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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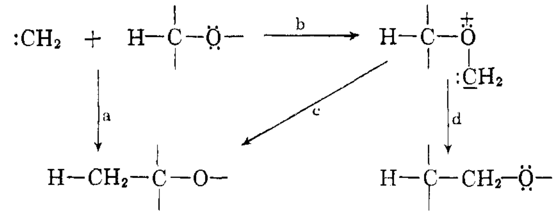
In their pioneer study of the photochemically induced reaction of methylene with organic molecules, Meerwein, Rathjen, and Werner[1] discovered that diethyl ether gave ethyl *n*-propyl and *i*-propyl ethers and that tetrahydrofuran gave α- and β-methyltetrahydrofuran. Here was the first example of the 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).

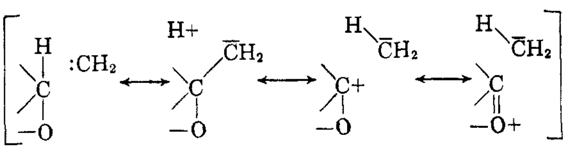
[3] R. Huisgen, *Angew. Chem.*, **67**, 439 (1955).

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

limits. Rearrangement of a hypothetically intermediate "ylid", urged so strongly by Meerwein and coworkers,[5] is therefore unimportant in the reaction of methylene with tetrahydrofuran and, presumably, with diethyl ether also.

The deviation from the statistical distribution in the reaction of methylene with the carbon-hydrogen bonds is small and lies in the direction of favoring the α-hydrogen atoms. Granting that the deviations are significant, one can rationalize their direction by comparing transition states of the type considered by Doering and Knox.[6] In the ethers, the transition state of reaction with the α-hydrogen could be favored by contribution of a resonance structure involving the oxygen atom.

It may be pointed out that appreciable carbon-rearrangement of the hypothetical diethyl ether-methylene "ylid" would have led to deviation in the opposite direction from that observed, whereas hydrogen-rearrangement from such an "ylid" would have led to deviation in the observed direction.[7]



These quantitatively more reliable results in no way change those reported by Meerwein and co-workers.[1] The conclusions are perhaps best expressed in a negative way: There is no new phenomenon in the reaction of these two ethers with methylene to compel one to consider the possible intervention of an "ylid" intermediate. It should, however, be pointed out that there are far more compelling reasons to consider an intermediate "ylid" in reactions of ethyl diazoacetate.[4,5,8]

EXPERIMENTAL

Photochemical decomposition of diazomethane in diethyl ether. An ethereal solution of diazomethane was prepared from 105 g. of crude nitrosomethylurea and 11 g. of purified diethyl ether and dried over potassium hydroxide at 0°. Irradiation with two General Electric sunlamps at 15–17° caused the smooth evolution of nitrogen and complete decolorization of the solution in 18 hr. The bulk of the solvent was removed by distillation through a 2-ft. column packed with glass helices. Total distillation of the residue gave 18.1 g. of a colorless product of b.p. 50–72°. Analysis and separation by g.l.p.c. afforded diethyl ether, ethyl *i*-propyl ether, and ethyl *n*-propyl ether. The substances were identified by comparing the infrared spectra with those of authentic materials. The ratio of *n*-propyl to *i*-propyl ether, determined by area measurement and corrected for differences in sensitivity, was 1.25.

Authentic ethyl *n*-propyl ether was prepared from sodium propoxide and ethyl iodide in boiling propanol-1; b.p. 63–64°; n^{25}_{D} 1.3698. Ethyl *i*-propyl ether was prepared in a similar fashion: b.p. 53.5°; n^{25}_{D} 1.3624.

Photochemical decomposition of diazomethane in tetrahydrofuran. In the same manner as described above, the irradiation of diazomethane in tetrahydrofuran (purified by boiling under reflux over sodium and distilling) gave 30.2 g. of crude product; b.p. 85–115°. Separation by g.l.p.c. showed recovered tetrahydrofuran, 2-methyltetrahydrofuran, and 3-methyltetrahydrofuran. The ratio of the latter compounds was 1.26. Identification was by comparison of infrared spectra with those of authentic materials.

Samples of tetrahydropyran (b.p. 86°; n^{25}_{D} 1.4206) and 2-methyltetrahydrofuran (b.p. 80°; n^{25}_{D} 1.4052) were obtained commercially and refractionated. 3-Methyltetrahydrofuran was obtained by the sequence of reactions in which methylsuccinic acid was converted to the dimethyl ester, b.p. 195–197.5°, by ethereal diazomethane; the diester was reduced with lithium aluminum hydride to 2-methylbutandiol-1,4, b.p. 95–97°/1 mm.; and the diol was treated with 60% sulfuric acid in a sealed tube at 100° according to Yur'ev and Gragerov.[9] A pure sample isolated by g.l.p.c. had b.p. 85–87° (reported[9] 86–86.5°) and n^{25}_{D} 1.4012.

The question of the possible presence of tetrahydropyran was examined. The retention time of authentic tetrahydropyran is slightly longer than that of 3-methyltetrahydrofuran on a column of dioctylphthalate under the conditions we used. No peak or shoulder at this retention time was observed. To eliminate the possibility of smaller amounts having been formed, 3 cc. of the crude reaction product (containing about 10% tetrahydrofuran) was separated on a 5-ft., 2″ I.D., silicone-firebrick column into starting material, 2-methyltetrahydrofuran and 3-methyltetrahydrofuran. The last quarter of the 3-methyltetrahydrofuran peak was collected and its infrared spectrum was measured neat in a 0.025 mm. cell. The strong absorption band of tetrahydropyran at 873 cm.$^{-1}$ is useful for detecting small amounts of this material. There is a slight discrepancy at this frequency corresponding to *ca.* 2%. When 0.011 g. of tetrahydropyran was added to 1.1 g. of the reaction product (bulk of tetrahydrofuran removed) the band was easily identifiable in the final quarter of the 3-methyltetrahydrofuran band and corresponded in intensity to about 6%.

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(5) H. Meerwein, H. Disselnkötter, F. Rappen, H. v. Rinteln, and H. van de Vloed, *Ann.*, **604**, 151 (1957).

(6) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **78**, 4947 (1956).

(7) Assuming that all hydrogen atoms react indiscriminately and that the "ylid" rearranges only to the α-methyl homologue, the reactivity of the oxygen atom towards methylene, relative to hydrogen taken as 1.00, becomes 1.04.

(8) G. B. R. de Graaff, J. U. Van Dijck-Rothuis, and G. van de Kolk, *Rec. trav. chim.*, **74**, 143 (1955).

(9) Yu. K. Yur'ev and I. P. Gragerov, *Zhur. Obschei (J Gen. Chem.)* **18**, 1811 (1948); *Chem. Abstr.*, **43**, 3818 (19

Dimethyl Dithiolfumarate and Some Copolymerization Reactions[1]

C. S. MARVEL AND J. F. PORTER

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Dimethyl dithiolfumarate (I) has been prepared from fumaric acid by the following series of reactions:

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(1) This is a partial report of work done under contract with three Utilization Research and Development Divisions, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division.