at 0°. The ether was evaporated in a stream of air, and a brown oil, which was insoluble in dilute sodium hydroxide solution, remained. The oil was mixed with 2% sodium hydroxide solution and refluxed for 30 min. The reaction mixture was acidified. The mixture was allowed to stand overnight, and the solid was crystallized from 50% ethanol; this gave 0.4 g. (20%) of product, m.p. 114–115°.

Anal. Calcd. for $C_8H_7BrO_3$: C, 41.56; H, 3.03; Br, 34.63. Found: C, 41.48; H, 3.07; Br, 34.41.

The **oxime of 5-bromoisovanillin** was prepared in quantitative yield by a standard procedure[17] and crystallized from water, m.p. 137.5–139°.

Anal. Calcd. for $C_8H_8BrNO_3$: N, 5.69. Found: N, 5.45.

2,6-Dibromoisovanillin.—6-Bromoisovanillin monohydrate (5 g., 0.0201 mole) was brominated in glacial acetic acid by a procedure similar to that used for the bromination of isovanillin; reaction time, 11 hr. (reflux temperature). The product was crystallized from glacial acetic acid; yield was 2.1 g. (34%), m.p. 160–161°.

Anal. Calcd. for $C_8H_6Br_2O_3$: C, 30.97; H, 1.94; Br, 51.61. Found: C, 31.01; H, 2.06; Br, 51.83.

As a derivative of the above aldehyde, **2,6-dibromoisovanillin triacetate** was prepared in nearly quantitative yield by treating a small sample of the aldehyde with an excess of acetic anhydride and 2 drops of concentrated sulfuric acid and crystallized from methanol, m.p. 145–146°.

Anal. Calcd. for $C_{14}H_{14}Br_2O_7$: C, 37.00; H, 3.08; Br, 35.24. Found: C, 37.05; H, 3.39; Br, 35.06.

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[17] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds" 3rd ed., J. Wiley and Sons, Inc., New York, 1948, p. 202.

Steric Effects in the Baeyer Ditolylethane Synthesis

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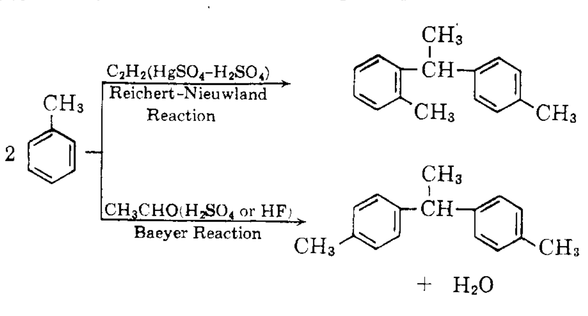
The effect of temperature on the isomer distribution of 1,1-ditolylethane from the Baeyer reaction has been examined. With paraldehyde as the alkylating agent, an increase in the ratio of 1,1-*p,p*-ditolylethane to other ditolylethane isomers is observed as the temperature is lowered. This temperature effect is not observed with acetaldehyde. The difference in the behavior between paraldehyde and acetaldehyde is believed to be due to differences in the steric requirements of the intermediate carbonium ions.

In an earlier publication[1] from these laboratories it was observed that the isomer distribution in 1,1-ditolylethane produced by the reaction of toluene in the Reichert-Nieuwland reaction with acetylene[2] differs greatly from that prepared in the Baeyer reaction with acetaldehyde.[3] The Reichert-Nieuwland product is predominantly 1,1-*o,p*-ditolylethane while the Baeyer product is predominantly 1,1-*p,p*-ditolylethane. Since the *para-para* isomer was desired as an intermediate, a study was made of the Baeyer reaction in an effort to increase the proportion of this isomer in the product.



Acetaldehyde and paraldehyde have been used interchangeably heretofore in our laboratories for the Baeyer reaction with no noticeable differences in yields or in isomeric compositions of the ditolylethane produced. This result was assumed to arise from a rapid acid-catalyzed depolymerization of paraldehyde to acetaldehyde to give the same alkylating species in both cases.[4] It has now been found that at very low reaction temperatures there is a significant difference in the isomeric compositions of the products from paraldehyde and from acetaldehyde. At the usual reaction temperature of 0°, the compositions of the products are identical, both containing about 78% of the *para-para* isomer. When the reaction temperature is lowered to −78°, the amount of the *para-para* isomer is increased to 87% in the paraldehyde reaction, but remains unchanged in the acetaldehyde reaction. The experiments at the lower temperatures were conducted with hydrofluoric acid as the catalyst to avoid the difficulty of freezing of sulfuric acid at these temperatures. Table I summarizes the results of these studies.

We feel that these results can be explained by considering the steric requirements of the carbonium ions involved in the reaction. The acid-

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[1] J. K. Dixon and K. W. Saunders, *Ind. Eng. Chem.*, **46**, 652 (1954).

[2] J. S. Reichert and J. A. Nieuwland, *Org. Syntheses*, **1**, 231 (1946).

[3] See O. Fischer, *Ber.*, **7**, 1193 (1874); O. Fischer and L. Castner, *J. prakt. Chem.*, [2], **82**, 280 (1910).

[4] The rate of depolymerization of paraldehyde in aqueous solutions of strong mineral acids is dependent on Hammett's acidity function H_0, with log k being linear in H_0 over the range of $H_0 = +1.4$ to -1.0 (R. P. Bell and A. H. Brown, *J. Chem. Soc.*, 774 (1954). If this linear relationship can be extended to 90% sulfuric acid with $H_0 = -8.27$, the first-order rate constant at 25° (the only temperature studied) is calculated to be 49,000 sec.$^{-1}$ with a half-reaction time of 1.4×10^{-5} sec. The rate in 90% hydrofluoric acid with $H_0 = -8.17$ (H. H. Hyman, M. Kilpatrick, and J. J. Katz, *J. Am. Chem. Soc.*, **79**, 3668 (1957), would be almost as rapid.

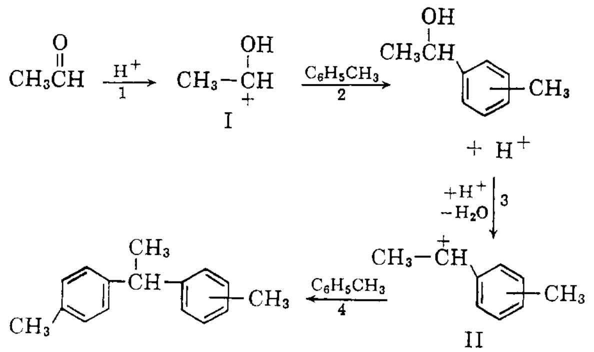
TABLE I

EFFECT OF TEMPERATURE ON THE ISOMER DISTRIBUTION OF 1,1-DITOLYLETHANE

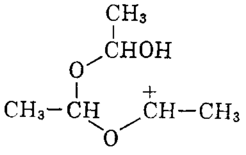
Experiment[a]	Alkylating[b] agent	Acid[c] catalyst	Reaction temperature, °C.	Conversion[d] of aldehyde, %	Ditolylethane isomer composition, %[e]				
					p,p	o,p		o,o + m,p[f]	o,m + m,m[g]
1	A	H_2SO_4	0	92	77.4		19.9		*ca.* 1
2	P	H_2SO_4	0	90	78.5		20.1		*ca.* 1
3	P	HF	0	100	78.6		21.4		*ca* .1
4	P	HF	0	95	75.3	9.5		13.1	2.1
5	P	HF	−38	88	82.3		17.7		<1
6	A	HF	−78	84	76.3	12.2		10.3	1.2
7	P	HF	−78	40	87.6		12.3		0
8	P	HF[h]	−78	48	86.9	6.5		6.5	0

[a] Yields of ditolylethane based on toluene consumed were in the range 88–94%. [b] A = acetaldehyde, P = paraldehyde. [c] 90–91% final hydrogen fluoride or sulfuric acid concentration. These concentrations are calculated values obtained by assuming a 100% reaction of the aldehyde and then assuming that the by-product water dilutes the original 100% hydrogen fluoride or 94.3% sulfuric acid to the 90–91% level. [d] Also yield of ditolylethane based on aldehyde charged. [e] Analyses by gas-liquid chromatography; see Experimental. The numbers placed between the columns designated *o,p* and *o,o* + *m,p* indicate results from a chromatography column unable to resolve this ternary mixture completely. Estimated error of analyses = 1% absolute. [f] Although this pair of isomers was not resolved on the gas-liquid chromatograph it is most probable that the major or perhaps the sole component is the *m,p*. The almost exclusive *para* orientation of the second alkylation step (see text) rules out the formation of very much *o,o* product. There is no reason to believe that the second alkylation of the *ortho* intermediate is less selectively *para* than is the second alkylation of the *para* intermediate. [g] This pair of isomers was unresolved. [h] 95.5% final hydrogen fluoride concentration. See *c* for method of calculation.

catalyzed Baeyer condensation of toluene and acetaldehyde is believed to proceed *via* the following sequence involving the alkylation of two molecules of toluene in consecutive steps.[5–7] Because of the steric requirements of the bulky methyltolylcarbonium ion II, the last step, alkylation of the second molecule of toluene, is highly selective and results in predominant *para* substitution. This, we believe, accounts for the fact that in the major portion of Baeyer ditolylethane, one of the tolyl groups is oriented *para* regardless of the orientation of the other tolyl group. Most of the *ortho* and *meta* substituted materials in the final ditolylethane are the result of alkylation of the first molecule of toluene by the smaller, less selective carbonium ion I, as shown in step 2.

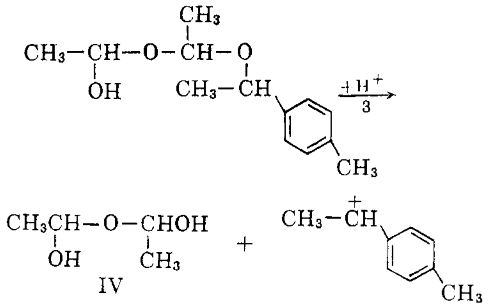


We believe that the increase in the amount of *para-para* isomer when the temperature is lowered in the paraldehyde reaction is the result of a marked decrease in the rate of depolymerization of paraldehyde to acetaldehyde.[8] The chief alkylating species in step 2 at low temperatures would therefore be the bulky carbonium ion of paraldehyde (III),[9] rather than the more compact carbonium



III

ion from acetaldehyde (I). The formation of some *ortho-para* and *meta-para* isomers even at −78° is thought to be due to alkylations by less hindered carbonium ion intermediates. These intermediates may be formed by the slow direct depolymerization of the paraldehyde but more certainly by the indirect depolymerization resulting from the reaction corresponding to step 3, wherein the dimer IV is



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[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, p. 348.

[6] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, 1944, p. 482.

[7] E. F. Pratt and L. Q. Green, *J. Am. Chem. Soc.*, **75**, 275 (1953).

[8] Unfortunately, there are no data available on the activation energy of the acid-catalyzed depolymerization of paraldehyde in aqueous solution to permit a calculation of the rate at the lower temperatures. Also, see ref. 9.

[9] See F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 960 (1957), for a discussion of the mechanism of acid catalysis for paraldehyde depolymerization. The low conversion of paraldehyde (40–50%) *vs.* that of acetaldehyde (84%) at −78° (see Table I) is consistent with both a low rate of depolymerization of paraldehyde and a difference in alkylating species in these experiments.

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.

Acknowledgment.—We gratefully acknowledge the assistance of Dr. R. Feinland in obtaining the gas-liquid chromatographic results and of Dr. A. T. Coscia in supplying the pure isomers of 1,1-ditolylethane for the calibrations.

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$[3.3.1.1^{3,7}]$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 absence 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.

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(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).