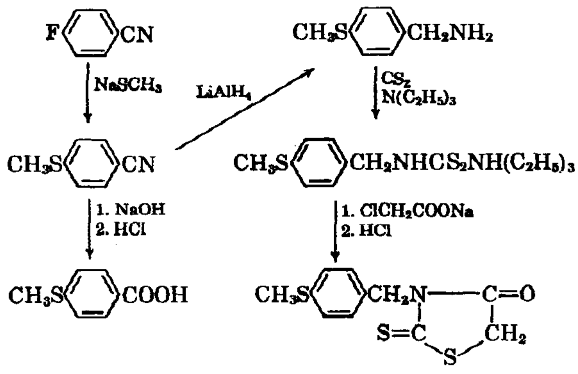

p-methylthiobenzoic acid, and subsequent conversion to *p*-methylthiobenzamide.

As with other benzylamines, *p*-methylthiobenzylamine reacts readily with carbon dioxide. It forms a picrate, and a dithiocarbamate with carbon disulfide and a base; the latter forms 3-*p*-methylthiobenzylrhodanine on reaction with sodium chloroacetate followed by cyclization in acid solution.

When the displacement reaction with sodium methylmercaptide and *p*-nitrochlorobenzene was tried, reduction of the nitro group took place instead of the desired reaction and a compound which gave an analysis corresponding to *p,p'*-dichloroazoxybenzene was isolated, thus confirming the similar action of sodium hydrosulfide and methyl sulfate on *p*-nitrochlorobenzene.[4]

EXPERIMENTAL

p-Methylthiobenzonitrile. A solution of sodium methoxide from 9.2 g. (0.4 g.-atom) of sodium and 200 ml. of methanol was surrounded by an ice bath and treated with chilled methyl mercaptan (23 g.; 0.48 mole). *p*-Fluorobenzonitrile (24.2 g.; 0.2 mole) was added and the reaction mixture was refluxed gently overnight and cooled. After the filtration of a slight amount of inorganic material, ice water was added, and 24.5 g. (82%) of white precipitate melting at 53–66° formed. Recrystallization from ligroin and a little acetone yielded 17.5 g. melting at 70–71°. From the filtrate an additional amount (4 g. melting at 51.5–57°) was obtained which on recrystallization gave 2.5 g. melting at 69.5–71° (lit.[3] m.p. 64°).

Anal. Calcd. for C_8H_7NS: C, 64.4; H, 4.69. Found: C, 64.51; H, 4.56.

p,p'-Dichloroazoxybenzene. A similar reaction between sodium methyl mercaptide and *p*-nitrochlorobenzene yielded a yellow solid, which after recrystallization from ethanol melted at 145° (lit.[4] m.p. 150°) and gave an analysis corresponding to *p,p'*-dichloroazoxybenzene. The infrared spectrum, with peaks at 6.38, 6.88, 7.18, 7.64, 7.70, 7.85, 8.67, 9.22, 9.87, 10.98, and 12.05 μ., is similar to that of azoxybenzene, while the ultraviolet spectrum shows bands at 235 mμ (log ε 3.80) and 330 mμ (log ε 4.19) [lit.[5] bands at 223 and 236 mμ (log ε 3.96) and 330 mμ (log ε 4.27)].

Anal. Calcd. for $C_{12}H_8Cl_2N_2O$: C, 53.96; H, 3.02; N, 10.49. Found: C, 54.65; H, 3.18; N, 10.68.

p-Methylthiobenzoic acid. A mixture of 1 g. of *p*-methylthiobenzonitrile and 20 ml. of 10% sodium hydroxide solution was refluxed for 1 hr. A white solid melting above 210° was removed by filtration and the filtrate acidified with 10% sulfuric acid. The precipitate, when placed on a preheated block, melted at 194° dec. (lit.[3] m.p. 192°). By treatment with thionyl chloride and ammonia, the acid was converted into *p*-methylthiobenzamide, melting at 186° (lit.[3] m.p. 191°), which is insoluble in cold sodium hydroxide solution and which on admixture with *p*-methylthiobenzoic acid melts at 160–165°.

p-Methylthiobenzylamine. To a suspension of 11.4 g. (0.3 mole) of lithium aluminum hydride in 500 ml. of sodium-dried ether was added dropwise a solution of 22 g. (0.15 mole) of *p*-methylthiobenzonitrile in 50 ml. of ether. The flask was cooled as necessary during the addition and subsequently stirred and refluxed overnight. The mixture was decomposed by water followed by 15% sodium hydroxide and water.[6] After filtration of the solid, the ether solution was dried and filtered. After removal of the ether, the product was vacuum distilled, yielding 16 g. (72%) of *p*-methylthiobenzylamine, b.p. 144–149° (6 mm.). For analysis, the amine was converted into its picrate, which after recrystallization from ethanol, melted at 216–218° with decomposition taking place above 210°.

Anal. Calcd. for $C_{14}H_{14}N_4SO_7$: C, 43.98; H, 3.69. Found: C, 44.12; H, 3.63.

3-(p-Methylthiobenzyl)rhodanine. This compound was prepared by the method described previously.[1] From 16 g. (0.107 mole) of the amine, which was added from a syringe to prevent absorption of carbon dioxide from the air, 5 g. (16.7%) of product melting at 118–121.5° was obtained. Recrystallisation from ethanol-acetone gave 3 g. of 3-(*p*-methylthiobenzyl)rhodanine, melting at 120.5–122°.

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Formation of a 1:1 Adduct from Allylbenzene and Diethyl Methylenemalonate

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When diethyl methylenemalonate is heated at 190° for two days in the presence of an excess of allylbenzene (4.5:1 molar ratio) a 32% yield of the 1:1 adduct 5,5-dicarbethoxy-1-phenylpentene-1 is obtained. This is obviously another example of a reaction taking place between a dienophile and an unconjugated olefinic bond.[5–10] The formation of

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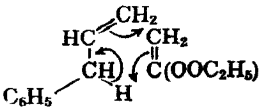
this adduct involves presumably a four-centered cyclic transition of this sort as has been shown in a previous publication from this laboratory.[5]



EXPERIMENTAL

Diethyl methylenemalonate.[11] A solution of 50 g. of diethyl ethoxymethylenemalonate (available from Eastman) in 100 ml. of ethanol was hydrogenated (in a Parr apparatus) at room temperature and 25 p.s.i. initial pressure, using 1.5 g. of 5% palladized carbon as the catalyst. The uptake of hydrogen, as indicated by the pressure gauge, was essentially over in approximately 0.5 hr. The reaction mixture was then filtered and the ethanol was distilled. The residue was then heated in an oil bath and the product, diethyl methylenemalonate, distilled at 205°, yield, 40 g.

Reaction of allylbenzene with diethyl methylenemalonate. Diethyl methylenemalonate (0.11 mole) and allylbenzene (0.49 mole) were heated together in a sealed glass bomb tube for 2 days at 190°. At the end of this time the tube was opened and the contents distilled. Eleven grams of a product, b.p. 141° at 1 mm., $n_D^{25°}$ 1.5117, was obtained (32% yield based on diethyl methylenemalonate).

Anal. Calcd. for $C_{17}H_{22}O_4$: C, 71.19; H, 7.56. Found: C, 71.11; H, 7.85.

The ultraviolet spectrum (major peak at 250μ and minor peaks at 285μ and 293μ) indicated that the double bond was now conjugated with the benzene ring.

Saponification. The 1:1 adduct (28 g.) was added to 150 ml. of 4*N* potassium hydroxide in 50% ethanol-water and the mixture was refluxed overnight. After acidification, extraction with ether, and evaporation of the ether, 19.5 g. of the free acid was isolated and recrystallized from nitromethane, m.p. 143°–144°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.03. Found: C, 66.65; H, 6.03.

Hydrogenation of the free acid. The free acid (2.408 g.) was hydrogenated in ethanol over palladium on charcoal. Hydrogen (245 ml.) was used up at room temperature. The saturated malonic acid prepared in this way was recrystallized from nitromethane, m.p. 111°–112°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.01; H, 7.01.

The neutral equivalent of the hydrogenated malonic acid was found to be 120 (theoretical neutral equivalent, 118).

Preparation of the barbiturate of the 1:1 adduct. The 1:1 adduct (20 g.) was added dropwise with stirring to a solution of 6 g. of sodium methoxide and 9.2 g. of urea, and dried at 60° overnight in 30 ml. of absolute methanol. The reaction mixture was refluxed for 6 hr. After this period of time the excess methanol was evaporated at reduced pressure and 67 ml. of ice water was added with vigorous stirring. Benzene was added, whereupon an emulsion benzene overnight. Three grams of a fine white powder that formed. After acidification, however, it was possible to separate the benzene layer in the form of a viscous semisolid slime. This was submitted to Soxhlet extraction with separated from the benzene extract were collected and an analytical sample was prepared by recrystallization from hot water, m.p. 188°–190°.

Anal. Calcd. for $C_{14}H_{14}O_3N_2$: C, 65.10; H, 5.46. Found: C, 64.89; H, 5.78.

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(11) This method of preparation was suggested by Prof. V. Boekelheide.

Heterocyclic Polynitro Compounds

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Received April 13, 1961

Aliphatic secondary amines containing *gem*-dinitro groups were prepared by the Mannich condensation of 2,2-dinitro-1-alkanols with ammonia, glycine, and hydrazine.[2] This work has now been extended to the synthesis of heterocyclic polynitro compounds. It was found that 2,2,4,4-tetranitro-1,5-pentanediol (I) condensed with ammonia to give 3,3,5,5-tetranitropiperidine (II). The condensation of I with 2,2,2-trifluoroethylamine, trimethylsilylmethylamine, 3-nitrazabutylamine, and 3,3,3-trinitropropylamine yielded the 1-substituted 3,3,5,5-tetranitropiperidines. The pronounced tendency for the formation of a six-membered ring takes precedence over the formation of the aliphatic secondary amines.[3] Nitration of II gave 1,3,3,5,5-pentanitropiperidine while the condensation of II with 2,2,2-trinitroethanol yielded 1-(2′,2′,2′-trinitroethyl)-3,3,5,5-tetranitropiperidine.

The reaction of 2,2-dinitro-1,3-propanediol with polynitro aliphatic primary amines and formaldehyde gave perhydropyrimidines.[4] Thus 1,3-bis-(3′,3′,3′ - trinitropropyl) - 5,5 - dinitroperhydropyrimidine and 1,3-bis(3′,3′-dinitrobutyl)-5,5-dinitroperhydropyrimidine were prepared from 3,3,3-trinitropropylamine and 3,3-dinitrobutylamine, respectively.

The condensation of methylenedinitramine and ethylenedinitramine with formaldehyde and 3,3-dinitrobutylamine gave 1-(3′,3′-dinitrobutyl)-3,5-dinitro-1,3,5-triazacyclohexane and 1-(3′,3′-dinitrobutyl)-3,6-dinitro-1,3,6-triazacycloheptane, re-

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(2) M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **79**, 2953 (1957).

(3) A similar type of reaction was observed by H. Feuer, G. B. Bachman, and W. May, *J. Am. Chem. Soc.*, **76**, 5124 (1954), who prepared *N*-carboxymethyl-3,3,5,5-tetranitropiperidine from the condensation of glycine with 2,2-dinitro-1,3-propanediol and sodium salt of 2,2-dinitroethanol.

(4) The formation of pyrimidines from the interactions of nitroparaffins with amines and formaldehyde has been reported by Senkus, *J. Am. Chem. Soc.*, **68**, 1611 (1946).