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A NEW SYNTHESIS FOR 3-CHLORO-
2,2',4,4',6,6'-HEXANITROBIPHENYL,
PIPICL (U)

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A NEW SYNTHESIS FOR
3-CHLORO-2,2',4,4',6,6'-HEXANITROBIPHENYL, PIPICL (U)

by

J. C. Dacons and M. J. Kamlet

ABSTRACT: 3-Chloro-2,2',4,4',6,6'-hexanitrobiphenyl, PIPICL, has been prepared by a three-step procedure from picryl chloride and m-chloro- or m-bromoanisole. The first step involved the formation of m-picrylanisole by means of a mixed Ullmann reaction. Using 90% nitric acid and 30% oleum, the picrylanisole was nitrated to 3-methoxy-2,2',4,4',6,6'-hexanitrobiphenyl which was in turn converted to PIPICL by treatment with pyridine and phosphorus oxychloride. When m-bromoanisole was used in the Ullmann reaction, the overall yield for the three steps was about 59%. The use of m-chloroanisole resulted in a lower yield in the first step and an overall yield of about 52%. Several variations in procedure are given for the preparation of m-picrylanisole. (U)

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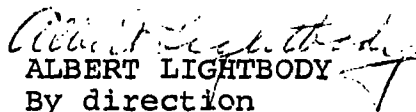
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This report describes a much simplified procedure for the preparation of 3-chloro-2,2',4,4',6,6'-hexanitrobiphenyl (PIPICL), which is used as a starting material in the preparation of 2,2',2'',2''',4,4',4'',4''',6,6',6'',6'''-dodecanitroquaterphenyl, DODECA, and azobis 2,2',4,4',6,6'-hexanitrobiphenyl, ABH. Both of the latter compounds are potentially useful heat resistant high explosives. This work was done under Task RMMO 62058/2121/F008 08 11 Problem 007, Desensitization of Explosives, and in part under Task R 360 FR 105/R011 01 01 Problem 044, High Energy Compounds.

J. A. DARE
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ALBERT LIGHTBODY
By direction

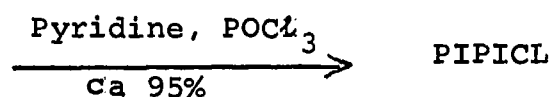
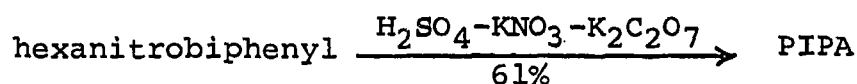
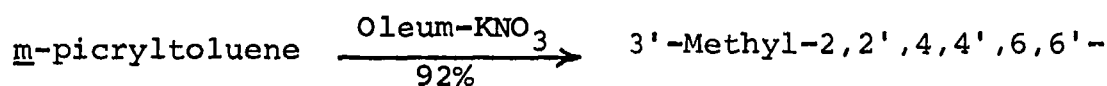
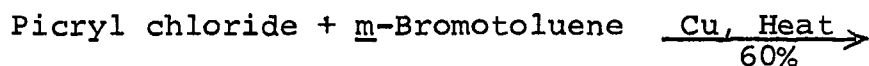
CONFIDENTIAL
NOLTR 65-215

TABLE OF CONTENTS

	Page
INTRODUCTION	1
RESULTS AND DISCUSSION	2
EXPERIMENTAL	
Preparation of 3-Methoxy-2',4',6'-trinitrobiphenyl; <u>m</u> -Picrylanisole	7
Preparation of 3-Methoxy-2,2',4,4',6,6'- hexanitrobiphenyl	9
Preparation of 3-Chloro-2,2',4,4',6,6'- hexanitrobiphenyl; PIPICL	11
REFERENCES	13

INTRODUCTION

The compound 3-chloro-2,2',4,4',6,6'-hexanitrobiphenyl (m-picrylpicryl chloride, PIPICL) was first prepared by Dacons, Adolph and Kamlet (1) as an intermediate in the conversion of 3-hydroxy-2,2',4,4',6,6'-hexanitrobiphenyl (m-picrylpicric acid, PIPA) to the corresponding 3-amino derivative. Although the yield was very good, this was but one step in a four-step synthesis; picrylpicric acid is available only through a three-step procedure starting with picryl chloride and m-bromotoluene.

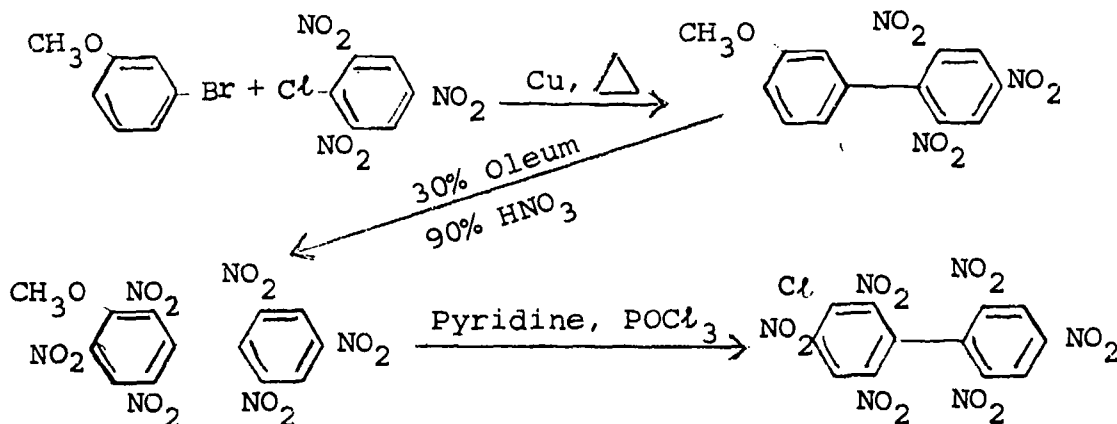


The second and third steps in this sequence were time-consuming, both requiring extended periods at elevated temperatures, and the overall yield from the four-step process was about 31%.

When it was discovered that PIPICL could be converted to 2,2',2'',2''',4,4',4'',4''',6,6',6'',6'''-dodecanitroquaterphenyl, DODECA, or to azobis 2,2',4,4',6,6'-hexanitrobiphenyl ABH,* a search for an easier synthesis was undertaken. Our prime purpose was to find a procedure in which the time-consuming steps could be simplified or eliminated. Unfortunately, a 3-halophenol could not be substituted for m-bromotoluene in step one as phenolic compounds undergo mainly dehalogenation and ether formation reactions when subjected to the conditions of the Ullmann synthesis (2,3). However, Johnson and Adolph (4) had found that on successively treating 1,3-dimethoxy-2,4,6-trinitrobenzene with pyridine and phosphorus oxychloride, it was

* These compounds have shown considerable promise as heat resistant explosives and will be the subjects of future reports from this Laboratory.

converted to 1,3-dichloro-2,4,6-trinitrobenzene in good yield. With this in mind, it seemed reasonable to believe that 3-methoxy-2,2',4,4',6,6'-hexanitrobiphenyl could be converted to PIPICL in a similar manner. Substituting *m*-bromoanisole for *m*-bromotoluene in the first step and nitrating the resulting *m*-picrylanisole to the hexanitro stage seemed a likely route to the desired 3-methoxy derivative.



This line of attack proved quite rewarding in that not only was the oxidation step completely eliminated, but the conditions required in the nitration step were much milder than those in the previous procedure. As a result, the total reaction time was reduced by a factor greater than seven and the overall yield was approximately doubled. The details of this synthesis are treated in the present report.

RESULTS AND DISCUSSION

3-Methoxy-2',4',6'-trinitrobiphenyl; *m*-Picrylanisole.

This compound is most conveniently prepared from a picryl halide and a *m*-haloanisole via the Ullmann reaction. An excess of the haloanisole favors the formation of the unsymmetrical product over the normal product, 2,2',4,4',6,6'-hexanitrobiphenyl, from two molecules of the picryl halide. The temperature is kept low enough that the haloanisole has little tendency to react with itself. It is likely that picryl iodide or picryl bromide could be used in this reaction as well as picryl chloride, and it may be that the greater reactivity of the halogens in these compounds (5) would facilitate the reaction. However, due to the ready availability of picryl chloride, it was used exclusively in this work. Both *m*-chloroanisole and *m*-bromoanisole were used as the second reactant. The latter gave about 17% greater yields and the crude reaction products melted slightly higher. For the most part, the reaction

temperatures were 170-180°C, but in one successful run with m-bromoanisole a reaction temperature of approximately 160°C was maintained.

The ratio of the bromoanisole to picryl chloride was varied from 200% excess to 700% excess without any noticeable effect on the yield or quality of product. The successful runs with m-chloroanisole were all made using a 700% excess of this reagent. A 100% excess of copper was used throughout, and all yields of picrylanisole are based on picryl chloride. The large excesses of anisoles not only served to enhance the formation of the unsymmetrical product, but also eliminated the need for additional solvents in the reaction mixtures, and the more dilute solutions gave more mobile slurries which made stirring and handling easier. Moreover, the temperature variations caused by the exothermic nature of the reaction were more easily controlled. On the other hand, since excess haloanisoles introduce difficulties into the isolation of the picrylanisole, they must be removed from the reaction mixtures before it is isolated, and product isolation is less time-consuming from the more concentrated solutions.

Three variations in procedure were used in combining the reactants, and again there were no apparent differences in yields or quality of products. However, the fact that the three methods were about equally successful allows one to make a selection based on equipment available, personal choice, etc. Our first method involved the conventional gradual addition of copper bronze to a stirred solution of the organic reactants. This is very convenient when done in the laboratory, but may present problems on a larger scale where it is necessary to operate remotely. In a variation of this procedure, involving the addition of solid picryl chloride to a stirred slurry of copper in the haloanisole, the reaction appeared to be a bit sluggish. Moreover, it would pose the same problems on a larger scale as the conventional method, and would probably increase the hazard involved. A further modification involved the addition of a solution of picryl chloride in the anisole to a stirred slurry of copper bronze in the anisole. The only problem here is that unless the ratio of haloanisole to picryl chloride was kept high, precipitation was likely to occur in the addition funnel.

The product could be precipitated as an oil containing considerable amounts of haloanisole and by-products of the reaction by the addition of n-hexane or carbon tetrachloride. However, to obtain reasonably pure m-picryl anisole, several extractions and recrystallizations were required. Although yields as high as 75% were isolated in this manner, the

procedure was too involved to be practical. Small amounts of either the chloroanisole or the bromoanisole made the product very difficult to crystallize.

As mentioned above, however, the isolation of m-picrylanisole from the reaction mixture can be simplified appreciable if the excess haloanisoles are first removed. The excess haloanisoles can be removed by steam distillation, vacuum distillation or "azeotropic distillation" with water. Steam distillation proved to be the fastest, but more complete recovery of the haloanisoles was realized using the other two methods. The low recovery was due in large measure to the lack of an efficient condenser in the steam distillation apparatus.** During steam distillation, the mixture was stirred vigorously and as the organic solvent was removed, the product separated as a finely divided solid. This was recovered by filtration or decantation and digested in a volume of boiling methanol insufficient to take it into solution. The suspension was then cooled and filtered giving a light brown crystalline product which usually melted above 114°C. However, in one case when m-chloroanisole was used, the product melted at 110-114°C. Several of these crude products, including the low melting one, gave good yields in the nitration step without further purification.

In three runs (two 0.1 molar and one 0.2 molar) using m-bromoanisole and the steam distillation procedure for isolation, the average yield of crude product melting above 114°C was 75.4%. In three 0.1 molar runs with m-chloroanisole using the same isolation procedure, the average yield of crude product melting above 110°C was 62%. Two 0.63 molar runs using m-bromoanisole, one where the excess solvent was removed by vacuum distillation and the other by "azeotropic distillation", gave yields of 69.5% and 72.2%, respectively, of recrystallized product melting at 118-120°C.

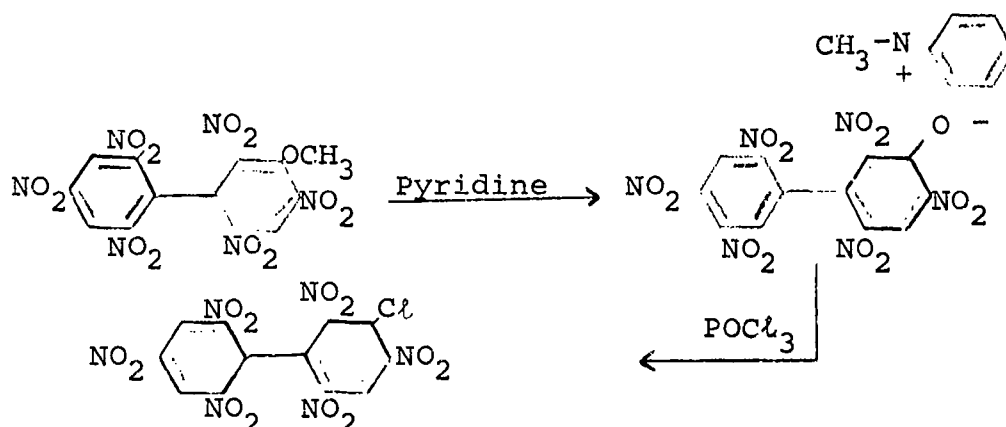
Thin-layer chromatographic examination of several of the residues after the picrylanisole had been removed indicated that the main by-products were 1,3,5-trinitrobenzene and 2,2',4,4',6,6'-hexanitrobiphenyl. There were also traces of picryl chloride and unidentified materials which remained at the origin on the silica gel plates when developed with benzene or benzene-n-hexane mixtures. The formation of 1,3,5-trinitrobenzene was

** The cost of the haloanisoles make their recovery necessary. When recovered by steam distillation or "azeotropic distillation", they must be refractionated before they can be reused. When the recovery is by vacuum distillation, the necessary fractionation can be done during the recovery.

probably the result of the dehalogenation of picryl chloride caused by the presence of small amounts of water or other active hydrogen compounds during the reaction (2). Efforts were made to dry and purify all reactants thoroughly before use and it seems likely that the compounds which promoted dehalogenation were formed during the reaction. This may have been the result of a small amount of oxidation-reduction taking place as a side reaction. The hexanitrobiphenyl was formed by the reaction of picryl chloride with itself, and its yield was apparently greater when *m*-chloroanisole was used. This was probably due to a slightly lesser tendency of the chloroanisole to react in the formation of the unsymmetrical product.

3-Methoxy-2,2',4,4',6,6'-hexanitrobiphenyl. Whereas the nitration of 3-methyl-2',4',6'-trinitrobiphenyl required treatment with nitrate-oleum mixtures at 135°C for 20 hours, good yields of 3-methoxy-2,2',4,4',6,6'-hexanitrobiphenyl were obtained from *m*-picrylanisole in shorter times and under milder conditions. Solid *m*-picrylanisole was added to a cooled mixture of 90% nitric acid and 30% oleum then warmed gently to 94-95°C (mild reflux) and held at that temperature for 1.5-2 hours. The product was isolated by either filtering the reaction mixture or drowning it in crushed ice. After thoroughly washing and drying, about a 90% yield of crude product melting in the region 175-185°C was obtained. When the crude product was recrystallized from acetone-*n*-hexane, acetone-methanol or acetone-carbon tetrachloride, the yields in two crops were about 85% of a cream colored crystalline product melting in the region of 190-195°C. Thin-layer chromatographic examination of the lower melting crops showed the presence of a small amount of a by-product which remained at the origin on silica gel plates when developed with benzene. The methoxyhexanitrobiphenyl showed an R_f value of 0.37 on the same plates. The contaminant was isolated by fractional crystallization and identified as 3-hydroxy-2,2',4,4',6,6'-hexanitrobiphenyl. This compound was probably formed as a result of oxidation and/or hydrolysis of the methoxyl group. However, this does not create a problem as the hydroxy derivative is readily converted to PIPICL by the treatment with pyridine and phosphorus oxychloride in the final step.

3-Chloro-2,2',4,4',6,6'-hexanitrobiphenyl; PIPICL. 3-Methoxy-2,2',4,4',6,6'-hexanitrobiphenyl is readily converted to PIPICL by successive treatments with pyridine and phosphorus oxychloride. The reaction probably proceeds via the methyl pyridinium salt of PIPA (4).



The preparation of the salt may be carried out in benzene solutions of pyridine either at room temperature or at reflux. At reflux, the reaction is complete in one hour, whereas several hours are required at room temperature. Since the reaction requires no attention at room temperature, it may be more conveniently done in this manner. On the other hand, it may be desirable to get it done as quickly as possible and in this case the reaction would be carried out at reflux. In either case, the yield is essentially quantitative and the choice may be made according to the situation at hand. For the conversion to PIPICL, the salt is dissolved in phosphorus oxychloride and heated on the steam bath for one hour. The product is recovered by slowly drowning in a large volume of crushed ice and water. The reaction of the excess phosphorus oxychloride with water is exothermic but slow at low temperatures. Our best results were obtained when the drowning temperature was kept between 40°C and 70°C. In order to accomplish this, the drownings were started in small volumes of water and the desired temperature range maintained by alternately adding small quantities of the reaction mixtures and ice. The products normally precipitated as waxy solids which on vigorous stirring solidified into dense spherical particles one to two millimeters in diameter. These usually occluded water and hydrochloric acid which could not be removed by drying. However, good results were obtained by the recrystallization of the damp or air dried products from acetone-hexane mixtures. The product was dissolved in acetone, and *n*-hexane was added until the solution clouded and an aqueous layer separated. The aqueous layer was then removed and the solution concentrated to precipitate the product. Two crops were taken in this manner and the yields were nearly quantitative. The products melted in the range 186-187°C and on slow heating, resolidified and melted again at 211-212°C. By grinding samples of the products under water and testing with Alkacid test paper,

CONFIDENTIAL
NOLTR 65-215

some of the products isolated in this manner (mainly second crops) were found to contain traces of acid. For some uses, e.g., the preparation of ABH, this is not objectionable. However, for use in Ullmann reactions, e.g., the preparation of DODECA, is essential that even traces of active hydrogen compounds be removed. The traces of acids can be removed by dissolving the samples in ethyl acetate, washing with 5% sodium bicarbonate, then with water and recrystallizing from ethyl acetate-n-hexane solution.

EXPERIMENTAL

Preparation of 3-Methoxy-2', 4', 6'-trinitrobiphenyl; m-Picrylanisole. Four procedures for the preparation of this compound are given below. These involve two methods for combining the reactants and basically three methods for the isolation of the products. It should be borne in mind that still other combinations of the various reaction and isolation steps can be used without marked effects on the quality or yield of the product.

Procedure I. To 70 ml of m-bromoanisole in a 300 ml 3-neck round bottom flask fitted with thermometer, mechanical stirrer, condenser and addition funnel was added 50.4 g (0.794 moles) of copper bronze.*** The slurry was heated to 160°C with vigorous stirring on an oil bath. A solution of 50 g (0.22 moles) of picryl chloride in 100 ml of warm m-bromoanisole was prepared and approximately one third of this was added to the stirred slurry in one portion. The temperature was raised to 170°C over a ten minute period and the copper began to lose its metallic luster, an indication that the reaction was under way. The remainder of the picryl chloride solution was added through the addition funnel over an additional ten minute period during which the solid phase changed to a dull brown then to a brownish grey. The reaction was slightly exothermic and the temperature was held between 170°C and 180°C by controlling the heating and the rate of addition. This temperature was maintained for thirty minutes after the addition was complete. The oil bath was then removed and the mixture allowed to cool to about 100°C. It was then filtered with suction and the inorganic residue was washed with suction on the funnel until the filtrate was almost colorless. The dark brown solution was treated with 25 g of Darco G-60, filtered and the carbon pad was washed with 250 ml of acetone

*** Venus Natural Copper Fine 44-F Manufactured by the United States Bronze Powders, Inc., Flemington, New Jersey.

CONFIDENTIAL
NOLTR 65-215

in several portions. The organic solvents were removed by steam distillation while the mixture was stirred vigorously. During the distillation, the product began separating as waxy solid which changed to a finely divided solid as the removal of the m-bromoanisole neared completion. When the distillate no longer contained bromoanisole, the distillation was stopped, the solid allowed to settle and the aqueous layer was removed by decantation. The damp product was stirred vigorously in 300 ml of boiling methanol for 30 minutes. The suspension was allowed to cool to room temperature, filtered with suction and the light brown crystalline product was washed with 150 ml of cold methanol on the funnel. After drying overnight at about 50°C, the product weighed 49 g (76%) and melted at 115-118°C. An analytical sample, m p 119-120°C, was prepared from a similar material by twice recrystallizing from acetone-n-hexane solutions.

Anal. Calc'd. for $C_{13}H_9N_3O_7$: C, 48.9; H, 2.84; N, 13.16.
Found: C, 49.23, 48.77; H, 2.00, 2.24; N, 13.33, 13.30.

The bulk of the crude product above was later nitrated without further purification. A second crop of 1.5 g was obtained by concentrating the mother liquor to a volume of 125 ml and chilling. Thin-layer chromatography showed this material to contain mainly m-picrylanisole but with two contaminants. It was not purified further.

Procedure II. Procedure I was repeated except that m-chloroanisole was used in place of m-bromoanisole. The yield was 42 g (66%) of a light brown crystalline product, m p 110-116°C. A second crop of 3.5 g was obtained by concentrating the mother liquor to 125 ml and cooling. Thin-layer chromatography showed it to be a mixture similar to the second crop in procedure I. As in procedure I, no attempt was made to purify this mixture.

Procedure III. A solution of 155 g (0.626 moles) of picryl chloride in 230 ml of m-bromoanisole was added to a 500 ml 3-neck round bottom flask fitted with thermometer, mechanical stirrer, condenser and addition funnel. The solution was heated to 160°C on an oil bath. An amount of 160 g (2.52 moles) of copper bronze was weighed out and about 30 g was added to the reaction mixture in one portion and stirred vigorously. After about eight minutes, the temperature had reached 170°C, the copper had begun to lose its metallic luster and the reaction was slightly exothermic. The remainder of the copper was then added in six approximately equal portions over a period of 35 minutes, the reaction temperature being held at 170-175°C by adjusting the external heating and controlling the rate of addition. The mixture was stirred at this temperature for one hour after the addition was complete. It was then allowed to cool to about

CONFIDENTIAL
NOLTR 65-215

60°C, 250 ml of acetone was added and the inorganic residue was removed by suction filtration. The residue was washed with acetone on the funnel until the filtrate was almost colorless. The acetone was boiled off on the steam bath and the m-bromoanisole was removed by vacuum distillation, b p 46-48°C/0.3 mm. When the pot temperature reached 110°, a volume of 145 ml of reusable m-bromoanisole had been recovered and the distillation was discontinued. The solid was dissolved in 400 ml of acetone, 3000 ml of methanol was added and the dark brown solution was treated with 50 g of Darco G-60. The carbon was removed by suction filtration, the filter cake was washed with 1000 ml of hot methanol and the amber filtrate was concentrated to a volume of about 800 ml. Crystallization started during concentration. The suspension was cooled with stirring on an ice bath then filtered with suction and the product was washed with cold methanol. After drying overnight at 50°C, the greenish yellow crystalline product weighed 125.2 g, m p 119-120°C. The mother liquor was treated with Darco G-60 and concentrated to about 300 ml. A second crop of 13.5 g, m p 118-120°C, after drying overnight at 50°C, was obtained. Total yield melting 118-120°C was 138.7 g (69.5%).

Procedure IV. This method of preparation is essentially the same as procedure III except that the reaction temperature was about 160°C and the product was isolated by azeotropic distillation. After the reaction mixture was filtered, the acetone was removed, 350 ml of water was added, and the excess m-bromoanisole was removed by "azeotropic distillation" and collected in a Dean-Stark trap.**** After about four hours, 162 ml of m-bromoanisole had been collected. The external heat was then removed and the mixture was seeded and allowed to cool with vigorous stirring. The product solidified and was collected by suction filtration and washed with water on the funnel. The damp solid was dissolved in 2750 ml of hot methanol, treated with 50 g Darco G-60, and the carbon pad was washed with two 500 ml portions of hot methanol. The filtrate was then concentrated to about 600 ml, cooled on an ice bath with stirring, filtered and the greenish yellow crystalline product washed with n-hexane. After drying in the oven at 80°C, the product weighed 146.6 g (74.2%), m p 119.5-120.5°C. Further concentration gave a mixture similar to those previously described.

Preparation of 3-Methoxy-2,2',4,4',6,6'-hexanitrobiphenyl.
A mixed acid solution was prepared in a 2000 ml 3-neck round

**** Good stirring is required during this step to prevent boiling-over.

CONFIDENTIAL
NOLTR 65-215

bottom flask fitted with a mechanical stirrer by slowly adding 140 ml of 90% nitric acid to 550 ml of 30% oleum with stirring while cooling on an ice bath. The reaction flask was then fitted with a condenser and the acid solution was cooled to 10°C. An amount of 83 g (0.26 moles) of accumulated crude batches of m-picrylanisole melting in the range of 110-118°C was added rapidly to the reaction flask. The temperature rose to 15°C during the addition and the solution became light brown. A small amount of solid remained undissolved. The ice bath was removed and the temperature leveled off at 25°C over a 10 minute period. The mixture was gently heated on a steam bath, the temperature rising to 94°C in 15 minutes. As the temperature reached 40°C, the solution became lighter in color and precipitation increased. At about 80°C, the precipitate became waxy but was immediately broken into fine particles with more vigorous stirring. When the temperature had reached 94°C, the mixture was light yellow and copious crystallization had occurred. After 90 minutes at 93-94°C, the mixture was cooled and drowned in a large volume of crushed ice.***** The crude product was recovered by suction filtration and washed with water until the filtrate was neutral. After thoroughly drying at 80°C, it weighed 110 g (93%) and melted at 179-185°C. The crude was dissolved in 500 ml of hot acetone, treated with 25 g of Darco G-60, filtered and the carbon residue was washed with 200 ml of acetone. While heating on the steam bath, 600 ml of n-hexane was added slowly with stirring. Precipitation started immediately. The suspension was cooled to room temperature on the bench, then on an ice bath for two hours and filtered with suction. The fine pale yellow crystalline product was washed with 200 ml of acetone-n-hexane 1:1 in three portions. The yield, after drying in the oven at 100°C, was 77.2 g, m p 193-5°C. The mother liquor was concentrated to about one third its volume by boiling on the steam bath with stirring. Further precipitation occurred during concentration. The suspension was cooled as above, filtered and the second crop was washed with hexane. After drying the yield was 27.2 g, m p 191-3°C. Total yield, melting at 191-5°C, was 104 g (88.4%). An analytical sample was prepared by recrystallizing a portion of the first crop from acetone-n-hexane. The melting point was not changed.

Anal. Calc'd. for $C_{13}H_6N_6O_{13}$: C, 34.4; H, 1.32; N, 18.5.
Found: C, 34.57, 34.69; H, 1.69, 1.70; N, 18.07, 18.05.

***** The product may also be recovered without drowning by filtration through a sintered glass funnel. It should be washed first with dilute sulfuric acid and then thoroughly with water.

CONFIDENTIAL
NOLTR 65-215

Preparation of 3-Chloro-2,2',4,4',6,6'-hexanitrobiphenyl;
PIPICL. An amount of 149 g (0.33 moles) of 3-methoxy-2,2',4,4',
6,6'-hexanitrobiphenyl was suspended in 1200 ml of benzene in a
2000 ml 3-neck round bottom flask fitted with mechanical stirrer,
condenser and addition funnel. A volume of 75 ml of pyridine
was added in a slow stream with stirring, and the mixture was heated
to mild reflux on a steam bath for one hour. During this time
the solid phase changed to a bright orange-yellow. After
cooling briefly on an ice bath, the mixture was filtered and the
orange-yellow crystalline product was thoroughly washed with
benzene and dried in the oven at 80°C for 90 minutes. The salt
weighed 174 g (99.4%).

The above product was dissolved in 400 ml of phosphorus
oxychloride and warmed on the steam bath for one hour. The
solution was dark red at the beginning but changed to amber
during the heating period. The crude product was isolated by
drowning the solution in about 4000 ml of ice and water. The
drowning was started by slowly adding a portion of the solution
to 1000 ml of water with vigorous stirring. When the temperature
reached 45°C, crushed ice and the remainder of the solution were
added at such a rate as to maintain a drowning temperature of
40-50°C. The mixture was then filtered with suction and the
crude PIPICL was washed thoroughly with water on the funnel.
After drying overnight at 80°C, the product, which was in the
form of dense roughly spherical particles, 1-2 mm in diameter,
weighed 172 g (114%) and had a strong acrid odor. It was
dissolved in 500 ml of acetone, treated with 40 g of Darco G-60,
the charcoal pad was washed with acetone and the volume adjusted
to 1200 ml by the addition of more acetone. A volume of 1400 ml
of n-hexane was then added whereupon a slight aqueous layer
separated. This was removed and the clear yellow solution was
concentrated by evaporation on the steam bath until the volume
was about 800 ml and crystallization occurred from the hot
solution. A volume of 500 ml of n-hexane was added and the
volume was again concentrated to about 800 ml. The suspension
was cooled on an ice bath, filtered and the pale yellow crystalline
product was washed with n-hexane. After drying several hours at
115°C, it weighed 126.9 g, m p 187-8°C. When the temperature
was increased slowly, the sample resolidified and melted again at
212°C. A second crop of 20.6 g, m p 186-8°C was obtained by
concentrating the mother liquor to 250-300 ml, cooling on ice
bath, filtering, washing the product with n-hexane and drying.
The total yield melting 186-8°C was 145.8 g (89%).

Small samples of the above crops were ground under water and
tested with Alkacid paper. The second crop was found to be
slightly acid. A 10.5 g sample of this crop was dissolved in

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NOLTR 65-215

75 ml of ethyl acetate and washed with two 25 ml portions of 5% sodium bicarbonate and twice with water. It was then dried over anhydrous magnesium sulfate and filtered. An equal volume of n-hexane was added and the solution was concentrated while adding more hexane until marked crystallization occurred. When the product was recovered by filtration, washed with n-hexane and dried, it weighed 8.5 g, m p 186-187.5° C. When tested as above, it was found to be neutral.

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REFERENCES

1. J. C. Dacons, H. G. Adolph and M. J. Kamlet, Tetrahedron 19, 791 (1963).
2. J. Forrest, J. Chem. Soc. 581 (1960).
3. F. Ullman and P. Sponagel, Ber. 38, 2211 (1905).
4. Bernard Johnson and H. G. Adolph, "A Novel Preparation of 1,3-Dichloro-2,4,6-trinitrobenzene", TN (NOL) 6164, 3 December 1963.
5. J. Forrest, J. Chem. Soc. 592 (1960).

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4. DESCRIPTIVE NOTES (Type of report and inclusive dates) ----		
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11. SUPPLEMENTARY NOTES ---	12. SPONSORING MILITARY ACTIVITY Bureau of Naval Weapons Washington, D. C.	
13. ABSTRACT 3-Chloro-2,2',4,4',6,6'-hexanitrobiphenyl PIPICL, has been prepared by a three-step procedure from picryl chloride and <u>m</u> -chloro- or <u>m</u> -bromoanisole. The first step involved the formation of <u>m</u> -picrylanisole by means of a mixed Ullmann reaction. Using 90% nitric acid and 30% oleum, the picryl anisole was nitrated to 3-methoxy-2,2',4,4',6,6'-hexanitrobiphenyl which was in turn converted to PIPICL by treatment with pyridine and phosphorus oxychloride. When <u>m</u> -bromoanisole was used in the Ullmann reaction, the overall yield for the three steps was about 50%. The use of <u>m</u> -chloroanisole resulted in a lower yield in the first step and an overall yield of about 52%. Several variations in procedure are given for the preparation of <u>m</u> -picrylanisole. (U)		

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
3-Methoxy-2,2',4,4',6,6'-hexanitrobiphenyl m-picryl anisole						
3-Chloro-2,2',4,4',6,6'-hexanitrobiphenyl						
Ullmann reaction						
Nitration						
Chlorination						

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Naval Ordnance Laboratory, White Oak, Md. (NOL technical report 65-215) A NEW SYNTHESIS FOR 3-CHLORO-2,2',4,4',6,6'-HEXANITROBIPHENYL, PIPCL (U) by J. C. Dacons and M. J. Kamlet. 18 Jan. 1966. v.p. BuWeps task RMO 62058/2121/FO08 08 11 and BuWeps task R 360 FR 105/ROLL 01 01. CONFIDENTIAL 3-chloro-2,2',4,4',6,6'-hexanitrobiphenyl, I, was prepared from picryl chloride and m-bromo- or m-chloranisole. The first step involved the formation of m-picrylanisole via a mixed Ullmann reaction. Using 90% nitric acid and 30% oleum, the picrylanisole was intrated to 3-methoxy-2,2',4,4',6,6'-hexanitrobiphenyl which was converted to I using pyridine and phosphorus oxychloride.	1. Chemical compounds - Nitration Chlorides Explosives - PIPICL Title Dacons, C. Joseph C. Kamlet, Mortimer J., jt. author Project Project Abstract card is unclassified.
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