Table II. Spectral Data of Acylstannanes

compd	^{13}C NMR,[a] $\delta_{C=O}$	^{119}Sn NMR,[b] δ	^{29}Si NMR,[a] δ	IR,[c] C=O
5a	244	−84		1615
5b	239.5	−80		1620
8a	230	−84		1600
8b	234	−87		1595
9b	236	−89		1590
10b	249	−90.5		1645
$PhCOSiMe_3$	234.2[d]		−7.9[d]	1617

[a] Spectra recorded in $CDCl_3$ (ppm) with respect to internal Me_4Si. [b] With respect to internal Me_4Sn. [c] In cm^{-1}, as $CDCl_3$ solutions. [d] Dexheimer, E. M.; Buell, G. R.; LeCroix, C. *Spectrosc. Lett.* **1978**, *11*, 751.

be used for subsequent reactions, without further purification.[10]

The relevant results of the above reactions are summarized in Table I. Worth mentioning, in particular, is the possibility of obtaining a general route to the still unreported heteroacylstannanes, which could prove to be, based on their correspondence with the silicon analogues,[5b] even more interesting and synthetically useful than the aromatic or aliphatic derivatives.

All the acylstannanes obtained throughout this work showed, as outlined in Table II, the unusual spectroscopic features previously noticed in the acylsilanes series.[5b,11] The ^{13}C NMR chemical shifts are indicative of an unexpectedly low electron density on the carbonyl carbon, whereas the high upfield shift of the ^{119}Sn suggests abnormally high electron density on the tin atom. The inadequacy of the ketonic structure for the description of the ground-state features of these compounds, already proposed in the case of acylsilanes,[5b] would also seem to apply to the acylstannane series, showing a close relationship between these two classes of acylmetallic derivatives.

Experimental Section

All reactions required dry conditions and were performed in oven-dried (110 °C for more than 2 h) glassware. The reactions as well as the workups, distillation, chromatography, and handling of acylstannanes were performed under a strictly inert atmosphere.

THF was freshly distilled from $LiAlH_4$ prior to use. ^1H, ^{13}C, and ^{119}Sn NMR spectra were obtained on Perkin-Elmer R-32 and Varian VXR-300 spectrometers (operating respectively at 90 and 300 MHz), IR spectra on a Perkin-Elmer 283 spectrophotometer, and GC/MS analysis on an HP5970-HP5790 GC selective ion detector, equipped with a high-performance dimethylsilicone fluid 25-m capillary column.

NMR spectra were recorded as $CDCl_3$ and CCl_4 solutions. Column chromatography was performed on Florisil, under a nitrogen stream.

Bu_3SnLi and Me_3SnLi were prepared according to Still's procedures.[12,13]

Procedure A: Reactions of (Trialkylstannyl)lithium with Esters. (Trialkylstannyl)lithium (0.68 mmol) in 2 mL of THF was treated at −78 °C with the appropriate alkyl carboxylate (0.34 mmol) in 1 mL of THF, followed by addition of $BF_3{\cdot}Et_2O$ (0.8 mmol). The orange solution obtained was stirred for 1 h at −78 °C, diluted with 3 mL of ether, and quenched with saturated NH_4Cl. After reaching room temperature, the aqueous layer was removed and the organic phase was washed with water and brine. Drying over Na_2SO_4 and removal of the solvent afforded the crude acylstannane.

Procedure B: Reactions of (Trialkylstannyl)lithium with Thioesters. (Trialkylstannyl)lithium (0.68 mmol) in 2 mL of THF was treated at −78 °C with an equimolar amount of thioester in 1 mL of THF and stirred for 1 h at −78 °C. Progress of the reactions was monitored by GC/MS analysis, and the reaction mixture was quenched at −78 °C with saturated NH_4Cl and worked up according to the above procedure. Evaporation of the solvent usually led to a thick, orange oil, which was purified by column chromatography (Florisil, hexane, N_2).

Benzoyltrimethylstannane (5b). To a cooled solution (−78 °C) of Me_3SnLi (0.60 mmol) was added dropwise 91.2 mg of PhCOSMe (0.60 mmol, 73 μL) in 1 mL of THF over 3 min. The reaction mixture was stirred for 1 h at −78 °C, diluted with 5 mL of ether, quenched with saturated NH_4Cl, and then slowly warmed to room temperature. The aqueous layer was removed with a syringe, and the organic phase was washed three times with water and brine. The yellow solution obtained was dried over Na_2SO_4, and the solvent was removed under vacuum, giving 250 mg of crude material, which was purified by elution under nitrogen on Florisil with hexane–ether 10:1 as the eluant, yielding 155.7 mg (57.6%) of benzoyltrimethylstannane: IR (CCl_4) 3100–2840, 1620, 1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 7.27–7.35 (m, 3 H), 7.86–8.1 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) δ 239.5 (C=O), 131.8, 129.3, 127.5 ppm; ^{119}Sn NMR ($CDCl_3$) δ −80 ppm; MS *m/e* (relative intensity) 270 (3.1), 165 (56.5), 105 (100), 77 (47.3).

Acknowledgment. Technical assistance from L. Favaretto and A. Guerrini and Financial support by the "Progetto Finalizzato Chimica Fine" CNR, Rome, are gratefully acknowledged.

Registry No. **5a**, 114566-87-9; **5b**, 120086-07-9; **6a**, 120086-08-0; **7a**, 120086-09-1; **8a**, 120086-10-4; **8b**, 120086-11-5; **9b**, 120086-12-6; **10b**, 120086-13-7; PhCOOEt, 93-89-0; PhCOSMe, 5925-68-8; PhCOSPh, 884-09-3; MeC_6H_4-*m*-COSPh, 97839-38-8; $MeOCOC_6H_4$-*m*-COOMe, 1459-93-4; $PhSCOC_6H_4$-*m*-COSPh, 18953-23-6; C_3H_7COSMe, 2432-51-1; $(n\text{-}Bu)_3SnLi$, 4226-01-1; Me_3SnLi, 17946-71-3; 2-furancarboxylic acid ethyl ester, 614-99-3; 2-furancarbothioic acid *S*-phenyl ester, 17357-38-9; 2-thiophenecarbothioic acid *S*-phenyl ester, 28122-95-4; 2-phenyl-1,3-dioxane, 772-01-0; dioxolane, 646-06-0; *O*-trimethylsilyl benzaldehyde cyanohydrin, 25438-37-3; *O*-ethoxyethyl benzaldehyde cyanohydrin, 120086-14-8.

(10) The reactivity of acylstannanes toward several representative electrophiles will be discussed in a forthcoming paper.

(11) (a) Ramsey, B. G.; Brook, A. G.; Bassindale, A. R.; Boch, M. *J. Organomet. Chem.* **1974**, *11*, 751. (b) Dexheimer, E. M.; Buell, G. R.; Le Croix, C. *Spectrosc. Lett.* **1978**, *11*, 751.

(12) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.

(13) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4836.

Baeyer–Villiger Oxidation of Hexacyclo[10.2.1.$0^{2,11}$.$0^{4,9}$.$0^{4,14}$.$0^{9,13}$]pentadeca-3,10-dione Systems†

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Received September 8, 1988

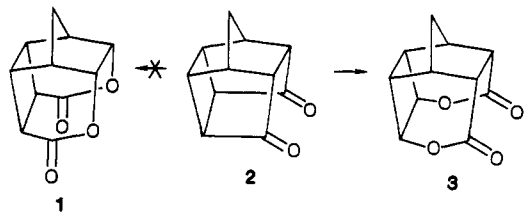
Baeyer–Villiger (B–V) oxidation of polycyclic ketones has received considerable attention in recent years from synthetic as well as mechanistic considerations.[2] Surapaneni and Gilardi[2a] have reported recently that the B–V oxidation of **2** gave exclusively **3** and not **1** (Scheme I). The structure **3** was unambiguously proved by single-crystal X-ray.

Since B–V oxidations in strained systems involved carbenium ion intermediates which are known to trigger various Wagner–Meerwein type rearrangements, we were interested in knowing whether such possibilities exist in hexacyclo[10.2.1.$0^{2,11}$.$0^{4,9}$.$0^{4,14}$.$0^{9,13}$]pentadeca-3,10-dione systems for the formation of rearranged products.[2c,d] Besides, we are especially interested in studying the B–V oxidation of hexacyclo[10.2.1.$0^{2,11}$.$0^{4,9}$.$0^{4,14}$.$0^{9,13}$]pentadeca-3,10-dione (**5**) (X = CH_2, Y = Z = CO) and hexacyclo-

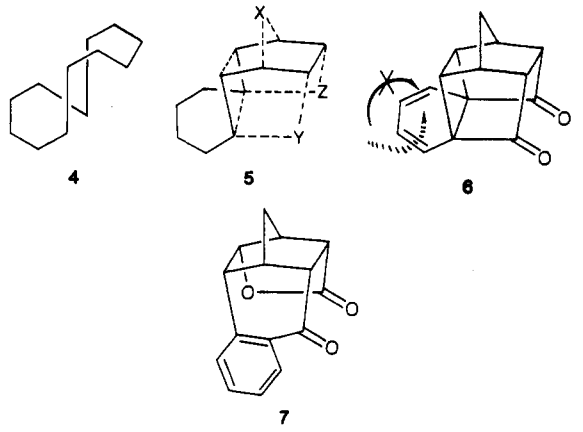
† NCL Communication No. 4529.

0022-3263/89/1954-2968$01.50/0

Scheme I



Scheme II



[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-diene-3,10-dione (**6**) because such systems can be considered as locked 12-membered rings such as **4**, which can offer considerable advantage for stereochemical manipulations (Scheme II).[3] Thus, the rigid frame in **5** and **6** fixes the stereochemistry of substituents adjacent to carbonyls and four-membered rings automatically. In the case of the diene **6**, we have shown recently that it exhibits π-facial stereoselectivity in the Diels–Alder reaction with various dienophiles, offering thereby an additional element of stereocontrol in this locked system.[5] The present paper records our studies in the B–V oxidation of **5** and **6**, which should help in unlocking the 12-membered ring.

The synthesis of **6** was carried out from the readily available cyclopentadiene and 1,4-naphthoquinone according to a literature procedure with a slight modification.[6] Initially, B–V oxidation of **6** was attempted as reported for pentacyclic dione **2**[2a] with (i) *m*-chloroperbenzoic acid and a catalytic amount of *p*-toluenesulfonic acid in benzene and (ii) 30% H_2O_2–*t*-BuOH in the presence of selenium dioxide. However, the reaction workup in both cases led to a mixture of unisolable products. Subsequently, treatment of **6** with peracetic acid and sodium acetate[7] in glacial acetic acid afforded a reasonable yield of a monolactone, which surprisingly was found to be **7**. It was presumed that the strain release[8] and aromatization are the driving force in this oxidative rearrangement.[9] To remove this possibility, the saturated analogue **5** was prepared by catalytic hydrogenation over PtO_2.[6] However, the B–V oxidation of **5** opened up various other possibilities for formation of rearranged products, e.g., **12**, **14**, and **15**, from carbenium ion **11** (Scheme III).

There is precedent for C_{14}–C_{13} to C_{14}–C_9 type bond migration in pentacyclic dione **2**[2c] and C_{14}–C_4 to C_{14}–C_9 type bond movement in 1,3-bishomocubanone,[2d] under B–V oxidation conditions. The cyclohexane ring in **11** might induce an additional C_5–C_4 to C_5–C_9 Wagner–Meerwein shift to give **12**. Surprisingly the reaction of **5** with *m*-chloroperbenzoic acid (2.5 equiv) and catalytic *p*-toluenesulfonic acid in benzene was highly regioselective and gave monolactone **10** (51%) and a symmetrical dilactone **13** (36%). On the basis of precedent[2a] and ^{13}C NMR arguments[10] where deshielded carbon due to monolactone formation is a quaternary carbon, structures **9** and **15** are discarded as probable structures for the monolactone.[11] The structure of the monolactone as **10** is further substantiated on the basis of the observation that B–V oxidation of **10** gave a dilactone **13**, which was symmetrical, as evidenced by eight lines in ^{13}C NMR spectrum. Besides, the deshielded carbons, due to dilactone formation, in **13** appeared at δ 82.48 as quaternary carbons. However, not only would the products derived from B–V oxidation of remaining probable monolactones **12** and **14** lose symmetry, but the δ value of quaternary carbons would exceed 100.[11] Subsequent B–V oxidation of **5** under exhaustive conditions using excess *m*-chloroperbenzoic acid (5 equiv) gave **13** (73%),[11] which was identical in all respects with the B–V product from **10**. This, again, proved the intermediacy and structure of the monolactone as **10**.[12]

Experimental Section[13]

Baeyer–Villiger Oxidation of Hexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-diene-3,10-dione (6). To a solution of diene dione **6** (300 mg, 1.33 mmol) and sodium acetate (139 mg, 1.7 mmol) in glacial acetic acid (5 mL) was added 19% peracetic acid (1.05 mL), and the reaction mixture was stirred for 24 h in the dark. Subsequently, the mixture was poured onto cooled, saturated sodium carbonate solution (10 mL) and extracted with ether (2 × 20 mL). The organic extract was washed with water (10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a crude mass, which was crystallized

(1) Dedicated to Professor M. V. George on the occasion of his 60th birthday.

(2) (a) Surapaneni, C. R.; Gilardi, R. *J. Org. Chem.* **1986**, *51*, 2382. (b) Mehta, G.; Pandey, P. N.; Ho, T. L. *J. Org. Chem.* **1976**, *41*, 953. (c) Mehta, G.; Singh, V.; Duddeck, H. *Tetrahedron Lett.* **1978**, 1223. (d) Miura, H.; Hirao, K.; Yonemitsu, O. *Tetrahedron* **1978**, *34*, 1805. (e) Butler, D. N.; Munshaw, T. J. *Can. J. Chem.* **1981**, *59*, 3365. (f) Mehta, G.; Singh, V.; Pandey, P. N.; Chaudhary, B.; Duddeck, H. *Chem. Lett.* **1980**, 59. (g) Krow, G. R. *Tetrahedron* **1981**, *37*, 2697 and references cited therein.

(3) We term X, Y, and Z in **5** as conformational protecting groups. The deprotection of these groups can be planned if X = CO or a heteroatom and Y = Z = CO. The four-membered ring opening in such systems can be accomplished via Mehta's thermal metathetic methodology.[4] Thus the dotted bonds in **5** can be synthetically manipulated.

(4) Mehta, G.; Srikrishna, A.; Reddy, A.; Nair, M. S. *Tetrahedron* **1981**, *37*, 4543.

(5) (a) Pandey, B.; Zope, U. R.; Ayyangar, N. R. *Synth. Commun.*, in press. (b) Coxon, J. M.; O'Connell, M. J.; Steel, P. J. *J. Org. Chem.* **1987**, *52*, 4726.

(6) (a) Kushner, A. S. *Tetrahedron Lett.* **1971**, 3275. (b) The qualitative yield of the photocyclization step was studied at 254, 300, and 350 nm in a Srinivasan-Rayonet photochemical reactor in various solvents, and the best results (98%) were obtained at 300 nm in acetonitrile (1 mg/1 mL concentration).

(7) Meinwald, J.; Frauenglass, E. *J. Am. Chem. Soc.* **1960**, *82*, 5235.

(8) By constructing molecular models of **5** and **6**, one clearly observes that **5** is less strained than **6**.

(9) Mehta, G.; Singh, V. *Tetrahedron Lett.* **1978**, 4591.

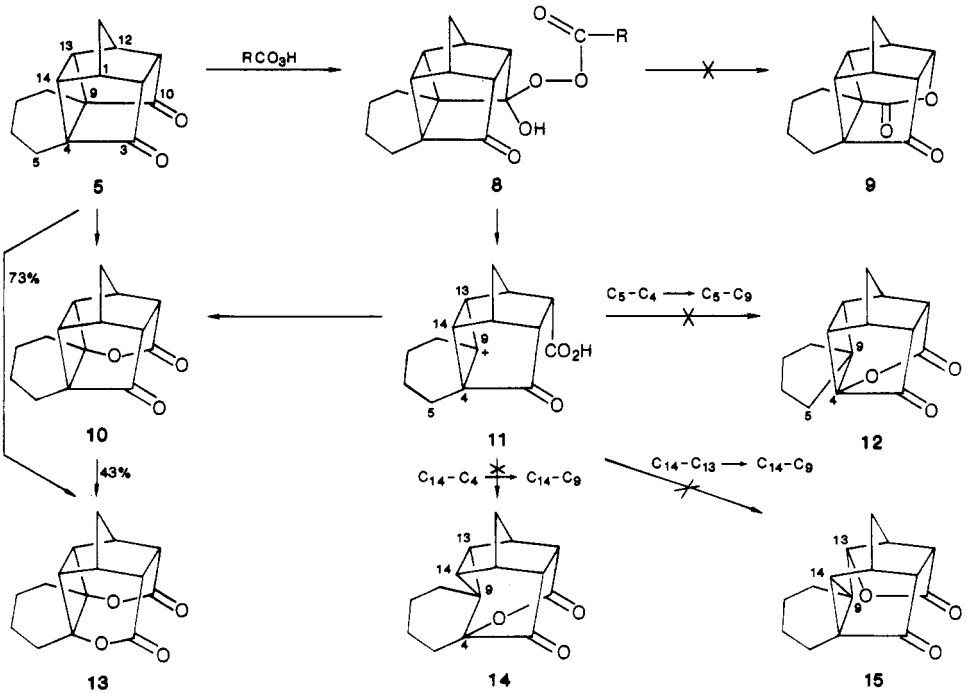
(10) The quaternary carbon in ^{13}C NMR moves from δ 49.58 in **5** to δ 78.05 in **10**.

(11) Many other minor spectroscopic arguments, e.g., absence of cyclopropyl protons and carbons in ^{1}H and ^{13}C NMR, absence of cyclopropyl carbonyls in IR, fragmentation patterns in mass spectrometry data, etc., substantiate our structural assignments.

(12) One of the referees has suggested that the failure of rearranged product (**12**, **14**, **15**) formation from **5** could be an argument against the intermediacy of carbocation **11** and in favor of a concerted B–V mechanism for formation of **10** and **13** in this system.

(13) Melting points were determined with a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 683 grating infrared spectrophotometer. Proton and ^{13}C NMR spectra were recorded on Varian Ft-80A, Brucker WH-90 FT NMR, and Brucker MSL-300 SC-FT NMR spectrometers. The chemical shifts are reported in parts per million (δ) with tetramethylsilane as internal standard. Mass spectra were obtained with a Finnigan MAT-1020-B 70-eV mass spectrometer. Elemental analyses were performed by the NCL analytical facility.

Scheme III



from methanol to give the rearranged lactone **7** (138 mg, 43%). The melting point, IR, ^{1}H NMR, and MS characteristics of **7** were similar to those reported by Mehta and Singh.[9]

Catalytic Hydrogenation of Hexacyclo-[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-5,7-diene-3,10-dione (6). A solution of unsaturated dione **6** (300 mg, 1.33 mmol) in dry methanol (25 mL) was hydrogenated over preactivated platinum dioxide (100 mg) at a hydrogen pressure of 30 psi for 8 h. The reaction mixture was filtered to remove the catalyst, and the filtrate was concentrated in vacuo to give a residue, which was chromatographed over a silica gel column (10 g). The purified material was recrystallized from a minimum amount of methanol to give white crystals of the reduced dione **5** (185 mg, 60%): mp 70 °C; IR (neat) 2900 (s), 2840 (s), 1740 (s), 1720 (s), 1450 (m), 1440 (m), 1370 (w), 1100 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05–2.20 (m, 10 H), 2.75 (s, 2 H), 2.85 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 213.297 (s), 55.046 (d), 49.587 (s), 44.193 (d), 43.543 (d), 41.073 (t), 22.616 (t), 19.172 (t); mass spectrum *m/e* (relative intensity) 228 (100) M$^+$, 200 (23), 135 (27), 129 (29), 107 (34), 91 (44), 77 (40), 66 (33). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.94; H, 7.01. Found: C, 78.76; H, 7.12.

Baeyer–Villiger Oxidation of Hexacyclo-[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]pentadeca-3,10-dione (5). (i) With 2.5 equiv of *m*-Chloroperbenzoic Acid. To a solution of dione **5** (290 mg, 1.27 mmol) in dry benzene (20 mL) were added *m*-chloroperbenzoic acid (540 mg, 3.17 mmol) and *p*-toluenesulfonic acid (10 mg). The mixture was stirred at room temperature for 8 h, poured into water (20 mL), and extracted with ether (3 × 20 mL). The combined organic extracts were washed with aqueous sodium bicarbonate (2 × 10 mL) and brine (10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a product mixture, which was separated by silica gel column chromatography. Elution with acetone–petroleum ether (15:85) gave a white solid, which was recrystallized from methanol to give monolactone **10** (160 mg, 51%): mp 93 °C; IR ($CHCl_3$) 2920 (s), 2840 (s), 1760–1740 (br s), 1450 (m), 1300 (s), 1050 (s), 750 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05–2.2 (br m, 10 H), 2.35–3.19 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 213.232 (s), 172.743 (s), 78.053 (s), 57.841 (s), 52.317 (d), 47.637 (d), 43.218 (d), 42.828 (d), 41.268 (d), 39.708 (d), 39.579 (t), 32.560 (t), 20.796 (t), 17.677 (t), 16.962 (t); mass spectrum *m/e* (relative intensity) 244 (40) M$^+$, 216 (43), 179 (44), 151 (49), 122 (72), 91 (100), 66 (90). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.77; H, 6.55. Found: C, 73.43; H, 6.69.

Further elution with the above solvent mixture gave the dilactone **13** (120 mg, 36%, after recrystallization from methanol): mp 160 °C; IR (Nujol) 2920 (s), 2840 (s), 1750 (s), 1460 (s), 1330 (s), 1180 (s), 1070 (s), 790 (w); ^{1}H NMR ($CDCl_3$) δ 1.1–2.1 (m, 10 H), 2.72 (br s, 2 H), 2.81 (s, 2 H), 3.20 (s, 2 H); ^{13}C NMR ($CDCl_3$ 270 MHz) δ 169.993 (s), 82.482 (s), 44.603 (d), 40.260 (d), 40.265 (d), 39.159 (t), 30.289 (t), 14.688 (t); mass spectrum *m/e* (relative intensity) 260 (20) M$^+$, 161 (50), 117 (32), 100 (26), 91 (100), 79 (26), 66 (51), 55 (30). Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.23; H, 6.15. Found: C, 69.63; H, 6.69.

(ii) With 5 equiv of *m*-Chloroperbenzoic Acid. Exhaustive B–V oxidation of dione **5** (300 mg, 1.33 mmol) with *m*-chloroperbenzoic acid (1.13 g, 6.65 mmol) and catalytic *p*-toluenesulfonic acid was carried out by stirring in benzene (20 mL) for 8 h. The usual workup and purification as above gave **13**, 250 mg (73%).

Baeyer–Villiger Oxidation of Monolactone 10. To a solution of monolactone (100 mg, 0.4 mmol) in dry benzene (10 mL) were added *m*-chloroperbenzoic acid (180 mg, 1.09 mmol) and catalytic *p*-toluenesulfonic acid (10 mg), and the reaction mixture was stirred for 4 h. The usual workup and purification as above gave 52 mg (48%) of dilactone **13**.

Acknowledgment. P.V.D. thanks Dr. L. K. Doraiswamy, Director NCL, for financial support in the form of JRF. We are thankful to Dr. N. R. Ayyangar and Prof. G. Mehta for discussions and encouragement.

Registry No. **5**, 33741-25-2; **6**, 24402-96-8; **7**, 70157-07-2; **10**, 120231-22-3; **13**, 120231-21-2.

Oxidation of Diols with Alkali Hypochlorites Catalyzed by Oxammonium Salts under Two-Phase Conditions

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Received January 9, 1989

Several procedures for the oxidation of alcohols to carbonyl derivatives mediated by oxammonium salts have been described.[1] We recently reported a catalytic cycle

0022-3263/89/1954-2970$01.50/0