hr. and poured with stirring into a 1:1 mixture of ice and concentrated hydrochloric acid. An ethereal solution of the product was washed with water and dried over calcium sulfate to give 1.26 g. (67%) of white solid, m.p. 110–115°. The solid was dissolved in cyclohexane and chromatographed on a 1 × 20 cm. column of Mallinckrodt analytical grade activated silica gel. Development and elution with cyclohexane gave 0.76 g., m.p. 115.8–116.4° from cyclohexane; 116.8–117.8° from methanol. The infrared spectrum in carbon tetrachloride and in a potassium bromide pellet exhibited a carbonyl peak at 5.77 μ. These constants did not correspond to those of methyl trityl ketone, m.p. 138°, C=O absorption maximum at 5.84 μ. Ethyl triphenylacetate has been reported to melt at 116–117°[11] and at 120–121°.[10] The above product was recovered unchanged after 13 hr. reflux with 10% sodium hydroxide solution; however, esters of triphenylacetic acid saponify with difficulty.[10]

Ethyl triphenylacetate was prepared by heating for one hour 2.56 g. of triphenylacetic acid in 15 ml. of purified[9] thionyl chloride, then refluxing the acyl halide for 21.5 hr. with 5 ml. of absolute ethanol. The product was treated with hot alcoholic potassium hydroxide to remove any excess acyl halide, and poured into water. The solid ester, obtained by extraction into ether and crystallization from 95% ethanol, melted at 115–116.5°. A carbon tetrachloride solution of the ester was chromatographed on a 1 × 20 cm. column of silica gel to give a product melting at 116–117° after recrystallization from methanol. The infrared spectrum of this material was identical with that from the reaction of triphenylacetyl chloride and methylmagnesium iodide in ethyl ether.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.54; H, 6.33. Found: C, 83.86; H, 6.40.

Reduction of triphenylacetyl chloride by ethylmagnesium iodide. To 5.0 g., 0.017 mole, of acyl halide in 50 ml. of dry ether was added slowly 60 ml. of 1.4 M ethylmagnesium iodide. Heat and gas were evolved. The gas was collected in a trap cooled by liquid nitrogen and was later expanded at 25° into a 1160-ml. storage system. The final pressure in the system was 424 mm. The infrared spectrum was identical to that of pure ethylene except for a small peak at 8.8 μ which was probably due to ether vapor. Comparison of the absorbancy at 10.98 μ with that of a sample of Matheson C.P. ethylene showed that the gas was 96.5% ethylene. The amount corresponds to 0.026 mole or 76% based on the reduction of the acyl halide through the aldehyde to the primary carbinol.

The residue was hydrolyzed by the addition of 35 ml. of water and 25 ml. of hydrochloric acid. The water layer was extracted with four 20-ml. portions of carbon tetrachloride and concentrated by fractionation through a 12-plate column. The residue from the distillation was made up to 50.0 ml. with carbon tetrachloride. The infrared spectrum contained a strong, sharp OH peak at 2.83 μ and no absorption in the carbonyl region. The solution was washed with sodium thiosulfate, concentrated to 15 ml., diluted hot with an equal volume of ethanol and cooled to 0°. Crystals weighing 1.8 g. were isolated and recrystallized six times from hexane to give 2,2,2-triphenylethanol, m.p. 103–105°.[12]

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.59; H, 6.57. Found: C, 87.29; H, 6.41.

A sample of the carbinol was converted to the acetate, m.p. 135–137°; reported m.p. 136°.[13] The absorbance of the carbinol at 9.43 μ obeyed Beer's law and was used to estimate the total yield of carbinol in the original carbon tetrachloride extract. This amount, 1.3 g., represents a yield of 30% of the primary alcohol. The OH peak at 2.83 μ, however, was larger than that calculated from this amount of carbinol and indicates the presence of another more soluble alcohol in the mother liquors. One possibility is ethyltritylcarbinol from the addition of ethylmagnesium iodide to the intermediate triphenylacetaldehyde.

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Improved Procedure for Condensation of Alkyl Azides with Phenylacetonitrile to Form *vic*-Triazoles

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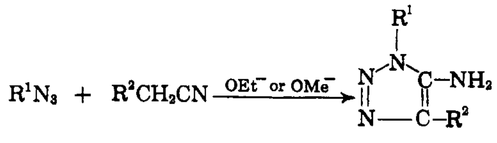
The elegant method for the synthesis of 1,4-disubstituted-5-amino-1,2,3-triazoles, III, first described by Dimroth,[2] involving the reaction of an organic azide, I, with an acetonitrile, II, in the presence of stoichiometric quantities of sodium ethoxide gives excellent yields for those cases in which the R substituent of I is an aromatic ring.[3] The yields were found to be poor when the benzyl and alkyl azides were employed. In the case of benzyl azide long periods of heating were required to effect condensation; even greater difficulties were experienced for alkyl azides in which R^1 was C_2H_5 and n-C_6H_{13}. Only in the case of ethyl azide was it possible to obtain a small quantity of the expected triazole; the major product when R^1 was C_2H_5 and n-C_6H_{13} consisted of an unknown substances[3a] whose elemental composition corresponded to the addition of two moles of II ($R^2 = C_6H_5$) and one mole of I ($R^1 = C_2H_5$ and n-C_6H_{13}). This communication reports on a significant improvement in the synthesis of III ($R^1 = C_6H_5CH_2$) and a new triazole, $R^1 = n$-C_6H_{13}, hitherto unattainable by the previous procedures.[3]


I II III ($R^2 = C_6H_5$)

When n-hexyl azide was stirred at room temperature with II ($R^2 = C_6H_5$) in anhydrous tetrahydrofuran (THF) as solvent in the presence of an equimolar amount of potassium *tert*-butoxide (KTB), a practically quantitative yield of III ($R^1 = n$-C_6H_{13}) was obtained. Previous experiments[3a] using benzyl azide gave a 59% yield of a very impure and difficultly purifiable III ($R^1 = C_6H_5CH_2$)

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(1) To whom all correspondence should be addressed.

(2) O. Dimroth, *Ber.*, **35**, 1034 (1902).

(3) (a) E. Lieber, T. S. Chao, and C. N. R. Rao, *J. Org. Chem.*, **22**, 654 (1957); (b) E. Lieber, T. S. Chao, and C. N. R. Rao, *Org. Syntheses*, **37**, 26 (1957).

after a reaction time of *ninety hours* at 60–65°. Repetition of this experiment in THF using KTB at *room temperature* for twelve hours gave a 78% yield of a 1:1 condensation product readily yielding pure III ($R^1 = C_6H_5CH_2$) identical with the product previously reported.[3a]

EXPERIMENTAL

Melting points are uncorrected. Micro-analyses by Dr. C. Weiler and Dr. F. B. Straus, Oxford, England.

1-n-Hexyl-4-phenyl-5-amino-1,2,3-triazole. To a mixture comprising 1.27 g. (0.01 mole) of *n*-hexyl azide,[3a] 1.17 g. (0.01 mole) of phenylacetonitrile in 50 ml. of dry THF was added a solution of 1.12 g. (0.01 mole) of KTB (dissolved in 50 ml. of THF) over a period of 30 min. The mixture was stirred at room temperature for a period of 12 hr. and then poured into ice water (400 ml.). The precipitated yellow crystals were filtered and vacuum dried; 2.3 g. (98%); m.p. 79–81°. Recrystallization from benzene gave m.p. 87–88°.

Anal. Calcd. for $C_{14}H_{20}N_4$: C, 68.82; H, 8.25; N, 22.93. Found: C, 68.57; H, 8.46; N, 23.10.

1-Benzyl-4-phenyl-5-amino-1,2,3-triazole. The reaction mixture comprised 5.85 g. (0.05 mole) of phenylacetonitrile, 6.65 g. (0.05 mole) of benzyl azide,[3a] and 5.6 g. (0.05 mole) of KTB in a total volume of 200 ml. of THF. The procedure used above was followed yielding 9.5 g. (78%) of the desired compound which on recrystallization melted at 156–156.5°. Mixture melting point with an authentic specimen[3a] showed no depression.

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Reaction of Primary Aliphatic Amines with Maleic Anhydride

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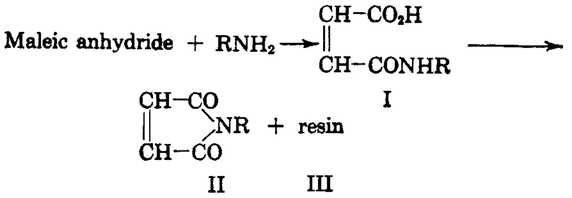
The reaction of primary amines with maleic anhydride has been known for many years[1]; however, with the exception of methyl and ethylamine,[2] the use of aliphatic primary amines has been reported only recently in the patent literature.[3,4] The reactions described in these patents are incomplete in nature and the products are not characterized. The reaction proceeds through the maleamic acid (I) intermediate to the maleimide (II) and a resinous by-product (III) as shown in the equation:

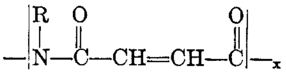


$$\text{Maleic anhydride} + RNH_2 \rightarrow \begin{array}{l} CH{-}CO_2H \\ \| \\ CH{-}CONHR \end{array} \longrightarrow \underset{\text{II}}{\begin{array}{l} CH{-}CO \\ \|\quad\;\; \rangle NR \\ CH{-}CO \end{array}} + \underset{\text{III}}{\text{resin}}$$

I

We have prepared a series of seven maleamic acids by reacting maleic anhydride with the appropriate amine in toluene at 90°. Amines containing from 4 to 18 carbon atoms were used. The acids were isolated in good yields as white crystalline solids.

Four *N*-alkyl maleimides were prepared by reacting maleic anhydride with the appropriate amine in xylene at 170–180°. The maleimides could also be prepared under the same conditions by starting with the *N*-alkyl maleamic acid. Low yields of product were obtained due to a concurrent polymerization reaction. The preparation of *N*-butyl maleimide was studied more extensively than the others. Yields of product were increased to 50% by removing solvent and then product and water under vacuum. In attempts to reduce the polymer formed in this reaction, hydroquinone and *p*-*t*-butylcatechol were added as inhibitors but were ineffective, suggesting that the reaction is not catalyzed by free radicals. The polymer appears to be a condensation product of the *N*-alkyl maleamic acid intermediate with the structure IV.



$$\left[-\overset{R}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-CH{=}CH-\overset{O}{\overset{\|}{C}}-\right]_x$$

IV

The infrared spectrum of IV showed the presence of unsaturation and differed from a spectrum of a free radical-catalyzed homopolymer of *N*-butyl maleimide which showed no unsaturation.

The *N*-alkyl maleamic acids and the corresponding maleimides have been investigated as monomers and details will be reported elsewhere.

EXPERIMENTAL[5]

Maleamic acids. General procedure: Maleic anhydride (0.5 mole) and 100 g. toluene were mixed at 90°. The appropriate amine (or Armeen[6]) (0.5 mole) was added slowly over a 2-hour period and the mixture was heated an additional hour at 90°. The mixture was cooled and the product was filtered. After washing with benzene and naphtha, the product was dried and then recrystallized from methanol-water as white crystals. The products are characterized in Table I.

Maleimides. Maleic anhydride and xylene were mixed at 80° and the appropriate amine was added at 80–90°. Equimolar amounts were used. Xylene was stripped off until the reaction temperature reached 180°, and the mixture was

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(1) R. Anschütz, *Ber.*, **20**, 3214 (1887).

(2) A. Piutti and E. Giustiniani, *Gazz. chim. ital.*, **26**, I, 431 (1896).

(3) J. M. Weiss and R. P. Weiss, U.S. Patent **2,306,918** (December 29, 1942).

(4) J. J. Giammaria, U.S. Patent **2,727,862** (December 20, 1955).

(5) All melting and boiling points are uncorrected.

(6) "Armeen" is the trade name for the primary aliphatic amines marketed by Armour and Co. The distilled samples were used in this study.