thank Miss Carol Hartke for technical assistance, Dr. C. H. Robinson for advice, and the Mass Spectrometry Laboratory, Department of Pharmacology and Experimental Therapeutics, Johns Hopkins School of Medicine. We also extend our thanks to the NIH Gerontology Research Center for the use of their nmr facilities. We acknowledge support by NCI Grant CA06973 and the Eli Lilly Co.

Registry No. **8**, 942-01-8; **9**, 42540-51-2; **10**, 42540-52-3; **11**, 42540-53-4; **12**, 42540-54-5; **13**, 41058-67-7; **14**, 42540-56-7; **16**, 42540-57-8.

Supplementary Material Available. Full nmr data for compounds **10**, **12**, and **16** will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-69.

References and Notes

(1) W. O. Godtfredsen and S. Vangedal, *Acta Chem. Scand.*, **10**, 1414 (1956).
(2) P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 2047 (1969).
(3) P. G. Gassman, G. A. Campbell, and G. Mehta, *Tetrahedron*, **28**, 2749 (1972).
(4) G. Büchi and R. E. Manning, *J. Amer. Chem. Soc.*, **88**, 2532 (1966).
(5) H. Zinnes and J. Shavel, Jr., *J. Org. Chem.*, **31**, 1765 (1966).
(6) N. Finch and W. I. Taylor., *J. Amer. Chem. Soc.*, **84**, 3871 (1962).
(7) J. B. Patrick and B. Witkop, *J. Amer. Chem. Soc.*, **72**, 633 (1950).
(8) S. G. P. Plant, R. Robinson, and M. Tomlinson, *Nature (London)*, **165**, 928 (1950).
(9) B. Witkop and J. B. Patrick, *J. Amer. Chem. Soc.*, **75**, 2572 (1953).
(10) R. F. Moore and S. G. P. Plant, *J. Chem. Soc.*, 3475 (1951).
(11) H. Sakakibara and T. Kobayoshi, *Tetrahedron*, **22**, 2475 (1966).
(12) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Nmr spectra were obtained on a Varian A-60 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were determined on a CEC-110 spectrometer. Microanalyses were performed by Galbraith Laboratories. Ir spectra were run on a Perkin-Elmer 700 spectrometer. Uv spectra were obtained on a Beckman DB spectrometer.
(13) See paragraph at end of paper regarding supplementary material.

Condensations of Enol Ethers of β-Dicarbonyl Compounds with Dimethylsulfonium Methylide and Dimethyloxosulfonium Methylide

Constance M. Harris, Joseph J. Cleary, and Thomas M. Harris*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

Received June 27, 1973

Condensations of dimethylsulfonium methylide with β-alkoxy-α,β-unsaturated ketones have been studied. The reactions of this ylide with the enol ethers of acyclic β diketones gave 2,4-disubstituted furans. Attack by the ylide occurred at the carbonyl carbon atoms. Easily rearranged epoxides are postulated as intermediates in furan formation. With the enol ether of a cyclic β diketone, 1,3-indandione, furanization of the epoxide intermediate was sterically prohibited and the condensation gave 3-(hydroxymethyl)indenone. The enol ethers of β-keto aldehydes reacted with dimethylsulfonium methylide to give two products. In addition to 3-substituted furans, the condensations gave 5-substituted 3,6-dihydro-(2*H*)-pyran-2-ols. Formation of the latter compounds has been rationalized to involve attack by one molecule of the ylide at the β positions of the unsaturated carbonyl compounds followed by a second molecule attacking the carbonyl groups. Rearrangement and hydrolysis of the resulting cyclopropyloxiranes would give the dihydropyran derivatives. β attack by dimethylsulfonium methylide on α,β-unsaturated ketones does not normally occur but is facilitated with the enol ethers of β-keto aldehydes by the reduced steric hindrance at the β positions. The condensations of dimethyloxosulfonium methylide with enol ethers of β diketones were also investigated. Twofold attacks occurred here, as well, but both attacks were by the same ylide molecule. Initial attack by the ylide at the β position, followed by formation of a new ylide by ionization of one of the remaining methyl groups, and finally intramolecular attack of the new ylides on the carbonyl groups, led to 3,5-disubstituted 1-methylthiabenzene 1-oxides.

The reactions of sulfonium ylides with α,β-unsaturated ketones have been employed widely subsequent to the observations by Corey and Chaykovsky that dimethylsulfonium methylide preferentially attacks the carbonyl group to give epoxides, whereas dimethyloxosulfonium methylide attacks the β position to give cyclopropyl ketones.[1,2] The corresponding reactions of β-alkoxy-α,β-unsaturated ketones were of interest to us because both the epoxide and cyclopropane products should be capable of rearrangement to furans or to the related 1,4-dicarbonyl compounds. The reactions of both of the ylides with these enol ethers have now been investigated.[3]