The reaction mixture was extracted with petroleum ether, the extract being treated with Norit. The solvent was removed *in vacuo*, and the residue was recrystallized from benzene-ethanol to yield 0.8 g. (14%) of III (X = H), m.p. and mixed m.p. 106°.

Run 36 was similar except that the reaction time was 12 hr.

Reaction of hydrazobenzene (V. X = Y = H) at low temperature. Run 41. A mixture of 1.8 g. (0.01 mole) of V (X = Y = H) and 2.1 g. (0.01 mole) of II was heated at 130° for 6 hr. The reaction mixture was dissolved in benzeneethanol, and was allowed to stand for several days in an ice box. The precipitate was filtered and recrystallized from water-ethanol to give 0.6 g. (66% yield based on Step 2) of I (X = Y = H), m.p. and mixed m.p. 68°.

Reaction of hydrazobenzene (V. X = Y = H) at high temperature. Run 43. One and eight-tenth grams (0.01 mole) of V (X = Y = H) was heated with 2.1 g. (0.01 mole) of II at 195° for 12 hr. The reaction mixture was treated similarly as in run 35, and the resulting mass was recrystallized from benzene-ethanol to give 0.5 g. (18%) of III (X = H), m.p. and mixed m.p. 106°.

Reaction of hydrazobenzene (V. X = Y = H) with benzil (IV). Run 51. A mixture of 1.8 g. (0.01 mole) of V (X = Y = H) and 2.1 g. (0.01 mole) of IV was heated at 195° for 12 hr., and the reaction mixture was treated with petroleum ether and Norit similarly as in run 35. Recrystallization of the resulting mass afforded 0.45 g. (16%) of III, m.p. and mixed m.p. 106°, and 0.5 g. (56% based on Step 2) of I (X = Y = H), m.p. and mixed m.p. 68°.

Condensation of aniline (VI. X = H) and N,N-dimethylp-phenylenediamine (VI. $X = (CH_3)_2N$) with benzil (IV). A mixture of 0.01 mole of amine (VI) and 2.1 g. (0.01 mole) of IV was heated at 130° for 6 hr. The reaction mixture for VI (X = H) was at once recrystallized from benzene-ethanol to give 1.2 g. (42%) of III (X = H), m.p. and mixed m.p. 106°.

The reaction mixture for VI (X = $(CH_3)_2N$) was treated with petroleum ether and Norit, and recrystallized from benzene-ethanol to yield 2.0 g. (61%) of III (X = $(CH_3)_2N$), m.p. and mixed m.p. 140°.

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[CONTRIBUTION FROM THE PLASTICS & RESINS DIVISION STAMFORD RESEARCH LABORATORIES, AMERICAN CYANAMID CO.]

The Synthesis of 2,2-Ditolylpropane from α ,p-Dimethylstyrene¹

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2,2-Di(*p*-tolyl)propane has been obtained in high yields for the first time by the alkylation of toluene with 2-chloro-2-(*p*-tolyl)propane, a derivative of α ,*p*-dimethylstyrene. Complexes of aluminum chloride with nitromethane or nitrobenzene were found to be specific catalysts for this reaction. Other Lewis acids and complexes were found to favor the competing reaction—*i.e.*, the formation of 1,3,3,6-tetramethyl-1-(*p*-tolyl)indane and other dimers of α ,*p*-dimethylstyrene.

1,1-Diarylalkanes are readily prepared by the acid catalyzed alkylation of aromatic compounds with aldehydes² or with styrenes.³ On the other hand, alkylations leading to non-terminal diaryl-alkanes which employ simple ketones or α -methyl-styrenes, have been limited to active aromatic compounds such as phenols⁴ and aniline.⁵ Toluene, for example, has not been alkylated in high yields with acetone or with α -methylstyrenes.⁶ The al-kylating agents appear to condense with themselves rather than with toluene under the conditions investigated.

The present work is a study of conditions which led to the successful alkylation of toluene by a derivative of α ,*p*-dimethylstyrene, 2-chloro-2-(*p*tolyl) propane to give 2,2-ditolylpropane in high yield.

DISCUSSION OF EXPERIMENTAL RESULTS

As early as 1890 Spiller and co-workers alkylated toluene with styrene in the presence of sulfuric acid to give a 1,1-diarylalkane.³ We have found that when this reaction is carried out using α ,p-dimethylstyrene (DMS) in place of the styrene, the major product (80%) is the dimer, [1,3,3,6tetramethyl-1-(p-tolyl)]indane.⁷ Only a small quantity (4%) of the desired product, 2,2-ditolylpropane (DTP) is obtained. The course for these reactions is shown below. Apparently the carbonium ion derived from α ,p-dimethylstyrene (in contrast to the styryl carbonium ion) attacks the double bond of another α ,p-dimethylstyrene molecule in preference to the toluene ring, $k_1 < < k_2 + (k_3, k_4, \text{ or } k_5)$.

In an effort to suppress dimerization other reaction conditions and catalysts were studied.

⁽¹⁾ Presented at the 135th Meeting of the American Chemical Society, Boston, Massachusetts, April 10, 1959.

⁽²⁾⁽a) A. Baeyer, Ber., 6, 220 (1873); (b) O. Fischer, Ber. 7, 1193 (1874).

⁽³⁾⁽a) G. Kraemer, A. Spiller, and P. Eberhardt, *Ber.*, 23, 3269 (1890); (b) A. Spiller and W. Schade, *Ber.*, 65B, 1686 (1932).

⁽⁴⁾⁽a) Th. Zincke and M. Grueters, Ann., 343, 85 (1905);
(b) J. B. Niederl, J. Am. Chem. Soc., 50, 2230 (1928);
(c) J. B. Niederl and R. Casty, Monatsh., 51, 86 (1929).

⁽⁵⁾ J. von Braun, Ann., 472, 1 (1929).

⁽⁶⁾ A. B. Bakalar in U.S. Pat. 2,455,643 (Dec. 7, 1948) reports the isolation of a product of molecular weight 224 (corresponds to 2,2-ditolylpropane) by the condensation of toluene with acetone in the presence of sulfuric acid. However, several independent attempts in these laboratories to condense acetone with toluene using a variety of acid catalysts, including sulfuric acid, were unsuccessful.

⁽⁷⁾ For a discussion of the acid catalyzed dimerization of the styrene see A. Muller, J. Org. Chem., 17, 1077 (1952), and J. C. Petropoulos and J. J. Fisher, J. Am. Chem. Soc., 80, 1938 (1958).

THE REACTION OF α , p-DIMETHYLSTYRENE WITH TOLDENE IN THE PRESENCE OF ACID CATALYSTS							
	Weight Ratio	Mole Ratio	Conditions		% Yield Products		
Catalyst	Catalyst: DMS	Toluene: DMS	Time, Hrs.	Temp.	DTP	Dimers	Residue
H_2SO_4 97%	0.5	70	2	5	4	80	6
$H_{2}SO_{4} = 70\%$	9	60	8	100	1	71	
RSO ₃ H ^a	1	30	3.5	27	1	80,	20
H_2SO_4 97%	20	300	6	0	35	59	

TABLE I

^a Mixture of methane, ethane, and propane sulfonic acids manufactured by Indoil Co.

The Reaction of α , p-Dimethylstyrene and 2-Chloro-2-(p-tolyl) propane⁹ with Toluene in the Presence of Lewis ACIDS AT 0°

TABLE II

	Alkylating	Mole Ratio Cat.: Alkylating	Mole Ratio Toluene: Alkylating	Product		
Catalyst	Agent	Agent	Agent	DTP	Dimers	Other ^a
AlCl ₃	DMS	0.1	1	0.1	26	74
AlCl ₃ CH ₃ NO ₂	DMS	0.2^{b}	30	4	54	40
AlCl ₃ ·HCl·3C ₇ H ₈	Chloropropane	0.06	9	40°	46°	
AlCl ₃ ·HCl·3C ₇ H	Chloropropane	0.25	115	48	59	
SnCl.	Chloropropane	0.08	14	0	37	18 ^d
TiCl	Chloropropane	0.08	14	2	94	_
GaCl₃	Chloropropane	0.08	33	10.5	68.5	

^o DMS oligomers, b.p. 200° at 2 mm. ^b Based on AlCl₃. ^c Calculated from Ref. 8. ^d Also 45% unreacted 2-chloro-2-(ptolyl)propane.



The data are summarized in Table I. Higher yields of 2,2-ditolylpropane were obtained only in one run, wherein the α , *p*-dimethylstyrene was added dropwise to a sulfuric acid dispersion in a very large excess of toluene, over an extended period of time.

The crude products were distilled and then identified by infrared and mass spectrographic analyses. The residues failed to distill below 200° at 2 mm. Infrared analyses suggested that these viscous oils were oligomers of α , *p*-dimethylstyrene.

Attention was directed to the use of Lewis acids. When aluminum chloride was used as a catalyst in the reaction of α , *p*-dimethylstyrene with toluene, the major product was a nondistillable viscous oil. The oil had the infrared characteristics expected of α , *p*-dimethylstyrene oligomers. Some dimers were formed, but only negligible amounts of 2,2-ditolylpropane were isolated. When the aluminum chloride was solubilized in the toluene by the addition of two mole equivalents of nitromethane, a smaller amount of non-volatile products was obtained but the yield of 2.2-ditolylpropane was increased to only 4%.

Hiatt⁸ reported a method for the preparation of 2,2-ditolylpropane starting with 2-chloro-2-(p-tolyl) propane a derivative of α , p-dimethylstyrene. By adding this tertiary chloride to a toluene dispersion of an oily catalyst consisting of a complex of aluminum chloride, hydrogen chloride and toluene, this worker obtained approximately equimolar yields of 2,2-ditolylpropane and the indane dimer of α , p-dimethylstyrene. The reaction paths are visualized below:



A high dilution modification of this procedure carried out as in the last run of Table I failed to produce any significant increase in the alkylation of toluene.

In other attempts to promote the alkylation reaction and to suppress dimerization, toluene soluble catalysts such as stannic chloride, titanium tetrachloride, and gallium chloride were employed under reaction conditions essentially similar to those of Hiatt.⁸ In each of these runs dimerization occurred in preference to the alkylation of the toluene. The data from the Lewis acid runs are compiled in Table II.

Because nitromethane lowers the catalytic activity of aluminum chloride¹⁰ while at the same time solubilizing it in toluene, an aluminum chloridenitromethane complex was tested as catalyst in the reaction of 2-chloro-2-(p-tolyl)propane with toluene. Using the conditions of Hiatt⁸ a surprisingly high yield (80%) of 2,2-ditolylpropane was obtained. Similar results were obtained with a toluene solution of an aluminum chloride-nitrobenzene complex as catalyst, dimer formation falling as low as 5%.

Other mixtures of Lewis acids with nitromethane were examined under the same conditions. Titanium tetrachloride promoted the formation of an insignificant amount of 2,2-ditolylpropane whereas gallium trichloride, in combination with nitromethane, afforded 2,2-ditolylpropane in modest yields (32%). Boron trifluoride coupled with nitromethane appeared to be too weak a catalyst to promote alkylation since after two hours of reaction only a small amount of the chloropropane had reacted. Because some of the boron trifluoride might have been swept out of the reactor (all reactions were maintained under an atmosphere of dry hydrogen chloride) additional but unmeasured quantities of boron trifluoride were fed into the reaction flask. Consequently, it is not certain whether reaction was caused by boron trifluoride alone or by the nitromethane complex. This run also gave a low yield of 2,2-ditolylpropane. The results are compiled in Table III.

The data indicate that nitromethane and nitrobenzene complexes of aluminum chloride are specific catalysts for the alkylation of toluene by 2-chloro-2-(p-tolyl)propane. Apparently these catalysts function without promoting dehydrohalogenation and dimerization of the resultant dimethyl-

TABLE III

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TODUENE AT U IN THE FRESENC.	EOF	f Nitro	Сомре	DUNDS

	% Yield of Products			
Catalyst	DTP	Dimers		
CH ₃ NO ₂ ·AlCl ₃	81	12		
C ₆ H ₅ NO ₂ ·AlCl ₃	81	5.5		
$CH_{3}NO_{2} + GaCl_{3}$	32.5	57.5		
$CH_{3}NO_{2} + TiCL$	0.5	68ª		
$CH_3NO_2 + BF_3$	10	82		

^a 13% residual oligomers were also obtained.

styrene. With gallium chloride, the addition of nitro compounds does not appreciably alter the course of reaction; dehydrohalogenation with subsequent dimerization is still preferred. The observed difference between the two metal halides suggests that aluminum has a greater affinity for oxygen than for chlorine, whereas the reverse situation may exist with gallium.¹¹

In the case of boron trifluoride, the nitro compound is believed to be so tightly bound to the boron trifluoride that the complex is too weak a catalyst to promote alkylation or dimerization, the actual species in our experiment being excess boron trifluoride.

With respect to isomer distribution during the alkylation of toluene with 2-chloro-2-(p-tolyl)-propane, it is interesting to note that the reaction proceeds with a high degree of selectivity for the *para* position. No more than 5% of the alkylation occurred at the *meta* position and no evidence could be found for alkylation at the *ortho* position. This was true whether nitro compounds were present with the aluminum chloride or not.

The reaction course may be contrasted with the benzylation of toluene which affords a significant amount of meta isomer as well as ortho isomer (41%)ortho, 19.4% meta and 39.5% para).12 The difference in selectivity is perhaps best explained by the additional stabilization given the benzyl carbonium ion or intermediate by the p-methyl substituent and the two α -methyl groups of the 2chloro-2-(p-tolyl)propane. If the para-meta ratio observed in this study is fitted in the typical log p_f vs. S_f plots compiled by H. C. Brown and coworkers¹³ one obtains S_f of 1.56 for the α, α, p trimethylbenzyl intermediate. This intermediate is more selective than the nitronium ion $(S_f =$ 1.37) and significantly more selective than that reported for the t-butylation of toluene $(S_t = 1.10)$ by t-butyl chloride catalyzed by an aluminum chloride-nitrobenzene complex.14

⁽⁸⁾ R. R. Hiatt, U. S. Pat. 2,719,871 (Oct. 4, 1955).

⁽⁹⁾ It was desirable to establish some definite evidence for the existence of 2-chloro-2(p-tolyl)propane as the reaction intermediate, and to investigate its stability. Although this compound has been mentioned in the literature—e.g., H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, J. Am. Chem. Soc., 79, 1897 (1957)—no specific physical properties have been reported. The chloropropane was found to distill at relatively low temperatures without decomposition. A distilled sample was characterized by its chlorine analysis and infrared spectrum (see experimental section). While not stable for any length of time at room temperature, dilute solutions in toluene were found to be stable for weeks if stored at 5°C. under an atmosphere of hydrogen chloride.

⁽¹⁰⁾ L. Schmerling, Ind. Eng. Chem., 40, 2072 (1948) has shown that nitroparaffins form 1:1 addition compounds with aluminum chloride and these are milder catalysts. R. E. VanDyke and H. E. Crawford, J. Am. Chem. Soc., 73, 2018 (1951) describe the aluminum chloride-nitrobenzene complex as a 1:1 addition compound.

⁽¹¹⁾ This has been previously suggested by F. R. Jensen and H. C. Brown, J. Am. Chem. Soc., 80, 3039 (1958).

⁽¹²⁾ H. C. Brown and B. A. Bolto, J. Am. Chem. Soc., 81, 3320 (1959).

⁽¹³⁾ See L. Stock and H. C. Brown, J. Am. Chem. Soc., 81, 3323 (1959) for $\log p_f$ data on electrophilic substitution reactions of toluene.

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EXPERIMENTAL^{1b}

Reactants. α , p-Dimethyl styrene (Newport Industries) was purified by distillation through a Todd apparatus, b.p. 71° at 10 mm.

2-Chloro-2-(p-tolyl) propane. Toluene (100 ml.) was placed in a three neck round bottom flask equipped with stirrer, thermometer and dropping funnel, and gaseous hydrogen chloride was led in. When the toluene was saturated, a solution of α, p -dimethylstyrene (40 g.) in 40 ml. of toluene was added dropwise with stirring at such a rate that the temperature did not exceed 10° (1 hr. and 10 min.). The resultant solution was kept at 0° under excess hydrogen chloride until used in alkylation experiments.

In one alkylation, a portion of the solution was separated and the excess hydrogen chloride and toluene were stripped *in vacuo* at 25°. Upon further heating 2-chloro-2-(p-tolyl)propane distilled at 60° and 1 mm. Microanalyses were run immediately, as the product fumed in air.

Anal. Calcd. for $C_{10}H_{13}$ Cl: Cl, 21.05. Found: Cl, 21.28. Infrared on the sample displayed peaks at 820, 1095, 1130, 1270, 1373, 1390 and 1517 cm.⁻¹ among others. There were no —OH absorptions and no 890 cm.⁻¹ band (vinyl absorption in α , p-dimethylstyrene).

Catalysts. Commercially available reagent grade Lewis acids were employed except for gallium chloride which was prepared as follows: A known amount of gallium metal was added to a flask equipped with gas inlet thermometer and adapter leading to a long 3/4" pyrex tube. This tube, in turn, was connected by adapter to a 3 neck round bottom flask containing toluene. The metal was heated slowly to 190° under a stream of hydrogen chloride gas. As the gallium reacted, needles of gallium chloride appeared in the connecting tube. When all the gallium had reacted the hydrogen chloride gas was replaced by a stream of nitrogen and the system was purged. The gallium chloride was then sublimed through the tube and into the vessel of toluene. The catalyst solution was used directly in the alkylation experiments.

Complexing agents. Commercial nitrobenzene and nitromethane were purified by distillation.

Alkylations. All alkylations were carried out in three neck round bottomed flasks equipped with stirrer, thermometer, pressure equalized dropping funnel, and in experiments where hydrogen chloride gas was employed, gas inlet and outlet. Toluene was used both as solvent as well as reactant. Unless otherwise noted, a 9- to 15-mole excess was employed. The catalyst was added to the toluene and the resultant mixture maintained at the desired temperature while the alkylating agent $(\alpha, p-\text{dimethylstyrene} \text{ or } 2-\text{chloro-}2-(p$ tolyl)propane) was added dropwise over a 15 to 60-min. period, unless indicated otherwise. To obtain a high speed of stirring in the two runs at high dilution, a Palo 5,000 r.p.m. motor and creased flask were employed. Following is the procedure using an aluminum chloride-nitromethane complex as catalyst (the work-up is typical of all the alkylation experiments): To the reactor described above was added 2000 ml. of toluene, 4 g. of aluminum chloride, and 5 ml. of nitromethane. The resultant clear, orange solution was agitated, saturated with hydrogen chloride and cooled to 0°. The solution of 2-chloro-2-(p-tolyl)propane in toluene

(15) All melting points are uncorrected.

was now added in 20 min. with vigorous stirring under a steady stream of hydrogen chloride gas. The mixture was stirred an additional 40 min. under dry hydrogen chloride at 0°. Cold water was then added with stirring at such a rate that the temperature did not rise above 30°. The organic layer was separated, washed with 10% sodium hydroxide solution and with water and was dried over anhydrous potassium carbonate. The toluene and nitromethane were removed under reduced pressure. The alkylated product was distilled at 135–140° at 2 mm. and crystallized upon cooling below 70°. The yield was 60 g. There was no residue. Although the p,p'-isomer of 2,2-ditolylpropane boils at 183° and 20 mm., this mixture (~7% by weight of dimers) was not separated by distillation.

The infrared absorption bands at 820, 1087, 1370, 1390, and 1515 cm.⁻¹ were used to identify p,p'-ditolylpropane. The absence of appreciable absorption at 1310, 1320, and 1515 cm.⁻¹ indicated the presence of only small amounts of indane dimer. The total dimer content (6.5 mole %) and 2,2-ditolylpropane content (93.5 mole %) were determined by mass spectrographic analysis. This is an 81% yield of 2,2-ditolylpropane and 11% of dimers.

Isomer distribution of alkylated products. Meta isomers of 2,2-ditolylpropane were detected by absorption at 710 and 790 cm.⁻¹ in the infrared. The extent of absorption at these wave numbers remained essentially constant in the runs where aluminum chloride was used alone or in conjunction with nitro compounds. From the absorption, the amount of meta alkylation was estimated to be around 2% to 5% of the para. In the run using aluminum chloride-nitrobenzene complex as catalyst, vapor phase chromatography on an Apiezon L column separated a mixture consisting of 4.8 parts of α, p -dimethylstyrene dimer, 4.5 parts of m, p'ditolylpropane and 90.7 parts of p, p'-ditolylpropane. The identity of the m, p'-isomer was established by comparison in the infrared with a known standard.

2,2-Di(p-tolyl) propane. A crude sample prepared as described above was recrystallized three times from methanol to give large plates, m.p. 80°, reported⁸ m.p. 78-79°. Further characterization involved the preparation of the dibasic acid and ester derivatives as follows.

2,2-Bis(p-carboxyphenyl) propane. To a refluxing mixture of 10 g. of crude 2,2-ditolylpropane, 250 ml. of acetic acid, 300 ml. of water and 50 ml. of sulfuric acid, 70 g. of chromic acid were added *cautiously* in small portions over a 10-min. period. After 16 hr. reflux the mixture was diluted with water and filtered to remove 8 g. (63%) of white crystalline product. Two recrystallizations from 90% acetic acid gave crystals, m.p. 313-315°, reported¹⁶ m.p. 315-316°.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 71.83; H, 5.63; neut. equiv., 142. Found: C, 72.04; H, 5.79; neut. equiv., 141.8.

The crude acid was dissolved in methanol and the solution saturated with hydrogen chloride gas. The crystals of methyl ester which separated during overnight standing were recrystallized three times from methanol, m.p. 107-107.5°, reported m.p. $101-102^{\circ}$.¹⁶

Anal. Calcd. for C₁₉H₂₀O₄: C, 73.08; H, 6.41. Found: C, 73.22; H, 6.54.

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(16) C. E. Schweitzer, U.S. Pat. 2,794,822 (June 4, 1957).

⁽¹⁴⁾ M. J. Schlatter and R. D. Clark, J. Am. Chem. Soc., 75, 361 (1953). H. C. Brown and C. R. Smoot, J. Am. Chem. Soc., 78, 6255 (1956) report a S_f of 0.624 for the *t*-butylation of toluene with *t*-butyl bromide catalyzed by gallium tribromide. The latter value is in some doubt, however, due to difficulties in temperature control during the alkylation [private communication with Professor H. C. Brown. See also S. U. Choi and H. C. Brown, J. Am. Chem. Soc., 81, 3315 (1959) footnote 10].