eliminated instead of water upon the formation of the methyltolycarbonium ion. The steric requirements of this dimer will be less than that of paraldehyde. The dimer, in turn, will be depolymerized to acetaldehyde during its sequence of reactions of protonation, alkylation, and formation of another methyltolycarbonium ion. On the basis of this reasoning, it is apparent that the production of 100% 1,1-*p,p*-ditolylethane by the Baeyer reaction of paraldehyde and toluene is highly improbable.

Experimental

Materials.—Acetaldehyde and paraldehyde were purchased from Distillation Products Industries and used without purification. Anhydrous hydrogen fluoride was obtained in cylinders from the Matheson Co. and nitration grade toluene from Stoney-Mueller, Inc. The sulfuric acid was reagent grade from J. T. Baker Chemical Co.

Gas-Liquid Chromatographic Analysis of Ditolylethane.— The analyses were performed on a Podbielniak Chromacon, Series 9580, gas-liquid chromatograph equipped with a 12-ft column packed with Apiezon L grease on acid-washed Chromosorb W solid support. The column was operated at 241° with helium flow rate of 73 ml./min. measured at room temperature. The relationship between actual weight percentages and peak areas was obtained by calibration with known mixtures of the pure 1,1-ditolylethane isomers. All of the six possible pure isomers were available for this calibration and the error of the analyses was estimated to be 1% absolute.

A. Employing Hydrofluoric Acid Catalyst.—A specially fabricated 2-l. copper flask fitted with a stainless steel impeller, stainless steel thermowell, a Dewar condenser, and a dropping funnel was used for these experiments.

In a typical run (run 8, Table I) 44.2 g. (0.33 mole) of paraldehyde was diluted to 100 ml. with toluene and placed in the dropping funnel. The remainder of the toluene (to a total of 552 g.; 6.0 moles) was placed in the reaction vessel. The flask was then placed in a Dry Ice-acetone bath at −78° and anhydrous hydrofluoric acid (360 g.; 18.0 moles)

added. The toluene–paraldehyde solution was then added at a constant rate during 120 min. to the stirred reaction mixture. After an additional hour of stirring the product was allowed to warm to about +5° and about 1 l. of water was added cautiously. The organic phase was separated and washed with several portions of 5% sodium hydroxide solution and several portions of water.

After drying over anhydrous calcium sulfate there was obtained 556 g. of product which was distilled. After stripping of the unchanged toluene (452 g.) the pressure was reduced to 10 mm. of mercury where the ditolylethane (101 g.) distilled at 150°. This product corresponds to an 88.5% yield based on the toluene consumed and a 48% yield based on the paraldehyde charged. No effort was made to recover unconverted paraldehyde.

B. Employing Sulfuric Acid Catalyst.—The apparatus used for these experiments was substantially the same as described above, except that the flask was of glass and the Dewar condenser was replaced by a second dropping funnel. The second dropping funnel was used to add the sulfuric acid continuously and thus maintain a constant acid concentration during the reaction.

In a typical experiment with this catalyst (run 1, Table I) 77 g. (1.75 moles) of acetaldehyde was diluted to 420 ml. with toluene and placed in one dropping funnel. The remainder of the toluene (total 921 g.; 10.0 moles) was added to the reaction vessel. In the other dropping funnel was placed 655 g. of 94.3% sulfuric acid. The reaction vessel was cooled and maintained at 0° with stirring while the contents of both dropping funnels were added simultaneously at a constant rate so that at the end of 120 min. both funnels were exhausted. After 1 hr. of additional stirring, the product was isolated as described above for the hydrofluoric acid-catalyzed reaction. In this case there was isolated 613 g. of unchanged toluene and 331 g. of ditolylethane corresponding to a 94% yield based on toluene consumed and 90% on acetaldehyde charged.

Biadamantane and Some of Its Derivatives

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Several 3,3'-disubstituted biadamantane derivatives were prepared from 3,3'-dibromo-1,1'-biadamantane. The structure of the compounds synthesized was determined by means of crystal structure analysis and nuclear magnetic resonance studies.

Adamantane (tricyclo[3.3.1.1³,⁷]decane) which can readily be prepared from tetrahydrodicyclopentadiene and aluminium trichloride or aluminum tribromide[1,2] has a carbon-carbon arrangement as in a diamond lattice. The molecule is highly symmetrical and has good chemical and thermal stability. Bromination of the adamantane in the ab-

sence of a catalyst leads to 1-bromoadamantane exclusively.[3] Therefore biadamantane was chosen as the obvious means to difunctional derivatives containing the adamantane structure. Subsequent to our own work, a publication by Stetter and Wulff[4] describes the synthesis of higher brominated adamantane by the use of special catalysts.

(1) P. von R. Schleyer, *J. Am. Chem. Soc.*, **79**, 3292 (1957).
(2) P. von R. Schleyer and M. M. Donaldson, *ibid.*, **82**, 4645 (1960).

(3) H. Stetter, M. Schwarz, and A. Hirschhorn, *Ber.*, **92**, 1629 (1959).
(4) H. Stetter and C. Wulff, *ibid.*, **93**, 1366 (1960).

Biadamantane (I), which has been previously prepared by Landa and Hala[5] from 1-bromoadamantane and sodium in ethyl ether, was more readily prepared from 1-bromoadamantane[3] and sodium dispersion in xylene or dioxane in yields of about 40%.
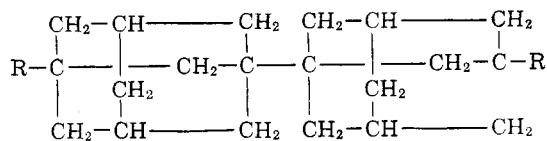
The bromination of biadamantane in the absence of added catalysts with elemental bromine gave a dibromobiadamantane in yields of more than 80%. No monobromobiadamantane formation was observed. The positions of the bromine atoms were determined *via* two-dimensional Patterson projections.[6] Using these bromine coördinates for the calculation of the signs of the structure factors for subsequent Fourier projections, it was possible to determine, after minor modifications, the positions of all carbon atoms. The Fourier projections indicated that the "diamond-like" arrangement of secondary and tertiary carbon atoms, as reported by Novacki,[7] for adamantane is preserved in the dimer derivatives. The two adamantane molecules are linked by tertiary carbon atoms. Substitution by two bromine atoms occurs at the tertiary carbon atoms to give a dibromobiadamantane which has a center of symmetry and can be described in the crystalline form as *trans*-3,3'-dibromo-1,1'-biadamantane (II).

The n.m.r. spectrum of 1,1'-biadamantane at 56.4 mc./sec. shows one peak at −100 c.p.s. and a shoulder at −99 c.p.s. from tetramethyl silane. The spectrum is in accord with the n.m.r. spectrum of adamantane which shows two hydrogen peaks at −101 and −100 c.p.s. from tetramethylsilane. 3,3'-Dibromo-1,1'-biadamantane gives three peaks at −130, 120, and −94 c.p.s. from tetramethylsilane which is in agreement with the n.m.r. spectrum of 1-bromoadamantane published by Stetter and co-workers.[3]

The area ratio of the hydrogen peaks of the n.m.r. spectrum of II should be 3:1:3 (twelve secondary hydrogens adjacent to the bromine substituent, four tertiary hydrogens, and twelve isolated secondary hydrogens), if the bromine substituents are located at tertiary carbon atoms and if the two adamantane molecules are bonded at tertiary carbon atoms. We found an area ratio of 3:1:3 which proves that all substitutions occurred on tertiary carbon atoms. This is in agreement with the results of the Fourier projections.

Crystallographic characterization[6] was made by use of the polarizing microscope and by precession camera and rotating film technique. Compound II crystallizes at room temperature in colorless crystals of tabular habit. The crystals are biaxial negative and belong to the monoclinic prismatic system. The cell dimensions are $a = 19.82$, $b =$

6.87, $c = 13.035$ Å, $\beta = 102°\ 37'$ with space group C_2/c. There are four molecules in the elementary cell which give a calculated density of 1.642 g./cc. in comparison with pycnometrically measured density of 1.61 g./cc.


I. R = H
II. R = Br
III. R = CN
IV. R = COOH
V. R = COCl
VI. R = COOCH₃
VII. R = CH₂OH

VIII. R = C₆H₄OCH₃
IX. R = C₆H₄OH
X. R = C₆H₅
XI. R = CH₂NH₂·HCl
XII. R = CH₂NH₂
XIII. R = OH

Methods similar to those described by Setter and co-workers[3,9] and von R. Schleyer and Nicholas[8] for the preparation of monoadamantane derivatives were used in the synthesis of the biadamantane derivatives.

The biadamantane dibromide (II) was treated with a copper cyanide–pyridine complex and 3,3'-dicyano-1,1'-biadamantane (III) was obtained. Hydrolysis of III with sulfuric acid–acetic acid–water led to 3,3'-dicarboxy-1,1'-biadamantane (IV). Compound IV reacted with thionyl chloride and the diacid dichloride (V) formed reacted with methanol to give dimethyl 1,1'-biadamantane-3,3'-dicarboxylate (VI). The reduction of VI with lithium aluminum hydride resulted in the formation of 3,3'-dimethylol-1,1'-biadamantane (VII).

Compound II reacts very readily with compounds having reactive hydrogens in the molecule such as phenol, anisole, diphenyl ether, diphenyl sulfide, etc., in the absence of added catalysts. The ease of these reactions suggests an ionic reaction mechanism involving the formation of a biadamantane carbonium ion as postulated by Stetter and co-workers[9] for the hydrolysis of 1-bromoadamantane in aqueous ethanol without added base. The reaction of II and anisole at 150° leads, *e.g.*, to the formation of 3,3'-(*p*-anisyl)-1,1'-biadamantane (VIII) in 92% yield. The infrared spectrum of
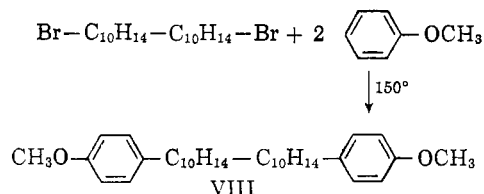
VIII indicates that the substitution occurred in the position *para* to the activating oxygen atom (strong aromatic C=C stretching band at 6.6 μ and also aromatic substitution bands in the 12-μ region).

(5) S. Landa and S. Hala, *Chem. Listy*, **51**, 2325 (1957).

(6) Crystal structure analysis and evaluation of results were carried out by Dr. G. Teufer, Engineering Department, E. I. du Pont de Nemours & Company, Inc.

(7) W. Novacki, *Helv. Chim. Acta*, **28**, 1233 (1945).

(8) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).

(9) H. Stetter, F. Mayer, M. Schwarz, and K. Wulff, *Chem. Ber.*, **93**, 226 (1960).

There is no indication for *ortho-* or *meta*-substitution.

Phenol reacts with II readily at temperatures above 50° in the absence of an added catalyst in nearly quantitative yield with formation of IX. 1-Bromoadamantane reacts under similar conditions with anisole and phenol with formation of the corresponding 1-anisyladamantane and 1-(*p*-hydroxyphenyl)adamantane. Trifluoromethoxybenzene, however, did not react with II on heating to reflux for three hours under the conditions applied above.

The reaction of II with excess benzene, in the presence of anhydrous ferric chloride, yields 3,3'-diphenyl-1,1'-biadamantane (X) in 50% yield. The dicyano derivative (III) could be reduced with lithium aluminum hydride to 3,3'-di(aminomethyl)-1,1'-biadamantane (XII), which was isolated as its dihydrochloride (XI).

3,3'-Dihydroxy-1,1'-biadamantane was obtained from II and silver nitrate in dioxane.

Experimental

1,1'-Biadamantane (I).—1-Bromoadamantane (107 g.) was dissolved in 200 ml. of xylene and heated to reflux in a three-neck flask fitted with thermometer, nitrogen inlet, anchor stirrer, and reflux condenser, under a slow stream of nitrogen. Then a total of 11.5 g. of small pieces of sodium metal was added to the stirred reaction mixture over a period of 4 hr. After all sodium had been added, the mixture was refluxed for an additional hour and then filtered in the hot state. On cooling to room temperature, 20 g. of biadamantane crystallized from the filtrate. Concentration of the filtrate to 75 ml. gave an additional 12 g. of biadamantane (48.7%). The biadamantane obtained was recrystallized from benzene, giving a microcrystalline powder, m.p. 288–290° (lit.,[1] m.p. 296°).

Anal. Calcd. for $C_{20}H_{30}$: C, 88.82; H, 11.18. Found: C, 88.78; H, 11.21.

3,3'-Dibromo-1,1'-biadamantane (II).—Biadamantane (I) (3.75 g.), was charged into a round-bottom flask fitted with a long reflux condenser. Then 20 ml. of bromine was added with stirring, and hydrogen bromide was formed. Hydrobromic acid evolution ceased after 15 min. The reaction mixture was then heated to reflux (61° pot temperature) for 2 hr. The cooled reaction product was diluted with 75 ml. of carbon tetrachloride and transferred to a separatory funnel. The carbon tetrachloride solution was then shaken with ice water, and sodium bisulfite was added until excess bromine was destroyed. The carbon tetrachloride layer was separated and the water layer extracted twice with 50 ml. carbon tetrachloride. The combined carbon tetrachloride solutions were dried over sodium sulfate, and the solvent was stripped under slight vacuum. The semisolid reaction product in the pot was precipitated with methanol, filtered off, and recrystallized from dioxane; yield 4.8 g. (81%), monoclinic prisms, m.p. 236–237°, soluble in benzene, carbon tetrachloride, ethyl ether; insoluble in methanol.

Anal. Calcd. for $C_{20}H_{28}Br_2$: C, 56.08; H, 6.58; Br, 37.31, mol. wt. 428. Found: C, 56.09; H, 6.68; Br, 37.19, mol. wt. 415.

3,3'-Dicyano-1,1'-biadamantane (III).—To 15 g. of cuprous cyanide charged into a round-bottom flask fitted with a distilling head, thermometer, and stirrer 75 ml. of pyridine was added. To the pyridine–copper cyanide complex which had formed immediately 20 g. of 3,3'-dibromo-1,1'-biadamantane (II) was added and the reaction mixture heated slowly to 230°, whereby most of the pyridine distilled. The

reaction product was maintained at 230° for an additional 10 min. After cooling to room temperature, a hard, black solid was obtained. This was powdered and extracted with 250 ml. of refluxing benzene for 36 hr. The dark brown solution was filtered hot and allowed to cool to room temperature. The tan product which precipitated from the benzene solution was repeatedly recrystallized from benzene until a colorless product was obtained with a yield of 12 g. (80%). Recrystallization from benzene gave transparent needles, m.p. 261–262°.

Anal. Calcd. for $C_{22}H_{28}N_2$: C, 82.45; H, 8.81; N, 8.74. Found: C, 82.72; H, 8.88; N, 8.75.

The infrared spectrum of the compound shows a CN band at 4.5 μ.

3,3'-Dicarboxy-1,1'-biadamantane (IV).—To 2 g. of III was added a mixture of 15 ml. of concentrated sulfuric acid, 15 ml. of glacial acetic acid, and 15 ml. of water. This was heated to reflux for 1.5 hr. (pot temperature was 125°) with stirring. The white, creamy reaction product was filtered off, carefully washed with water and methanol, and then dried under vacuum. Recrystallization from dimethylacetamide yielded 2.2 g. (98%) of the diacid, m.p. 352–355°.

Anal. Calcd. for $C_{22}H_{30}O_4$: C, 73.71; H, 8.43. Found: C, 73.70; H, 8.78.

3,3'-Dimethylol-1,1'-biadamantane (VII).—To a mixture of 0.5 g. of lithium aluminum hydride in 20 ml. of tetrahydrofuran charged into a round-bottom flask fitted with stirrer, reflux condenser with drying tube, and thermometer was added a solution of 3.86 g. of VI in 15 ml. of tetrahydrofuran over a period of 10 min., whereby the temperature of the reaction mixture rose to 50°. The reaction mixture was then heated to reflux for 1 hr. and, after cooling to room temperature, was poured onto a mixture of 10 ml. of concentrated hydrochloric acid in 125 ml. of ice water. The solids were filtered off, washed with water, and dried. Recrystallization from benzene yielded white needles of (VII), yield 3.1 g. (94%), m.p. 217–218°.

Anal. Calcd. for $C_{22}H_{34}O_2$: C, 79.94; H, 10.36. Found: C, 80.09; H, 10.29.

3,3'-(*p*-Anisyl)-1,1'-biadamantane (VIII).—To 5 g. of II was added 25 ml. of anisole and the mixture was heated to reflux (155° pot temperature) for 5 hr. After 15 min. of refluxing, hydrogen bromide was evolved. The evolution of hydrobromic acid ceased after about 1 hr. The reaction product was filtered hot and on cooling to room temperature, small flakes were obtained which were recrystallized from xylene. We obtained 5.17 g. of (VIII) (95%), m.p. 263–263° which was soluble in aromatic hydrocarbons; insoluble in acetone, ethanol, and carbon tetrachloride.

Anal. Calcd. for $C_{34}H_{42}O_2$: C, 84.59; H, 8.77. Found: C, 84.61; H, 8.61.

3,3'-Di-(*p*-hydroxyphenyl)-1,1'-biadamantane (IX).—Five grams of 3,3'-dibromo-1,1'-biadamantane and 30 g. of phenol were heated under a slow stream of nitrogen (to remove hydrobromic acid as formed) with stirring. Hydrobromic acid formation began at 50° and at temperatures above 85° was rapid. After 36 min., the refluxing temperature was 182°. The product was refluxed an additional 30 min. On cooling to room temperature, a white solid precipitated and was refluxed with about 500 ml. of methanol. The solid remaining in the pot was filtered hot and washed with methanol. The yield was 5.2 g. (98%). The product was recrystallized from dimethylacetamide and tetrahydrofuran to give fine leaflets, m.p. 343–344°, which were soluble in hot dimethylacetamide and tetrahydrofuran; insoluble in water, dioxane, methanol, benzene, carbon tetrachloride, cyclohexane, and 50% aqueous sodium hydroxide.

Anal. Calcd. for $C_{32}H_{38}O_2$: C, 84.53; H, 8.42. Found: C, 84.58; H, 8.52.

3,3'-Diphenyl-1,1'-biadamantane (X).—A mixture of 5 g. of II and 60 ml. of benzene containing 2 g. of sublimed ferric chloride was charged into a three-neck flask (thermometer and nitrogen, stirrer, reflux condenser) and heated to reflux for 2 hr. under a slow stream of nitrogen. The formation of

hydrogen bromide began after reaching a temperature of 50°. The reaction product after cooling to room temperature, was poured onto 150 g. of wet ice containing 10 ml. of conc. hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with 50 ml. of benzene. The combined benzene solutions were dried over sodium sulfate, filtered, and concentrated to a volume of 60 ml. The crystals which precipitated from the concentrated benzene solution were recrystallized from benzene, yield 2.5 g. (51%), m.p. 270–271°.

Anal. Calcd. for $C_{32}H_{38}$: C, 90.93; H, 9.06. Found: C, 90.95; H, 8.94.

3,3'-Bisaminomethyl-1,1'-biadamantane (XII).—Powdered lithium aluminum hydride (0.6 g.) was charged into a three-neck flask (fitted with a thermometer, nitrogen inlet, addition funnel, and reflux condenser) together with 15 ml. of anhydrous tetrahydrofuran. A solution of 2.5 g. of 3,3'-dicyano-1,1'-diadamantane in 20 ml. of anhydrous tetrahydrofuran was added over a period of 15 min. The reaction product, after cooling to room temperature, was poured onto wet ice containing dilute hydrochloric acid. Recrystal-

lization from dilute hydrochloric acid gave about 2 g. (64%) of the dihydrochloride of 3,3'-diaminomethyl-1,1'-biadamantane (XI) in the form of fine white needles. The compound does not melt at temperatures up to 320°.

Anal. Calcd. for $C_{22}H_{38}Cl_2N_2$: C, 65.81; H, 9.54; Cl, 17.66. Found: C, 65.32; H, 9.63; Cl, 17.32.

The free diamine was obtained from the dihydrochloride by reaction with ammonia. It is a white solid melting below 50°.

3,3'-Dihydroxy-1,1'-biadamantane (XIII).—Eleven and five-tenths grams of II, 20 g. of silver nitrate, 120 ml. of dioxane, and 40 ml. of water were charged into a three-neck flask fitted with thermometer, stirrer, and reflux condenser. The mixture was heated to gentle reflux for 3.5 hr. with stirring. The reaction product was then cooled to room temperature and filtered. The solids were extracted with refluxing dioxane and, on cooling to room temperature, 3.5 g. (93%) of 3,3'-dihydroxy-1,1'-biadamantane crystallized as transparent needles, m.p. 271–272° (sealed tube).

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 9.99. Found: C, 79.53; H, 9.98.

Physical and Chemical Properties of Hydroxyflavones. II. 3-Aroyl-5-hydroxyflavones. Synthetic and Infrared Spectral Studies[1,2]

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The Baker-Venkataraman rearrangement with the dibenzoate and bis(methoxybenzoates) of 2,6-dihydroxyacetophenone at the reflux temperature of pyridine or 2,6-lutidine, with subsequent ring-closure, resulted in the 3-aroyl-5-hydroxyflavones as principal product. The carbonyl region of the infrared spectra of 3-aroyl-5-hydroxyflavones contains two absorption bands, of which the high frequency one is assigned to the carbonyl function of the 3-aroyl group.

In the synthesis of flavones by the Kostanecki-Robinson, (Allan-Robinson) reaction, the 3-aroylflavone often is obtained as a by-product.[4] In many instances, the 3-aroyl group is removed readily by subsequent treatment with alcoholic alkali. The present paper reports an investigation of the Baker-Venkataraman rearrangement,[5] with subsequent ring-closure, as a synthetic route to 5-hydroxy-*n*-methoxyflavone (*n* = 2', 3', or 4'), and infrared spectral data which in virtually all instances afford a method for distinguishing between the 5-hydroxyflavone and its 3-aroyl derivative. The spectral method is of added significance since combustion analyses will not always distinguish between these two classes.[6]

The dibenzoate or bis(methoxybenzoate) was
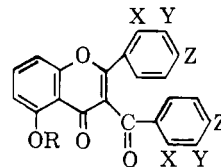
I.   X = Y = Z = R = H
II.   X = Y = Z = H;   R = COCH₃
III.   Y = Z = R = H;   X = CH₃O
IV.   Y = Z = H;   R = CH₃CO;   X = CH₃O
V.   X = Z = R = H;   Y = CH₃O
VI.   X = Z = H;   R = CH₃CO;   Y = CH₃O
VII.   X = Y = R = H;   Z = CH₃O
VIII.   X = Y = H;   R = CH₃CO;   Z = CH₃O

prepared from 2,6-dihydroxyacetophenone and excess acid chloride (benzoyl, *o*-methoxybenzoyl, *m*-methoxybenzoyl, or anisoyl chloride) in pyridine solution. The Baker-Venkataraman rearrangement was carried out with potassium carbonate in 2,6-lutidine or pyridine at reflux temperature, and the products (presumably a mixture of diaroylmethane, triaroylmethane, and possibly some flavone and 3-aroylflavone from thermal ring-closure) were isolated but not purified. Cyclization to the mixture of flavone and its 3-aroyl derivative was effected with sulfuric acid–acetic acid. The 3-aroylflavone was obtained as the major product by crystallization from ethyl acetate.

(1) From a portion of the Ph.D. thesis of Walter William Hanneman, The University of Nebraska, 1958.

(2) This investigation was supported in part by a research grant (E-1703) from the National Institute of Allergic and Infectious Diseases, Public Health Service, and in part by a grant from the University of Nebraska Research Council.

(3) Dow Chemical Fellow, 1956–57; Public Health Service Research Fellow of the National Institute of Dental Research, 1957–58.

(4) W. Baker, G. Flemans, and R. Winter, *J. Chem. Soc.*, 1560 (1949).

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(6) K. M. Gallagher, A. C. Hughes, M. O'Donnell, F. M. Philbin, and T. S. Wheeler, *J. Chem. Soc.*, 3777 (1953).