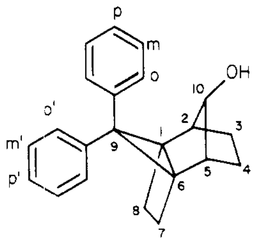
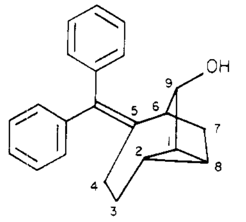
Table I. Lanthanide Shift Data



4-OH

proton	chemical shift, ppm calcd[a]	chemical shift, ppm obsd[b]	multiplicity (J, Hz)
10	12.9	9.0	s
3x, 4x	10.5	4.65	d (8)
2, 5	9.5	4.6	s
3n, 4n	5.4	2.65	d (8)
7n, 8n	2.7	1.9	d (8)
7x, 8x	2.5	1.5	d (8)
o	2.2	1.85	
m	1.2	0.55	
p	0.77	0.55	
o'	2.1	1.2	
m'	1.0	0.55	
p'	0.8	0.55	

correlation coefficient:[c] aliphatic H's, 0.992; aliphatic and aromatic H's, 0.984



9	12.8	20	s
6	11.2	14.4	d (9)
1	9.3	11.9	t (7)
7x	6.6	11.2	m
7n	4.4	6.3	m
3x	4.2	6.3	m
4x	3.4	3.4	m
8	3.0	3.6	m
3n	2.9	3.1	m
4n	2.5	3.4	m
2	2.0	3.1	m
aromatics[d]	0.8-2.8	2.7, 0.9	m

correlation coefficient:[c] 0.985

[a] $10^3(3 \cos \theta - 1)/r^3$. [b] $\Delta\delta$/(moles of LSR/moles of alcohol). The value of the denominator used to extrapolate to a 1/1 complex was 1.55 for 4-OH and 0.8 for 5-OH. [c] The CHOH pair of protons did not correlate well, as expected,[25] and was omitted from the calculation. [d] The aromatic protons were too complex for secure assignment. The LSR study of 4-OH and 5-OH showed clearly the symmetry of the former and the dissymmetry of the latter.

Table II. ^{1}H and ^{13}C NMR Data

alcohol	position	δ_H (J, Hz)	δ_C
4-OH	1, 6		28.1
	2, 5	2.20 br s	45.2
	3, 4	2.05 m	24.1
	7, 8	2.46 d (8),[a] 1.25 d (8)[b]	20.4
	9		35.9
	10	3.56 br s	77.6
	OH	1.20 br s	
	Ar	7.33-7.16 m	144.6-125.6[c]
5-OH	1	*d*	29.6
	2	*d*	21.4
	3	*d*	24.6
	4	*d*	32.0
	5	*d*	143.8
	6	2.92 d (8.5)	50.6
	7	*d*	30.0
	8	*d*	18.0
	9	4.30 s	78.7
	$Ph_2C=$		137.5
	OH	*d*	
	Ar	7.40-7.10 m	140.7-120.0[e]

[a] Exo. [b] Endo. [c] Eight resonances in this range, mostly unassigned. [d] Complex multiplet, δ 2.6-0.8. [e] Complex, with not all eight resonances assigned.

Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05. Found: C, 83.89; H, 7.18.

Addition of palladium(II) acetate (trimer, Alfa, ~15 mg) to an ethereal solution of the diphenyldiazomethane-photocyclized material prior to the 6-h heating period, followed by the above isolation procedure, led to ill-defined tarry material with no spectral evidence of either propellane product or 3-H. This contrasted with the palladium(II) acetate promoted reaction[16] of diphenyldiazomethane to norbornene, from which was isolated hydrocarbon 13[27] in 20% yield, along with benzophenone–azine (20%).

Pyrolysis Studies. A solution of pyrazoline alcohol **3-OH** (1 mmol) in benzene (10 mL) was refluxed in the presence of copper(II) fluoborate[17] (Alfa, ~3 mg) until the evolution of nitrogen stopped. Analysis of the evaporated reaction material by TLC showed **5-OH** as the only identifiable product. No **4-OH** was detected.

Pyrolysis of pyrazoline **3-H** as a neat solid led to a very complex mixture which was not extensively investigated. Reaction of **3-H** (200 mg) in xylene (15 mL) under reflux for 30 min led to nitrogen evolution (92%). Removal of the xylene and elution of the residue through Florisil (10 g) with hexene followed. Evaporation of the hexane left a solid consisting of a major and very minor compounds by TLC. The mixture showed a complex NMR spectrum and clearly contained no propellane. The matter was not pursued intensively, but the provisional structural assignment of 5-(diphenylmethylene)bicyclo[4.2.1]non-2-ene [δ 5.63 (d, $J \simeq 5$ Hz), 5.41 (d, $J \simeq 1.5$ Hz, vinyl H's)] was given to the major product.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also are indebted to those individuals mentioned in the references for assistance and to the Department of Chemistry of Purdue University for some of the ^{13}C work.

Registry No. *anti*-1-OH, 38680-07-8; *syn*-1-OH, 38680-08-9; 1-OAc, 75347-89-6; 3-OH, 75347-82-9; 3-OAc, 75347-83-0; 4-OH, 75347-84-1; 4-OAc, 75347-85-2; 4-ODNB, 75347-86-3; 5-OH, 75347-87-4; 5-OAc, 75365-49-0; 6, 75347-88-5; 2,3-dimethylene-7-norbornane, 38680-06-7; diphenyldiazomethane, 883-40-9.

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(27) J. W. Wilt and T. P. Malloy, *J. Org. Chem.*, 38, 277 (1973).

A Facile Route to 1,3,5,7-Tetraaminoadamantane. Synthesis of 1,3,5,7-Tetranitroadamantane[†]

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Received August 18, 1980

Stetter and Krause[1] have reported that they were unable to convert 1,3,5,7-tetrabromoadamantane (1) to acetamido

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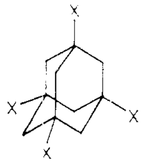
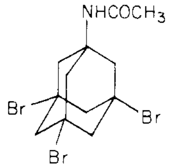
[†] Presented before the Division of Organic Chemistry, 180th National Meeting of the American Chemical Society, Las Vegas, NV, Aug 25-29, 1980, Abstract ORGN 327.

or carboxy derivatives, in contrast to the case of both 1-bromo- and 1,3-dibromoadamantanes. Nonetheless, they report the preparation of 1,3,5,7-tetraacetamidoadamantane (**3**) from 1,3,5,7-tetracarboxyadamantane in a straightforward manner via the tetraamino derivative (**4**).



1, X = Br
2, X = I
3, X = $NHCOCH_3$
4, X = NH_2
5, X = NO_2



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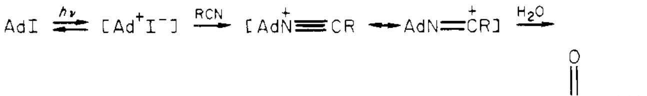
The tetracarboxy compound, however, was prepared in low overall yield by a laborious, multistep procedure involving the Meerwein ester synthesis. We report a new route to **4**, which makes this compound more readily accessible and report its conversion to the previously unknown tetranitroadamantane.

We have confirmed Stetter and Krause's finding that **1**, a compound readily obtained from adamantane by bromination, does not undergo the Ritter reaction[2] with acetonitrile and concentrated sulfuric acid to form amidic products.[3] An attempted reaction of 1,3,5,7-tetraiodoadamantane (**2**) under similar conditions was also unsuccessful. It was, therefore, somewhat surprising to find that **2**, a compound obtained in high yield from **1** by halogen exchange,[4] readily undergoes a photochemically initiated Ritter-type reaction with acetonitrile to produce the tetraamide **3**. In contrast, an attempted reaction of **1** with acetonitrile to produce **3** under identical conditions afforded only 1-acetamido-3,5,7-tribromoadamantane (**6**), a new compound, in 32% yield.

Perkins and Pincock[5] had previously reported that the amides are formed in high yields by the photolysis of 1-iodo- and 1,3-diiodoadamantanes in alkyl nitrile solvents and suggested that the reactions proceed via formation of Ritter-type intermediates. As in the Ritter reaction, the nitrilium ion, formed via interaction of the generated carbenium ion with the nitrile, is converted by water to the amide (eq 1).



$$\mathrm{AdI} \overset{h\nu}{\rightleftharpoons} [\mathrm{Ad^+I^-}] \xrightarrow{\mathrm{RCN}} [\mathrm{Ad\overset{+}{N}{\equiv}CR} \longleftrightarrow \mathrm{AdN{=}\overset{+}{C}R}] \xrightarrow{H_2O} \mathrm{AdNH\overset{\overset{\displaystyle O}{\|}}{C}R} \quad (1)$$

Perkins and Pincock found that the bromoadamantanes are slower to react than the iodides and are more susceptible to hydrogen atom (or ion) transfer under photolysis in methanol, but nevertheless they obtained replacement of all three halides by methoxide in 1,3,5-tribromoadamantane as well as in 1,3,5-triiodoadamantane via photolytically generated adamantyl cationic species. The marked difference in the reactivities of **1** and **2** observed in the present work may be due at least in part to the fact that the total power of the UV lamps used to initiate the reactions was less than that used by Perkins and Pincock.

The tetraamide **3**, obtained in yields as high as 60%, is presumably formed via successive, independent reactions at each iodide, as suggested for the photochemical substitution reactions of dihaloadamantanes.[5] Hydrolysis of **3** with 18% hydrochloric acid produced 1,3,5,7-tetraaminoadamantane (**4**) which was isolated in yields as high as 85% as the tetrahydrochloride.[6,7]

Permanganate oxidation of **4** afforded 1,3,5,7-tetranitroadamantane (**5**) in 45% yield. This oxidation is a standard one for converting tertiary-alkyl amines to the corresponding nitro compounds[8] but has apparently not been used in the past to prepare compounds containing more than two nitro groups. It has been used for the preparation of 1-nitroadamantane.[9] 1-Amino- and 1,3-diaminoadamantanes have been reported to undergo a tungstate-catalyzed oxidation to the nitro compounds with hydrogen peroxide.[10] The nitration of adamantane with concentrated nitric acid in glacial acetic acid at elevated temperature and pressure has been reported to produce 1-nitro-, 1,3-dinitro- and 1,3,5-trinitroadamantanes, the last in very low yield[11] The nitration of alkyladamantanes with nitrogen dioxide at elevated temperature reportedly yields 1-nitro and 1,3-dinitro derivatives,[12] while the photochemical reaction of N_2O_5 with adamantane affords only mononitration.[13]

Other potential routes to precursors of tetranitroadamantane were examined in this study but without success. These included treating **1** or **2** with formic acid in fuming sulfuric acid, with acetamide, with ammonia or amines (butyl, cyclohexyl, and dodecyl), with cuprous cyanide in the presence of pyridine, or with sodium *p*-toluenesulfonamide. These efforts represented attempts to extend reactions applicable to 1-bromo- or 1,3-dibromoadamantanes[14-17] or, as in the last case, tetrakis-

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(1) H. Stetter and M. Krause, *Justus Liebigs Ann. Chem.*, **717**, 60 (1968), and references cited therein.

(2) T. Sasaki, S. Eguchi, and T. Toru, *Bull. Chem. Soc. Jpn.* **41**, 236 (1968), and references cited therein.

(3) Novel nitrosonium- and nitronium-induced conversions of monohaloadamantanes with nitriles to the amides were recently reported: R. D. Bach, J. W. Holubka, and T. H. Taaffee, *J. Org. Chem.*, **44**, 1739 (1979); R. D. Bach, T. H. Taaffee, and S. J. Rajan, *Ibid.*, **45**, 165 (1980); G. A. Olah, B. G. B. Gupta, and S. C. Narang, *Synthesis*, 274 (1979). Possible extension to the tetrahaloadamantanes was not examined in the present study.

(4) J. W. McKinley, R. E. Pincock, and W. B. Scott, *J. Am. Chem. Soc.*, **95**, 2030 (1973).

(5) R. R. Perkins and R. E. Pincock, *Tetrahedron Lett.*, 943 (1975); R. R. Perkins, *Diss. Abstr. Int. B*, **37**, 3421 (1977) [cf. *Chem. Abstr.*, **86**, 105490 (1977)].

(6) 1,3-Diacetamidoadamantane was similarly hydrolyzed in 60% yield, using 10% hydrochloric acid under reflux for 6 h, despite the claim (R. E. Moore, U.S. Patent 3419611 (1968)) that the compound is hydrolyzed by mineral acids to only a minor extent.

(7) H. Stetter and C. Wulff, *Chem. Ber.*, **93**, 1366 (1960), have described the hydrolysis of 1,3-diacetamidoadamantane using concentrated hydrochloric acid without reporting the yield. H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, **92**, 1629 (1959), have reported that 1-acetamidoadamantane with concentrated acid yields only 1-chloroadamantane nearly quantitatively.

(8) N. Kornblum, R. J. Clutter, and W. J. Jones, *J. Am. Chem. Soc.*, 78, 4003 (1956); N. Kornblum and W. J. Jones, *Org. Synth.* **43**, 87 (1963).

(9) H. Stetter, J. Mayer, M. Schwarz, and K. Wulff, *Chem. Ber.*, **93**, 226 (1960); H. Stetter and E. Smulders, *Ibid.*, **104**, 917 (1971).

(10) G. L. Driscoll, U.S. Patent 3535390 (1970).

(11) G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26**, 2207 (1961); G. W. Smith and H. D. Williams, U.S. Patent 3053907 (1962).

(12) A. Schneider, U.S. Patent 3258498 (1966).

(13) I. Tabushi, S. Kojo, and Z. Yoshida, *Chem. Lett.*, 1431 (1974).

(14) Based on the procedure of R. E. Moore and G. L. Driscoll, *J. Org. Chem.*, **43**, 4978 (1978), who converted dibromodimethyladamantane to the dicarboxylic acid, reaction of 1,3-dibromoadamantane with formic acid in 15% fuming sulfuric acid in this study produced the dicarboxylic acid in 91% yield as compared to 80% reported by H. Stetter and C. Wulff, ref 7, for the reaction in concentrated sulfuric acid in the presence of silver sulfate.

(15) K. Gerzon, D. J. Tobias, Sr., R. E. Holmes, R. E. Rathbun, and K. W. Kattau, *J. Med. Chem.*, **10**, 603 (1967) (*Chem. Abstr.*, **67**, 73211 (1967)), reported the reaction of bromotrimethyladamantane with acetamide. This was extended successfully to both 1-bromo- and 1,3-dibromoadamantanes in the present study. Mono- and diacetamido derivatives were obtained in 60% and 64% yields from reactions of 6-h and 16-h durations, respectively, at 150 °C. The former yield was depressed due to sublimation of 1-bromoadamantane.

(bromomethyl)methane,[18] a sterically crowded molecule.

Experimental Section[19]

1,3,5,7-Tetrabromoadamantane (1). The tetrabromide was prepared by modification of a published procedure.[20] Adamantane (27.0 g, 0.2 mol) was added portionwise over 30 min to a stirred mixture of bromine (350 g, 2.2 mol) and anhydrous aluminum chloride (27.0 g, 0.2 mol) at 5–10 °C. The mixture was then heated to 70 °C over a period of 1 h and held at that temperature for 24 h. Hydrogen bromide was evolved copiously during the addition and heating. Excess bromine (180 g) was distilled on the water bath. The residue was triturated with aqueous sodium sulfite (to remove excess bromine) with hydrochloric acid added (to dissolve aluminum salts). The solids were removed by filtration, washed, air-dried, and weighed (91.0 g). Recrystallization from 1200 mL of glacial acetic acid gave 52.0 g (58%) of tan, powdery product: mp 245–247 °C (lit.[20] mp 246–247 °C); NMR [$(CD_3)_2SO$] δ 2.80 (s) (relative to $(CH_3)_4Si$); IR (KBr) 2960 (w), 1443 (m), 1317 (s), 1213 (m), 987 (w), 847 (s), 722 (s), 499 (w) cm^{-1}. Addition of 100 mL of water to the filtrate gave 10.3 g, mp 235–240 °C. The IR spectra of both crops were identical.

1,3,5,7-Tetraiodoadamantane (2). The tetraiodide was prepared by using the conditions cited by Pincock et al.[4] Bromine (1.3 mL, 0.025 mol) was added to small pieces of aluminum foil (20.0 g, 0.074 mol) in methylene iodide (240 mL), and the mixture was stirred for 35 min in a bath at 80 °C. Compound 1 (20.0 g, 0.044 mol) was added in one portion and allowed to react for 15 min at the same temperature. The reaction mixture was poured into 400 mL of cold water with stirring, and sodium bisulfite was added to remove the color of bromine. The methylene iodide phase was separated and washed with water, and the solvent was flash evaporated. The solid residue was washed with chloroform and then with acetone. Recrystallization from toluene yielded 21.2 g (75%) of 2 in the form of needles: mp 370–371 °C dec (lit.[4] mp 370 °C dec); IR (KBr) 2950 (w), 1441 (m), 1313 (s), 1200 (m), 979 (w), 828 (s), 692 (s), 489 (w) cm^{-1}.

Use of half quantities in the above procedure gave 2 in 81% yield.

1,3,5,7-Tetraacetamidoadamantane (3). In a quartz reaction flask, 7.7 g (0.012 mol) of 2 was stirred briskly in 800 mL of acetonitrile (Fisher, 0.1% H_2O, or Baker, 0.07% H_2O) with 1.0 mL of water added, and the mixture was photolyzed for 64 h in a Rayonet photochemical reactor (16 lamps[21]) at approximately 60 °C ambient temperature. The solids were collected on a filter, washed with fresh solvent, and dried. The tarry residue obtained from the acetonitrile filtrate by flash evaporation of the solvent was dissolved in acetone, and after several days the separated solids were collected, washed with fresh solvent, and dried. The combined solids were taken up in methanol with warming (to remove any unreacted starting compound), and the solution was filtered and evaporated to dryness. The residual solids were dissolved in hot water, and the solution was neutralized with aqueous sodium hydroxide and filtered. The aqueous filtrate was flash evaporated, and the residual solids were dissolved in warm methanol. After filtration the solution was evaporated to dryness, and the product was washed onto a filter with acetone and then washed briefly with acetone–water (50:50, v/v), rinsed with acetone, and air-dried, yielding 2.68 g (51%). The product crystallized from water in the form of needles and exhibited no melting to 360 °C (lit.[1] no melting to 360 °C). The product analyzed as the tetrahydrate: NMR [$(CD_3)_2SO$] δ 1.75 (12 H, s, CH_3), 2.06 (12 H, s, CH_2), 3.33 (8 H,[22] s, H_2O), 7.50 (4 H, s, NH); IR (KBr) 3430 (m), 3270 (s), 3040 (w), 2970 (w), 1650 (s), 1525 (s), 1449 (w), 1430 (w), 1367 (m), 1347 (s), 1326 (m), 1304 (m), 1283 (m), 1229 (w), 676 (w), 600 (m), 557 (m), 477 (m), 335 (m) cm^{-1}.

Anal. Calcd for $C_{18}H_{28}N_4O_4 \cdot 4H_2O$: C, 49.53; H, 8.31; N, 12.84; O, 29.32; H_2O, 16.51%; mol wt 436.5. Found: C, 49.97; H, 8.50; N, 12.46; O, 29.33; H_2O (by weight loss), 16.23%; mol wt (in H_2O), 421.

Use of half quantities in the above procedure gave 3 in 60% yield.

A sample of 3 was dried for 2 h at 100 °C in vacuo with phosphorus pentoxide present; IR (hexachlorobutadiene) 3260 (s), 3070 (w), 1620 (s), 1545 (s), 1430 (w), 1365 (m), 1350 (m), 1325 (m), 1310 (m), 1285 (sh, w), 1227 (w) cm^{-1}. A similar spectrum was obtained from the tetrahydrate on mulling in Nujol without predrying, indicating that the water was removed by that mulling process. The bands in the region 1380–1270 cm^{-1} were relatively unresolved, differing from the five sharp peaks characteristic of the tetrahydrate. Pelletizing the dried sample in KBr without excluding moisture caused conversion to the tetrahydrate as indicated by the IR spectrum.

1,3,5,7-Tetraaminoadamantane (4) Tetrahydrochloride. A solution of 3 tetrahydrate (7.9 g, 0.018 mol) in 18% hydrochloric acid (30 mL of water plus 30 mL of concentrated hydrochloric acid) was refluxed for 3 h with stirring. The separated product (4.9 g) was collected on a filter and washed with acetone; mp >360 °C (lit.[23] mp >360 °C). On standing overnight, the filtrate, containing the acetone wash, deposited an additional 0.1 g, mp >360 °C, for a combined yield of 5.0 g (79%): IR (hexachlorobutadiene) 2900 (s), 1585 (m), 1545 (m), 1535 (m), 1486 (m), 1373 (s), 1365 (s), 1305 (m), 1074 (w) [(Nujol) 954 (w), 946 (w), 811 (w)] cm^{-1}.

Anal. Calcd. for $C_{10}H_{20}N_4 \cdot 4HCl$: C, 35.11; H, 7.07; N, 16.38. Found: C, 35.35; H, 7.17; N, 16.01.

Use of half the quantity of 3 tetrahydrate in the above procedure gave 4 tetrahydrochloride in 85% yield.

No significant weight loss was obtained on drying a sample of the tetrahydrochloride of 4 in vacuo for 1 h at 110 °C with phosphorus pentoxide present. Conversion to a hydrated form occurred on pelletizing the sample in KBr without excluding moisture, as indicated by the changed IR spectrum: 3460 (s), 2980 (s), 2870 (s), 1580 (w), 1473 (s), 1455 (m), 1373 (s), 1302 (m), 1068 (w), 945 (w), 816 (w), 568 (w), 316 (m) cm^{-1}.

1,3,5,7-Tetranitroadamantane (5). The standard permanganate oxidation of tertiary alkylamines[8] was adapted to this preparation. The tetrahydrochloride of 4 (5.2 g, 0.015 mol) was dissolved in 200 mL of water and converted to the free base by adding equivalent aqueous sodium hydroxide. Magnesium sulfate (10.5 g, 0.087 mol) was added to the well-stirred mixture at 30 °C. The mixture was diluted with 150 mL of acetone, and potassium permanganate (57.0 g, 0.35 mol) was added portionwise with stirring over 30 min. Stirring was continued at 30 °C for 48 h. The insoluble solids were collected, washed with water, dried, and extracted eight times with boiling toluene, totaling 400 mL. The combined extracts were filtered and concentrated to approximately 75 mL to yield, after 3 days, 1.27 g of product in the form of truncated square pyramidal crystals, mp >360 °C dec. The filtrate yielded an additional 0.87 g of product for a total yield of 2.14 g (45%). For analysis, a sample was dissolved in acetone and precipitated as a powder by the addition of water: mp 361–363 °C dec; NMR [$(CD_3)_2SO$] δ 2.92 (s); mass spectrum, m/e 270 [$(M - NO_2)^+$, 100%], 178 [$(M - 3NO_2)^+$, 91.5%], 132 [$(M - 4NO_2)^+$, 39.5%]; IR (KBr) 3015 (w), 3000 (w), 2985 (w), 2880 (w), 1542

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(16) E. V. Krumkalns and W. Pfeifer, *J. Med. Chem.*, 11, 1103 (1968); F. N. Stepanov, Z. E. Stolyarov, *Zh. Org. Khim.*, **5**, 537 (1969) [*Chem. Abstr.*, 71, 12643 (1969)]; E. I. du Pont de Nemours and Co., Neth. App. 7402316 (1974) [*Chem. Abstr.*, **83**, 113776 (1975)].

(17) P. H. Owens, G. J. Gleicher, L. M. Smith, Jr., *J. Am. Chem. Soc.*, **90**, 4122 (1968). Reaction with CuCN and pyridine could not be extended to 1,3-dibromoadamantane in the present study.

(18) A. Litherland and F. A. Mann, *J. Chem. Soc.*, **1588** (1938). Sodium *p*-toluenesulfonamide was found to convert 1-bromoadamantane in sulfolane to 1-(*p*-toluenesulfonamido)adamantane in 40% yield after 7 h at 235 °C in the present study. The yield was depressed due to sublimation of bromoadamantane. The compound was previously prepared[9] from *p*-toluenesulfonyl chloride and 1-aminoadamantane.

(19) Melting points were determined with a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 457A grating infrared spectrophotometer. NMR spectra were obtained on a Varian T-60 NMR spectrometer using tetramethylsilane as internal standard. Chemical shifts are reported in parts per million. The mass spectrum was obtained on a DuPont 21-492 mass spectrometer using a solids probe. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

(20) A. P. Khardin, I. A. Novakov, and S. S. Radchenko, *J. Org. Chem. USSR* (*Engl. Transl.*), **9**, 435 (1973).

(21) Each lamp ca. 0.03 W, 1849 Å, and 2.2 W, 2537 Å (The So. New England Ultraviolet Co., Middletown, CT).

(22) Correction was made for water present in the solvent.

(23) H. Stetter and C. Wulff, ref 7.

(24) Correction was made for $CHD_2(CD_3)SO$ present in the solvent.

(s), 1457 (m), 1402 (w), 1362 (s), 1342 (w), 1256 (w), 1236 (m), 921 (w), 913 (w), 845 (w), 748 (m), 741 (m), 713 (m), 360 (w), 343 (m), 329 (m) cm^{-1}.

Anal. Calcd for $C_{10}H_{12}N_4O_8$: C, 37.98; H, 3.83; N, 17.72. Found: C, 38.30; H, 3.86; N, 17.50.

1-Acetamido-3,5,7-tribromoadamantane (6). The photolysis of 5.4 g (0.012 mol) of 1 in 800 mL of acetonitrile was carried out in the same manner as described above for the conversion of 2 to 3. The solids obtained by flash evaporation of the clear solution were extracted with boiling *n*-heptane several times, removing 0.9 g of unchanged 1 as confirmed by IR spectrum. The undissolved solids were taken up in methanol, and the solution was neutralized dropwise with aqueous KOH. The solution was dispersed in water, and the separated solids were collected on a filter. The dried solids were taken up in boiling acetone, and the solution was filtered, concentrated, diluted with water to the cloudpoint, and chilled overnight to give 1.68 g (32%) of 6, mp 286–289 °C dec. Recrystallization from acetone–water gave needles: mp 290–292 °C dec; NMR [$(CD_3)_2SO$] δ 1.78 (3 H, s, CH_3), 2.50 (6 H,[24] s, CH_2 β to $NHCOCH_3$), 2.73 (6 H, s, CH_2 δ to $NHCOCH_3$), 7.88 (1 H, s, NH); IR (KBr) 3280 (s), 3070 (w), 2940 (w), 1635 (s), 1550 (s), 1448 (m), 1371 (m), 1343 (m), 1320 (s), 1305 (m), 1214 (w), 850 (m), 725 (m), 608 (w), 486 (w) cm^{-1}.

Anal. Calcd for $C_{12}H_{16}Br_3NO$: C, 33.52; H, 3.75; Br, 55.75; N, 3.26. Found: C, 33.73; H, 3.74; Br, 55.83; N, 3.02.

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Registry No. 1, 7314-86-5; 2, 40950-19-4; 3, 21336-48-1; 4·HCl, 21336-47-0; 5, 75476-36-7; 6, 75476-37-8; adamantane, 281-23-2.

Oxidative Coupling of Ketone Enolates by Ferric Chloride[†]

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Metallic oxidants have been widely employed in oxidative couplings of phenols,[2] yet only recently have comparable methods appeared for oxidatively dimerizing ketones to give 1,4-diketones. Surprisingly, while cupric salts have been used to couple ketone enolates,[3-5] ferric chloride, commonly used in phenolic oxidations, is reported to be ineffective for such couplings.[3,6]

We find that in spite of previous observations, ferric chloride is an effective oxidant for the preparation of 1,4-diketones from ketone enolates. Examples of ketones whose enolates have been coupled with ferric chloride are given in Table I. Entry 10 demonstrates that esters can also be dimerized by this method. In most respects enolate dimerizations with ferric chloride are quite similar to those induced by cupric chloride. However, while dimerizations with cupric chloride are relatively sensitive to steric congestion around the carbanion,[3] the ferric system offers the advantage of not being so.

The coupling reaction is performed by adding a solution of anhydrous ferric chloride[7] in dry dimethylformamide to an enolate in tetrahydrofuran.[8] The enolates can be prepared in conventional ways, e.g., with lithium diisopropylamide (LDA) at dry ice temperatures (kinetic enolates) or with potassium hydride (thermodynamic enolates).[9] Stirring the mixture overnight at room temperature was generally sufficient to ensure completion of the oxidation.[10] After an extractive workup, the products could be isolated with standard techniques.

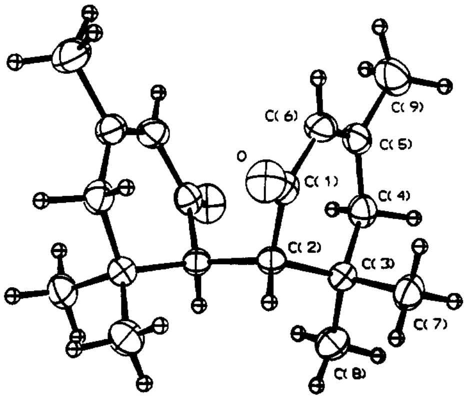

Figure 1. ORTEP drawing of *dl*-1,1′,5,5,5′,5′-hexamethyl[4,4′-bicyclohexenyl]-3,3′-dione. Selected bond distances (Å): C(1)–O, 1.229 (1); C(1)–C(2), 1.510 (2); C(1)–C(6), 1.461 (2); C(2)–C(2)′, 1.560 (2); C(2)–C(3), 1.560 (2); C(5)–C(6), 1.332 (2). The ring adopts a half-chair conformation in which C(2) and C(3) are 0.37 and −0.33 Å out of plane formed by C(1), C(4), C(5), and C(6). The C(1)–C(2)–C(2)′–C(1)′ torsion angle is 55.7°.

Where more than one enolate anion is possible, the structure of the product depended on the particular enolate prepared.[11] Thus, the structure of dimer 3 as shown in Table I was that expected from oxidation of the kinetic enolate. Spectral data for this compound, however, were not unequivocal, and a single-crystal X-ray structure de-

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[2] For reviews see T. Kametani and K. Fukumoto, *Synthesis*, **657** (1972), and references therein.

[3] Y. Ito, T. Konoike, T. Harada, and T. Saegusa, *J. Am. Chem. Soc.*, **99**, 1487 (1977).

[4] Y. Ito, T. Konoike, and T. Saegusa, *J. Am. Chem. Soc.*, **97**, 2912 (1975).

[5] Y. Kobayashi, T. Taguchi, and E. Tokuno, *Tetrahedron Lett.*, 3741 (1977); Y. Kobuzaski, T. Taguchi, and T. Morihawa, *ibid.*, 3555 (1978).

[6] Oxidation of propiophenone and butyrophenone with ferric chloride has been reported to give 1,4-diketones and products derived from these diketones along with other products. The enolate anions, however, were not oxidized, and, further, the reaction is not general since with acetophenone or aliphatic ketones only products derived from aldol-like condensations were obtained. H. Inoue, M. Sakata, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **46**, 2211 (1973).

[7] Ferric chloride must be anhydrous for successful couplings. In our experience, commercial anhydrous ferric chloride was often not sufficiently dry and was usually contaminated with insoluble iron oxides. We found it better to dry the hydrated reagent with thionyl chloride and, since the anhydrous solid is extremely hygroscopic, handle it under an atmosphere of dry nitrogen.

[8] If THF was substituted for DMF, the yields were much lower. Similar solvent effects have been noted for phenolic oxidations by ferric chloride [S. Tobinaga and E. Kotani, *J. Am. Chem. Soc.*, **94**, 309 (1972)] and by Saegusa for the cupric oxidation of ketone enolates.

[9] C. A. Brown, *J. Org. Chem.*, **39**, 3913 (1974).

[10] The reaction can be followed by various standard methods. We found gas chromatography particularly useful due to the large retention time differences between the starting materials and the dimers. Such analyses revealed that the reaction mixtures were composed of primarily dimers and undimerized starting materials. Smaller amounts, generally 10% or less, of self-condensation products were also observed. The dimer yields given, aside from losses due to isolation and purification, generally reflect the percent conversion to dimers. In experiments with cyclohexanone, increasing the amount of ferric chloride used did not substantially alter the conversion to the dimer.

[11] The oxidations presented here were done on enolates composed of essentially only one regioisomer. Under these conditions the dimerization appears to be regiospecific. When a mixture of enolates is present, oxidation with $FeCl_3$ will give a statistical distribution of all possible dimers based on the original concentrations of enolates.

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