Table I. Polycyclic Trisaminomethanes

compd		yield, %	δ methine H
1		88	5.03
2		91	4.04
3		90	2.49
4		90	2.31
5		81	3.74
(6, 7)			
6	X = O	81	4.31
7	X = NH	95	4.45

MHz NMR spectrum in toluene-d_8 showed line broadening, and at −37 °C, two eight-proton multiplets were resolved. At 0 °C in toluene-d_8, five sharp ^{13}C NMR absorptions were resolved, δ 99.8 54.3, 53.8, 51.3, and 49.7. When the sample was warmed to 90 °C, the methylene signals collapsed to a sharp singlet at δ 52.9. All eight equivalent isomers of **7** must interconvert to equilibrate the hydrogens syn to the methine with those anti as well as all the methylene carbons in the localized structure. The isomerization requires carbon–nitrogen bond exchange and methine hydrogen "flipping" through the macrocycle plane. The details of this isomerization are still under investigation.

The chemical shift of the methine protons in the series **1–4** varies over 2.7 ppm (Table I). The downfield shift of the methine hydrogens[7] of **1** and **2** can be ascribed to a dramatic anomeric effect of the nitrogen lone pairs.[8] The methine hydrogen of **1**
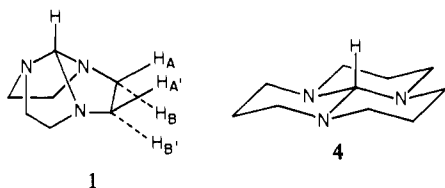
is highly deshielded by combined eclipsing interactions with all three lone pairs. The downfield methylene hydrogen absorption has been assigned to the exo-hydrogen, based on lone pair deshielding. The trans,trans,trans three-chair conformation of **4** places all nitrogen lone pairs anti to the methine hydrogen. The presence of Bohlmann bands[9] at 4.0 μm in the IR spectrum provides evidence for this conformation. With a high population of this lowest energy conformation,[10] the methine absorption of **4** appears at a much higher field than that of **1** or **2**. Compounds **1** and **4** may be the ultimate models for monitoring the anomeric effect of nitrogen lone pairs in syn (0° dihedral angle) and anti

(180° dihedral angle) conformations.

When the trisaminomethane moiety was incorporated into a small macrocyclic cage, as in **1**, its reactivity differed markedly from the model bicyclic analogue **5**. For example, when **5** was treated with excess methyl iodide, the trisaminomethane opened as expected to give a mixture of the formamidinium cations **8** and **9**,[4,11] resulting from double alkylation at the ring and bridgehead nitrogens, respectively.
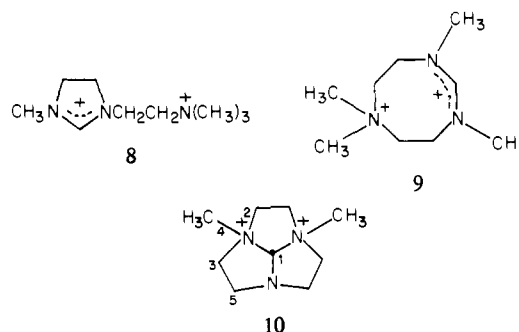
However, when **1** was treated with either methyl iodide or methyl fluorosulfate, the dication **10**[4] was formed. Compound **10** exhibited no IR absorptions near 6 μm; its ^{1}H NMR spectrum showed the methine hydrogen at δ 6.51 and a methyl singlet (6 H) at δ 2.96, and its ^{13}C NMR spectrum (D$_2$O) had absorptions at δ 106.8 (C$_1$), 53.9 (C$_2$), 52.2 (C$_3$), 41.9 (C$_4$), and 41.5 (C$_5$). In comparison, **1** had ^{13}C NMR absorptions (D$_2$O) at δ 93.2 and 41.9. Clearly, the tricyclic integrity of **1** has been preserved after alkylation. In addition, **1** was stable in water whereas **5** gave a vigorous exotherm with complete loss of the trisaminomethane moiety. The enhanced stability of **1** can be attributed to the high energy required to open one carbon–nitrogen bond to give an excessively strained formamidinium cation.

Thus, these readily available polycycles exhibited remarkable conformational effects and unusual reactivity. Further explorations of the chemistry of this novel class of compounds will be presented in a full paper.

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(11) The mixture of salts of **8** and **9** had IR absorptions in the 6 μm region and NMR absorptions at δ 8.46 and 8.16 in the ^{1}H NMR spectrum and at δ 147–150 in the ^{13}C NMR spectrum.

Thomas J. Atkins

Contribution No. 2636
Central Research and Development Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received December 26, 1979

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(7) The methine hydrogen of tris(dimethylamino)methane absorbs at δ 3.02 in C$_6$D$_6$; see: H. Weingarten and W. A. White, *J. Am. Chem. Soc.*, **88**, 850 (1966).

(8) For an empirical correlation of the ^{1}H NMR shift with amine and ether conformations, see: C. C. Price, *Tetrahedron Lett.*, 4527 (1971).

(9) (a) F. Bohlmann, *Angew Chem.*, **69**, 641 (1957); (b) T. A. Crabb, R. F. Newton, and D. Jackson, *Chem. Rev.*, **71**, 109 (1971).

(10) Calculations indicate this conformation to be ca. 6 kcal/mol more stable than the corresponding cis,cis,trans three-chair conformation: D. A. Pensak, private communication.

Transfer of Hydrogen from Orthoamides. Synthesis, Structure, and Reactions of Hexahydro-6bH-2a,4a,6a-triazacyclopenta[cd]pentalene and Perhydro-3a,6a,9a-triazaphenalene
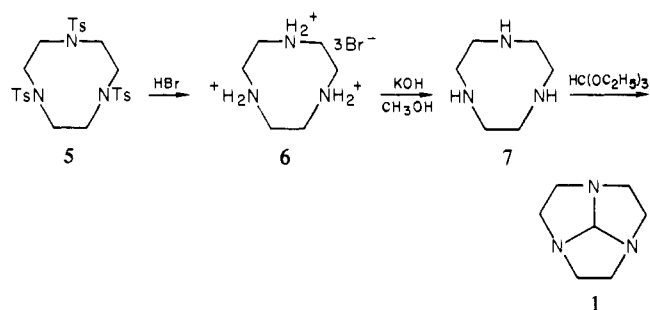
Sir:

The transfer of a proton and two electrons from one molecule to another is a common but puzzling process.[1] Important examples are enzymatic and nonenzymatic reductions involving 1,4-dihydropyridines.[2] Despite extensive study, not all the factors which promote these transfers have been identified. To provide

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(1) For reviews, see: Nenitzescu, C. D. *Carbonium Ions* **1970**, *2*, 463. Deno, N. C.; Peterson, H. J.; Saines, G. S. *Chem. Rev.* **1960**, *60*, 7. Stewart, R. "Oxidation Mechanisms", W. A. Benjamin: New York, 1964. Nenitzescu, C. D. *Usp. Khim.* **1957**, *26*, 399.

(2) For references, see: Sund, H. *Biol. Oxid.* **1968**, 603. *Enzymes 3rd Ed.* *11*, 1. Kill, R. J.; Widdowson, D. A. *Bioorg. Chem.* **1978**, *4*, 239. Sigman, D. S.; Hajdu, J.; Creighton, D. J. *Ibid.* **1978**, *4*, 385.

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Scheme I

**5** → (HBr) → **6** → (KOH/CH₃OH) → **7** → (HC(OC₂H₅)₃) →

1

complementary information, we have begun to study other simple compounds rivaling 1,4-dihydropyridines as reducing agents. Orthoamides were attractive candidates since loss of a proton and two electrons can convert them into stable guanidinium ions (eq 1). Unfortunately, however, this reaction does not ordinarily

$$(NR_2)_3CH \rightleftharpoons (NR_2)_3C^+ + H^+ + 2e^- \qquad (1)$$
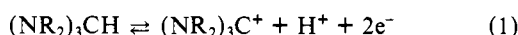
occur; electrophiles remove amide instead, yielding formamidinium ions (eq 2).[3] Orthoamide **1** promised to behave differently, since

$$(NR_2)_3CH \rightleftharpoons (NR_2)_2CH^+ + NR_2^- \qquad (2)$$

strain incorporated in bicyclic formamidinium ion **2** should prevent transfer of amide, permitting transfer of hydrogen (eq 3). Here

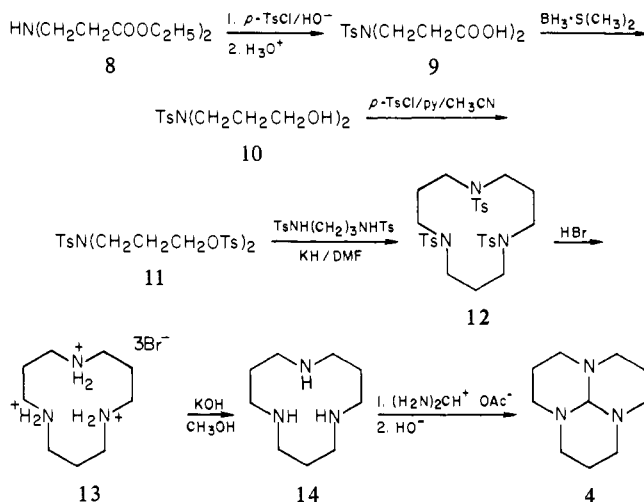$$\mathbf{2} \rightleftharpoons \mathbf{1} + R^{\cdot} \rightleftharpoons \mathbf{3} + RH \qquad (3)$$
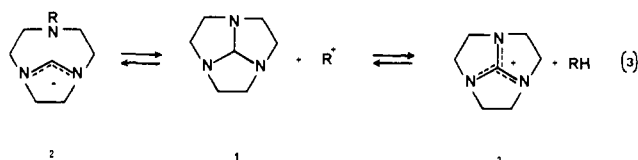
we describe the synthesis, structure, and reactions of orthoamide **1**, hexahydro-6b*H*-2a,4a,6a-triazacyclopenta[cd]pentalene, and the remarkable different behavior of a close relative, perhydro-3a,6a,9a-triazaphenalene (**4**).[4]


4
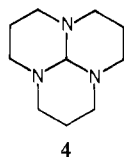
To synthesize orthoamides **1** and **4**, we used the sequences of reactions summarized in Schemes I and II. Standard procedures efficiently converted diethyl 3,3'-iminodipropionate (**8**)[5] into diacid **9**,[6] diol **10**,[6] tosylate **11**,[6] and trisulfonamide **12**.[7,8] The reactions of compounds **5**[7,8] and **12** with hydrogen bromide produced trihydrobromides **6**[7] and **13**,[7] from which 1,4,7-triazacyclononane (**7**)[6] and 1,5,9-triazacyclododecane (**14**)[6] could be liberated by neutralization with methanolic potassium hydroxide. Although orthoamides usually cannot be prepared directly from amines and orthocarboxylates,[9] compound **1** was exceptional. It was formed in 84% yield by the reaction of triamine **7** with triethyl orthoformate (THF, *p*-TsOH, 135 °C, 60 h).[6] The need for such extreme conditions did not surprise us, since the sequence of

Scheme II

$$HN(CH_2CH_2COOC_2H_5)_2 \xrightarrow[2. H_3O^+]{1. \, p\text{-TsCl/HO}^-} TsN(CH_2CH_2COOH)_2 \xrightarrow{BH_3 \cdot S(CH_3)_2}$$

8 → **9**

$$TsN(CH_2CH_2CH_2OH)_2 \xrightarrow{p\text{-TsCl/py/CH}_3CN}$$

10

$$TsN(CH_2CH_2CH_2OTs)_2 \xrightarrow[KH/DMF]{TsNH(CH_2)_3NHTs}$$

11

12 → (HBr) →

13 → (KOH/CH₃OH) → **14** → (1. (H₂N)₂CH⁺ OAc⁻; 2. HO⁻) → **4**

reactions probably includes one of the following two unfavorable steps: formation of the strained formamidinium ion **15** or direct

15 | **16** (R = C₂H₅) | **17**
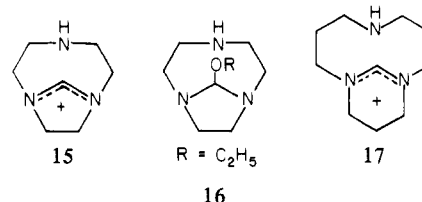
displacement of ethanol from the ester aminal **16**.[10] Unlike 1,4,7-triazacyclononane, triamine **14** failed to react with triethyl orthoformate under these conditions. However, treatment of the triamine with formamidinium acetate in ethanol and then with aqueous base produced orthoamide **4** in 71% yield,[6] probably from the intermediate formamidinium acetate **17**.[11]

Pronounced deshielding of the methine hydrogen [δ 5.03 (CDCl₃)] in the ¹H NMR spectrum of compound **1**[12] and the absence of Bohlmann bands in the infrared spectrum[13] indicated that this orthoamide adopts a conformation in which the lone pairs are syn periplanar or nearly syn periplanar to the central carbon–hydrogen bond. The behavior of perhydrophenalene itself suggested that perhydrotriazaphenalene **4** would adopt conformation **18** or possibly conformation **19**, in which the magnitude

18 | **19**

20
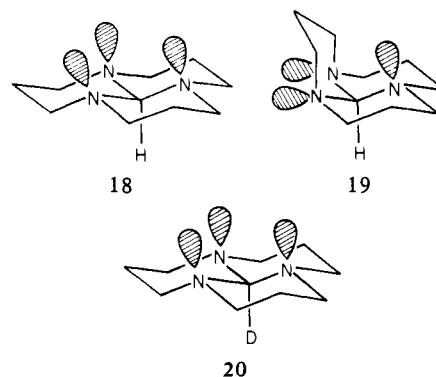
of the anomeric effect is reduced.[14,15] The simplicity of the ¹³C

(3) Meerwein, H.; Hederich, V.; Morschel, H.; Wunderlich, K. *Justus Liebigs Ann. Chem.* **1960**, *635*, 1.

(4) These compounds have been prepared independently by Dr. T. J. Atkins at du Pont. Dr. Atkins has generously shared his unpublished observations and agreed to submit our results for concurrent publication. See: Atkins, T. J. *J. Am. Chem. Soc.*, in press.

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(6) The assigned structure was consistent with the elemental analysis and the IR, NMR, and mass spectra of this new substance.

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(11) Brown, D. J.; Evans, R. F. *J. Chem. Soc.* **1962**, 4039.

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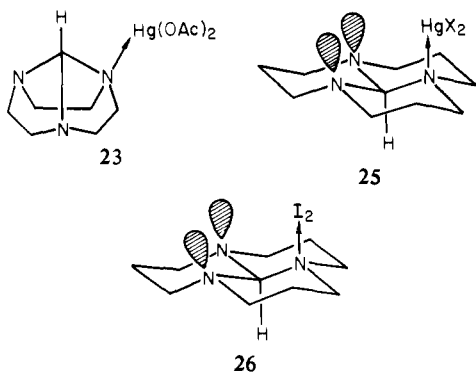
(14) Schneider, A.; Warren, R. W.; Janoski, E. J. *J. Am. Chem. Soc.* **1964**, *86*, 5365. *J. Org. Chem.* **1966**, *31*, 1617.

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NMR spectrum at −55 °C [δ 24.7, 54.6, 101.9 (acetone-d_6)] demanded a structure with the elements of effective C_{3v} symmetry. Since ring inversions in simple perhydropyrimidines are slow at this temperature,[16] conformer **18** must predominate (≥85%). The six equivalent axial carbon–hydrogen bonds adjacent to nitrogen in conformer **18** are responsible for the strong Bohlmann bands between 2690 and 2800 cm⁻¹ in the infrared spectrum.[13] An additional Bohlmann band appears at 2450 cm⁻¹, an extraordinarily low frequency. In the monodeuterated derivative **20**, this absorption is absent, and a new band appears near 1800 cm⁻¹. We therefore believe that the origin of these remarkable absorptions is the central carbon–hydrogen bond, which is anti periplanar to three lone pairs. This arrangement permits mixing of the lone-pair orbitals with $\sigma_{CH}*$, weakens the carbon–hydrogen bond, and increases the electron density at the methine hydrogen.[13] This hydrogen does in fact have a notably small chemical shift [δ 2.33 (CCl₄)].
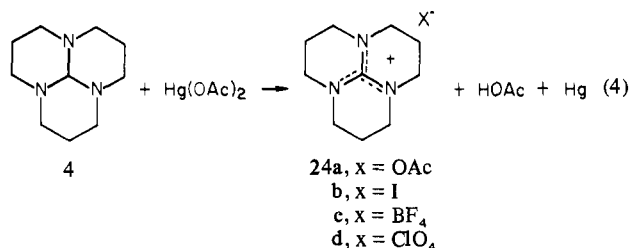
The superficial similarity of orthoamides **1** and **4** therefore conceals an important difference: one adopts conformation **21**, in which the central carbon–hydrogen bond is syn periplanar to

21

22
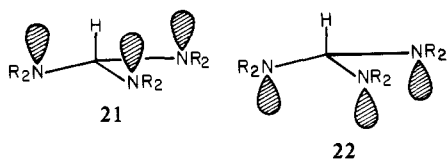
the adjacent lone pairs; and the other adopts conformation **22**, in which the carbon–hydrogen bond is anti periplanar. As a result, we expected the two orthoamides to react differently with electrophiles.[17] Orthoamide **1** did not react rapidly with mercuric acetate, even in boiling ethanol. Syn elimination of mercury and acetic acid from complex **23** therefore must be slow.[17b] In contrast, compound **4** cleanly reduced mercuric acetate in ethanol at 25

23

25

26

°C to mercury or mercurous acetate (eq 4). The presence of a strong band at 1590 cm⁻¹ in the infrared spectrum of the product

4

24a, x = OAc
b, x = I
c, x = BF₄
d, x = ClO₄

and the simplicity of its ¹H NMR (CDCl₃) spectrum [δ 2.03 (s, 3 H), 2.09 (qn, 6 H), 3.45 (t, 12 H)] indicated that oxidation had converted orthoamide **4** into guanidinium acetate **24a**. Similarly, iodine in methanolic potassium carbonate at 25 °C oxidized orthoamide **4** to guanidinium iodide **24b**.[6] Anti elimination of mercury and acetic acid from complex **25**,[17b] or of hydrogen iodide from complex **26**,[18] therefore must occur readily.

A solution of compound **1** in carefully dried chloroform at 25 °C reduced triphenylcarbenium tetrafluoroborate to triphenylmethane in 67% yield (eq 5). Since a similar reaction in chlo-

1

3

(5)
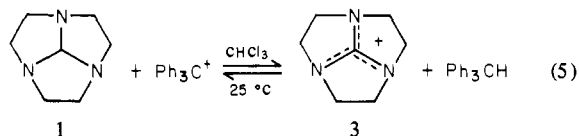
roform-d_1 produced no triphenylmethane-d_1, chloroform plays no important role in the reduction. The infrared spectrum of the product of oxidation displayed a strong band at 1655 cm⁻¹, and the ¹H NMR (CD₃CN) [δ 4.03 (s)] and ¹³C NMR (CD₃CN) spectra (δ 57.1, 190.9) at 25 °C required a structure with the elements of effective D_{3h} symmetry. Strained guanidinium tetrafluoroborate **3** satisfies these requirements.[6] If the ion is not planar, then inversion must be rapid at 25 °C. As we expected, the action of hot aqueous sodium hydroxide and p-toluenesulfonyl chloride cleanly converted guanidinum ion **3** into trisulfonamide **5** in 88% yield (eq 6). When an equimolar mixture of guani-

3

5

(6)
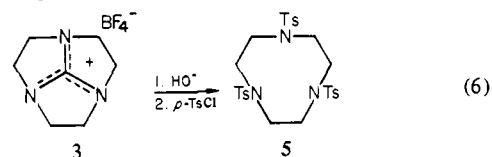
dinium tetrafluoroborate **3** and triphenylmethane in chloroform was stirred at 25 °C and treated later with water, triphenylmethane was recovered in 97% yield, and no triphenylmethanol could be detected. The equilibrium constant for the transfer of hydrogen in eq 5 therefore is greater than 100. This transfer could be direct, without the intervention of intermediates,[19a] it could involve the rearrangement of ammonium ions like compound **27**,[19b] or it could occur within the radical pair **28**.[19c]

27

28
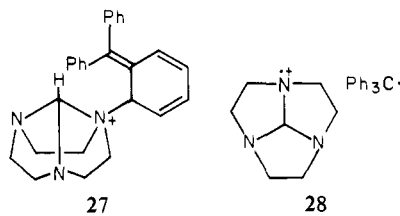
Like orthoamide **1**, orthoamide **4** reduced triphenylcarbenium tetrafluoroborate in chloroform at 25 °C to triphenylmethane in about 70% yield. We were surprised to find, however, that oxidation of orthoamide **4** produced only very small amounts (≤5%) of guanidinium tetrafluoroborate **24c**. Under the conditions of this reaction, tetrafluoroborate **24c** is inert. Therefore, hydrogen is transferred not from the central carbon atom but from one of the other six equivalent carbon atoms, presumably giving iminium tetrafluoroborate **29** or the isomeric imine **30** as the initial products of oxidation. These intermediates could not be isolated, however, and the final products of oxidation appear to be the asymmetric or dissymmetric isomers of oligomer **31**, derived from compound **30** by a rapid cyclotrimerization characteristic of imines.[20]

(15) Eliel, E. L. *Angew. Chem.* **1972**, *84*, 779. Lemieux, R. U. *Pure Appl. Chem.* **1971**, *25*, 527.

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(18) Deno, N. C.; Fruit, R. E., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 3502. Lee, D. G.; Srinivasan, R. *Can. J. Chem.* **1973**, *51*, 2546.

(19) (a) Olah, G. A.; Shen, J.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 4957. Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *Ibid.* **1973**, *95*, 4960. (b) Olah, G. A.; Svoboda, J. J. *Ibid.* **1973**, *95*, 3794. (c) Nelsen, S. F.; Kessel, C. R. *J. Chem. Soc., Chem. Commun.* **1977**, 490. For a review of the chemistry of aminium radicals, see: Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243.
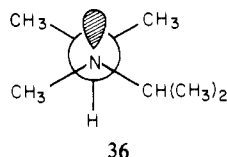
29　　　　　30　　　　　31
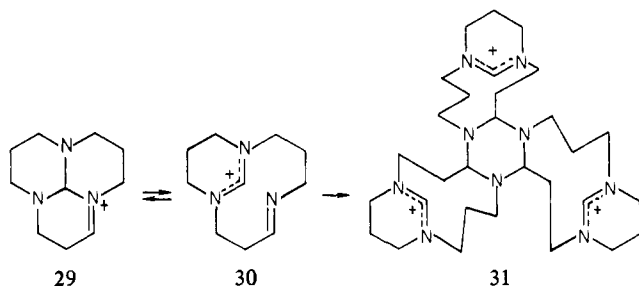
The low reactivity of the central carbon–hydrogen bond in orthoamide **4** can be explained in two ways: (1) Steric factors may make the methine hydrogen inaccessible to triphenylmethyl cations or radicals.[21] In oxidations of simpler amines, however, triphenylcarbenium does not always remove hydrogen from the least substituted carbon atom attached to nitrogen. Methyldiisopropylamine is converted into iminium tetrafluoroborate **32**,[22a] but dimethylisobutylamine yields iminium ion **33**.[22b]　(2) Al-

32　　　　　　　33
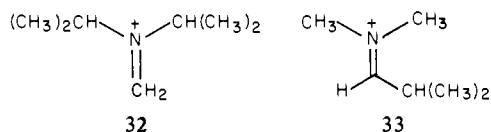
ternatively, the major products of oxidations by triphenylcarbenium may in general result from cleavage of carbon–hydrogen bonds gauche or syn periplanar to lone pairs. Two plausible mechanisms can account for this behavior; rearrangement of an intermediate similar to ammonium salt **34**[19b] or rapid transfer of

34　　　　　35
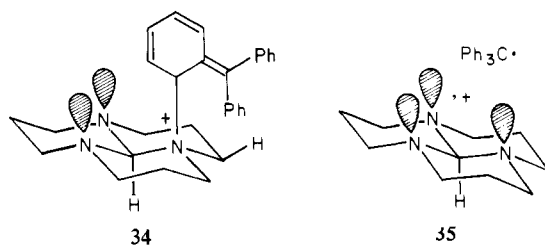
hydrogen within the radical pair **35**[19c] would lead only to iminium ion **29** or imine **30**, since the triphenylmethyl group and the methine hydrogen lie on opposite faces of the molecule. A similar effect may control oxidations of simpler amines. For example, if methyldiisopropylamine adopts conformation **36**,[23] only the

36

methyl group offers a carbon–hydrogen bond gauche to the lone pair. We are investigating the related possibility that pyramidal nitrogen in 1,4-dihydropyridines like NADH renders the hydrogens at prochiral C_4 intrinsically nonequivalent.[24]

Having demonstrated that orthoamides **1** and **4** could reduce electrophiles like carbenium ions, we wondered if they could reduce less active, uncharged compounds containing polar multiple bonds. Prompted by evidence suggesting that complexation with Zn^{2+} activates substrates at the binding site of liver alcohol dehydrogenase,[25] we investigated the reaction of equimolar amounts of magnesium perchlorate hemihydrate,[26] orthoamide **1**, and methyl phenyl glyoxylate. Guanidinium perchlorate **3** was present after the mixture had been heated in carefully dried acetonitrile at 165 °C for 12 h, and hydrolysis of the crude product provided mandelic acid in 45% yield. Like orthoamide **1**, orthoamide **4** reduced methyl phenyl glyoxylate in acetonitrile (105 °C, 92 h) containing an equimolar amount of magnesium perchlorate hemi-, tri-, or nonahydrate. Hydrolysis of the crude product provided mandelic acid in 55% yield, but in this case only traces (<5%) of guanidinium perchlorate **24d** were formed, possibly by direct perchlorate oxidation.[27] The predominant product of oxidation was the perchlorate salt of the oligomer obtained previously from imine **30**. Just as in the oxidation of orthoamide **4** by triphenylcarbenium, the carbon–hydrogen bond anti periplanar to three lone pairs is unreactive. The magnesium cation is essential in the reactions of both orthoamides, since little or no reduction occurred when equimolar amounts of orthoamides **1** or **4** and methyl phenyl glyoxylate alone were heated under similar conditions. Moreover, orthoamide **1** is not hydrolyzed by an equimolar amount of magnesium perchlorate hemihydrate in acetonitrile at 165 °C, and orthoamide **4** is not hydrolyzed by an equimolar amount of magnesium perchlorate mono- or trihydrate in acetonitrile at 105 °C, so formate cannot be the actual reducing agent in either case. These reductions are therefore not examples of the Leuckart reaction.[28] Several plausible mechanisms provide a role for the magnesium cation and account for the absence of guanidinium ion **24d**: direct transfer of a proton and two electrons within intermediates similar to the ternary complexes **37** and **38**,[29]

37　　　　　　　38
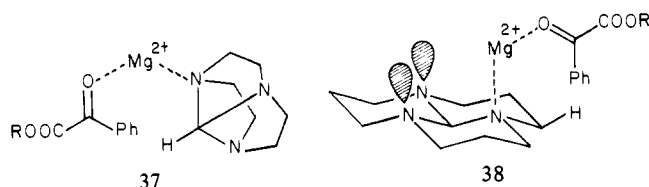
transfer of an electron from orthoamide **1** or orthoamide **4** to a complex of magnesium perchlorate and methyl phenyl glyoxylate, followed rapidly by the transfer of a proton and an electron,[30] or transfer of a proton and two electrons from complexes of magnesium perchlorate and orthoamide **1** or orthoamide **4** to uncomplexed methyl phenyl glyoxylate.[29]

Our observations are important because they show that 1,4-dihydropyridines are not the only simple organic molecules which can transfer a proton and two electrons efficiently to polar multiple bonds. In the case of orthoamide **4**, this reduction is efficient even though it does not appear to exploit the weakness of the central carbon–hydrogen bond or the stability of guanidinium ion **24**.[31] We are therefore investigating the reactions of molecules in which similarly activated carbon–hydrogen bonds are readily accessible to bound substrates.

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(27) We have demonstrated that under similar conditions, magnesium perchlorate itself can oxidize orthoamide **4** to guanidinium perchlorate **24d**: Erhardt, J. M.; Wuest, J. D., unpublished results.

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Jeanette M. Erhardt, Edward R. Grover, James D. Wuest*

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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Reactions with Olefins in Condensed Phases of O(^{3}P) Atoms Produced by Microwave Discharge

Sir:

The reactions of ground-state oxygen atoms with olefins in the gas phase have been investigated extensively by Cvetanović,[1] Havel,[2] and their co-workers, but only limited knowledge exists on these reactions in the condensed phases.[1h] Recently, Sakurai et al.[3] and Sato et al.[4] reported on oxidations of olefins dissolved in liquid CO_2 and irradiated with γ rays, which was attributed to O(^{3}P) atoms formed from CO_2.

We have found a simple and clean way to react O(^{3}P) atoms with olefins in condensed phases, including neat liquids, solutions, suspensions, and solids, thus enabling utilization of oxygen atoms as reagents for preparative organic chemistry.

Ground-state oxygen atoms were generated by discharge of either O_2[1c,d,5] or a mixture of N_2 and N_2O.[6] In the first method, the O(^{3}P) atoms formed are accompanied by O_2 molecules in their singlet and triplet states, and by O(^{1}D) atoms,[7] but the second method gives only almost pure O(^{3}P) atoms.[6]

The reaction vessel consisted of a quartz U-tube of 15-mm diameter, containing 1–5 g of magnetically stirred substrate, and connected to a microwave generator (Kiva, MPG-2, operating at 2450 MHz with 100-W output) by a gas-discharge cavity (15-mm diameter) placed ca. 5 cm above the level of the substrate. A steady flow of a mixture of gases consisting of He and O_2 in a 7:1 ratio (total flow 0.7 L/min) or a He, N_2, and N_2O mixture in a 10:6:1 ratio (total flow 1 L/min), maintained by means of a high-vacuum pump operating at a constant pressure of 4 torr, was passed through the U-tube; the temperature and the duration of the reaction were variable.

Reaction of neat *cis*-stilbene (**1**) with O atoms produced by O_2 discharge resulted in a mixture of *cis*-stilbene oxide (**3**), *trans*-stilbene oxide (**4**), and benzyl phenyl ketone (**5**).[8] At 0 °C, all

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(7) Wayne, R. P. *Adv. Photochem.* **1969**, *7*, 330–332.

(8) Diphenylacetaldehyde, the product of phenyl migration, was detected only in trace amounts (<0.5%).

Table I. Reactions of O(^{3}P) with *cis*-Stilbene **1**

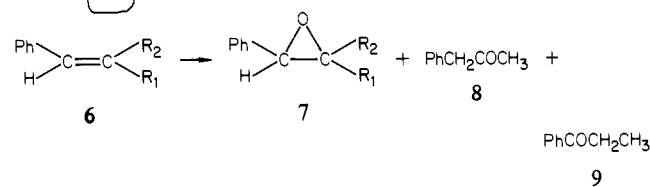| conditions[a] °C	yield, %	conversion, %	product distribution, %		
			3	4	5
−40[b]	85	50	37	37	26
0[b]	75	100	31	40	29
0[c]	71	60	36	41	29
0[d]	90	65	31	36	33
25[b]	72	63	27	44	29
60[b]	e	e	13	51	36

[a] Performed on 1.5 g of substrate for 30 min, except in solution where reaction time was 2 h. [b] Neat liquid, O_2 discharge. [c] Neat liquid, N_2O/N_2 discharge. [d] 30% decane solution, O_2 discharge. [e] Not determined.

Table II. Product Distributions (%) in the Reaction of O(^{3}P) with Styrene at −25 °C

conditions	Ph—⟨O⟩	PhCH$_2$-CHO	PhCOCH$_3$	PhCHO
O_2 (neat)[a]	44	25	12	19
O_2 (decane)[a]	57	27	9	7
N_2O/N_2 (neat)	62	31	2	5

[a] In addition, a small amount (<3%) of 1-phenylethanol and α-hydroxyacetophenone was isolated.

Scheme I

$$Ph{-}C{=}C{<}^{R_2}_{R_1} \longrightarrow Ph{-}C{-}C{<}^{R_2}_{R_1} + PhCH_2COCH_3 +$$

$$\mathbf{6} \qquad\qquad \mathbf{7} \qquad\qquad \mathbf{8}$$

$$PhCOCH_2CH_3$$

$$\mathbf{9}$$

[a] **a**, $R_1 = CH_3$, $R_2 = H$; **b**, $R_1 = H$, $R_2 = CH_3$. **6a** → **7a** (58) + **7b** (8) + **8** (18) + **9** (12). **6b** → **7a** (36) + **7b** (16) + **8** (23) + **9** (12). Product distribution percentage in parentheses.

Scheme II
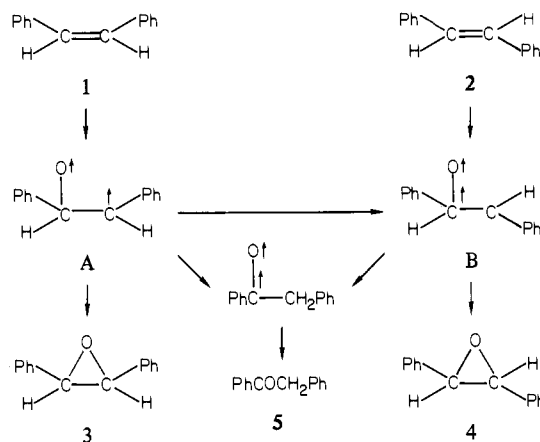
the starting material (1.5 g) was consumed within $^1/_2$ h; the total yield of characterized products was 75%, the rest consisting of an insoluble material (Table I). With shorter reaction times, the conversion was lower, but the relative yields were unchanged. As shown in Table I, similar product ratios were also obtained in a 30% *n*-decane solution, or when O atoms were produced by N_2/N_2O discharge. The product ratios were dependent on the reaction temperature: at higher temperatures, larger relative yields of both **4** and **5** were observed (Table I). In addition, we found a decrease in the reaction rate when the temperature was increased from 0 to 60 °C.[9]

(9) Negative temperature dependence of the reaction of O(^{3}P) atoms with several olefins was observed previously; ref 1i and Atkinson, R.; Pitts, J. N., Jr. *J. Chem. Phys.* **1977**, *67*, 38.