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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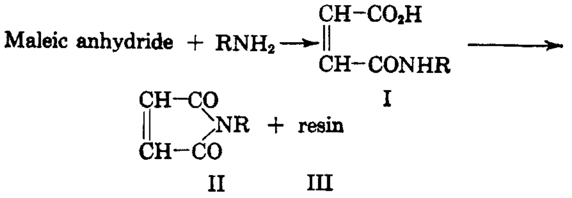
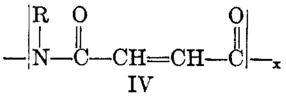
The reaction of primary amines with maleic anhydride has been known for many years[1]; however, with the exception of methyl and ethylamine,[2] the use of aliphatic primary amines has been reported only recently in the patent literature.[3,4] The reactions described in these patents are incomplete in 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:



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.



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

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.

TABLE I

N-Alkyl Maleamic Acids

Alkyl Group	Yield, %	M.P., °C.	% N Theory	% N Found
Butyl	97.5	79–80	8.19	8.20
Octyl	63.4	80–82	6.18	6.08
Decyl	83.5	83–84	5.49	5.27
Dodecyl	72	92–94	4.95	5.01
Tetradecyl	55	96–97.5	4.50	4.51
Hexadecyl	77.5	99–101	4.13	4.29
Octadecyl	86	102–104	3.81	3.87

held at this temperature for 2 hr. The residue was heated under reduced pressure and the water and product distilled off to a pot temperature of 210°/30 mm. The crude product was then redistilled under reduced pressure. The maleimides are characterized in Table II. The synthesis of *N*-butyl maleimide was improved by removing the xylene under reduced pressure. Yields of 50% were obtained.

TABLE II

N-Alkyl Maleimides

Alkyl Group	Yield, %	M.P., °C.	% N Theory	% N Found
Butyl	25	103–104[a]	9.15	9.04
Octyl	15	37–37.5	6.70	6.74
Decyl	20	46.5–48	5.91	6.01
Dodecyl	24	54.5–56.0	5.29	4.99

[a] B.p. at 20 mm. Hg.

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Reaction of Methylene with Diethyl Ether and Tetrahydrofuran

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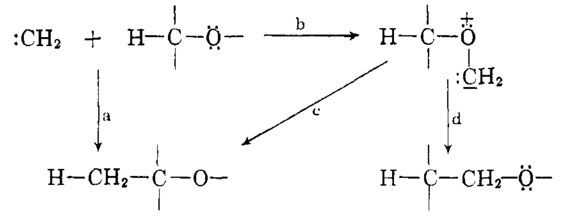
In their pioneer study of the photochemically induced reaction of methylene with organic molecules, Meerwein, Rathjen, and Werner[1] discovered that diethyl ether gave ethyl *n*-propyl and *i*-propyl ethers and that tetrahydrofuran gave α- and β-methyltetrahydrofuran. Here was the first example of the insertion of methylene into the carbon hydrogen bond. Later, this reaction was extended to saturated hydrocarbons by Doering, Buttery, Laughlin, and Chaudhuri.[2] In these instances methylene reacted indiscriminately with the various kinds of hydrogen atom. We wondered whether ether oxygen would permit the operation of the "ylid" mechanism discussed by Huisgen[3] (Chart 1, paths b and c) and thus cause the ratio of products to deviate from the statistical expected of the direct insertion mechanism (Chart 1, path a).

In the reaction with cyclopentane[2] participation of a direct insertion into the carbon-carbon bond, to form cyclohexane, was not observable. With ethers, however, intermediate "ylid" formation might be followed by rearrangement (Chart 1, paths b and d), with insertion into the carbon-carbon bond being the end result. As first pointed out by Gutsche and Hillman, tetrahydrofuran is an apt substrate for examination of this possibility.[4]



This note is, accordingly, concerned with the repetition of the Meerwein studies with the use of gas-liquid partition chromatography as a more refined analytical method than any conveniently available at the time of Meerwein's work.

The experiments were carried out in the usual way, by preparing a solution of diazomethane in a large excess of the substrate and irradiating with light of wave lengths greater than *ca.* 300 mμ. The bulk of the solvent was removed by distillation through a fractionating column. The concentrate of the product was analyzed by g. l.p.c. Retention times and sensitivities were determined on synthetic samples; identification was effected by comparison of infrared spectra.

From diethyl ether, ethyl *n*-propyl ether and ethyl *i*-propyl ether were obtained in the ratio 55.5 to 44.5. The deviation from the statistical value, 60:40 is small. The ratio of reaction of α-hydrogen to β- is 1.23. The ratio predicted on the basis of indiscriminate reaction of methylene is, of course, 1.00.

Tetrahydrofuran afforded α- and β-methyltetrahydrofuran in the ratio 1.26, in contrast again to the predicted value of 1.00. No tetrahydropyran could be found among the products. Especial care was exercised so that quite small amounts could have been detected. By the method described in the EXPERIMENTAL, 0.5% would have been detected easily, whereas the detection of 0.1% or less would have been equivocal. Reaction with the carbon-oxygen bond (or with the carbon-carbon bond) does not occur within these experimental

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(1) H. Meerwein, H. Rathjen, and H. Werner, *Ber.*, **75**, 1610 (1942).

(2) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.* **78**, 3224 (1956).

(3) R. Huisgen, *Angew. Chem.*, **67**, 439 (1955).

(4) C. D. Gutsche and M. Hillman, *J. Am. Chem. Soc.*, **76**, 2236 (1954).