distilled oil (benzene) gave 81 mg of crystalline *p*-tolyl disulfide (IV): mp 43–45° [mp (Eastman *p*-tolyl disulfide IV) 43–45°]; mmp 43–45°; ir and nmr identical. A later fraction (25% $CHCl_3$–75% C_6H_6), 0.132 g, was redistilled, mp 80–81°, white needles. Comparison with authentic *p*-toluene-3-methylbut-2-enyl sulfone prepared by the alkylation of *p*-toluenesulfinic acid with 1-bromo-3-methyl-2-butene showed that the compounds were identical in all respects. Nmr evidence on the crude ylide distillate indicated only the disulfide and sulfone present, and integration yielded weight per cents of 21 and 22%, respectively.

Preparation of 1,1-Dimethyl-1-benzyl-2-(*p*-toluenesulfonyl)-hydrazonium Bromide.—To 12.8 g (59.6 mmol) of 1,1-dimethyl-2-(*p*-toluenesulfonyl)hydrazine in a 50-ml flask was added 20 g (117 mmol) of benzyl bromide. The mixture was warmed on a steam bath until dissolved and allowed to stand for 10 hr at room temperature. The white solid formed was triturated with ether and filtered to yield 14.2 g (62%) of white salt. Recrystallization from ethanol yielded a white powder: mp 105–106°; ir (Nujol) 2750 (broad), 1600, 1700, 1090 cm^{-1}; nmr ($CDCl_3$) δ 2.37 (s, 3), 3.69 (s, 6), 5.52 (s, 2), 7.1–8.1 (m, 9), 9.0–10.5 (broad, 1).

Preparation of 1,1-Dimethyl-1-benzyl-2-(*p*-toluenesulfonyl)-hydrazonium Ylide (I, R = benzyl).—The previously prepared hydrazonium bromide (3.59 g, 9.32 mmol) was dissolved in 20 ml of absolute ethanol and 1.15 g (1.1 equiv) of potassium *tert*-butoxide in 10 ml of ethanol was added while stirring. After the solution was stirred for 4 hr at room temperature, it yielded a white solid, 3.92 g (113%). This was dissolved in hot chloroform and filtered, and the chloroform was removed giving a white solid, 2.12 g (75%). Recrystallization from ethanol yielded white prisms: mp 176–177° dec; ir (Nujol) 1600, 1260, 1130, 1090, 1000 cm^{-1}; nmr ($CDCl_3$) ϵ 2.30 (s, 3), 3.08 (s, 6), 4.55 (s, 2), 7.0–7.7 (m, 9).

Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.22. Found: C, 63.08; H, 6.49; N, 9.18.

Pyrolysis of the Ylide I (R = Benzyl).—When 1.403 g of this ylide (I, R = benzyl) was pyrolyzed (same manner and apparatus as previously described) at 185° for 15 min, 0.133 g of yellow oil was collected in the trap (−78°). This was not completely characterized, but nmr evidences indicated that *N,N*-dimethylbenzylamine was a major component. The nonvolatile portion, 1.24 g, a black oil, was chromatographed over alumina. Four components were identified: (benzene) 59 mg (4.2%) of *p*-tolyl disulfide; (benzene) 63 mg (4.5%) of benzaldehyde (the dimethylhydrazone was identical with that of the authentic sample); (25% chloroform–75% benzene) 313 mg (22.3%) of *p*-tolyl benzyl sulfone (V, R = benzyl) [recrystallized from carbon tetrachloride; mp 144–145° (lit.[9] 144.5°), nmr ($CDCl_3$) ϵ 2.40 (s, 3), 4.10 (s, 2) 6.95–7.69 (m, 9)]; and (2% ethyl acetate–98% chloroform) 183 mg (13.1%) of *p*-toluenesulfonamide [mp 136–137° (from water); mixture melting point with the authentic sample was undepressed].

Attempted Preparation of 1,1-Dimethyl-2-benzyl-2-(*p*-toluenesulfonyl)hydrazine (VIII, R = Benzyl).—Reaction of the lithium salt of 1,1-dimethyl-2-(*p*-toluenesulfonyl)hydrazine in ether with benzyl bromide (1 equiv) gave the previously described ylide I (R = benzyl) in 60% yield. With potassium *tert*-butoxide (1 equiv) in ethanol, this ylide also formed. Refluxing potassium *tert*-butoxide (1 equiv) in *tert*-butyl alcohol with the hydrazine (1 equiv) and benzyl bromide (1 equiv) yielded *p*-toluenebenzyl sulfone (V, R = benzyl) as the sole product.

Registry No.—I (R = 3-methyl-2-butenyl), 31529-11-0; I (R = benzyl), 31529-12-1; 1,1-dimethyl-1-(3-methyl-2-butenyl)-2-(*p*-toluenesulfonyl)hydrazonium bromide, 31529-13-2; 1,1-dimethyl-1-benzyl-2-(*p*-toluenesulfonyl)hydrazonium bromide, 31529-14-3.

Acknowledgments.—We wish to thank the U. S. Public Health Service, the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, Eli Lilly and Co., and Hoffmann-La Roche, Nutley, N. J., for support of this research.

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Carbomethoxy Radical from Photodecomposition of Carbomethoxymercury Compounds

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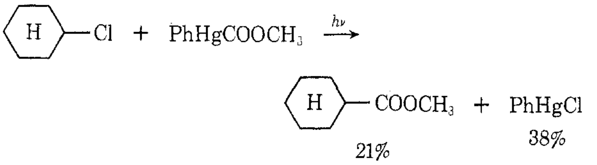
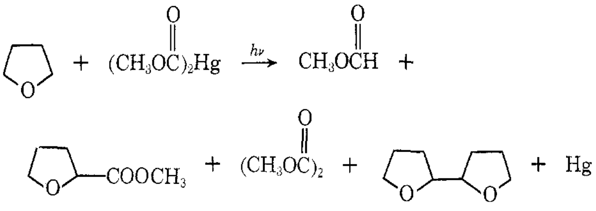
Although many species have been investigated in the study of free-radical chemistry, little work has been reported on carbomethoxy or carbethoxy radicals. These radicals are reportedly unstable and decompose readily to form carbon monoxide and alkoxy radicals or carbon dioxide and alkyl radicals. Gray and Thynne[1] reported that the activation energy of decomposition is only a few kilocalories/mole.

In a course of a study on the photochemical reaction of some mercury compounds,[2] it was found that the photochemical reaction of phenyl(carbomethoxy)mercury with cyclohexyl chloride gave methyl cyclohexylcarboxylate and phenylmercuric chloride, together with some metallic mercury (eq 1).[3] In a similar reaction Fanta[4] found that a photodecomposition of carbomethoxymercuric iodide in benzene produced methyl benzoate and toluene. However, it has not been elucidated whether this carbomethoxylation proceeds *via* formation of a free carbomethoxy radical and can be applied to saturated aliphatic compounds. Thus, we carried out the photochemical reaction of some carbomethoxymercury compounds in tetrahydrofuran (THF).



(1)

In a typical experiment, bis(carbomethoxy)mercury (0.015 mol) was irradiated in THF (82 ml) with a low-pressure mercury lamp for 12 hr under nitrogen. The products formed were methyl formate (50%), methyl tetrahydrofuroate (21%), dimethyl oxalate (5.3%), and α,α'-bistetrahydrofuranyl (43%), in addition to metallic mercury (quantitative yield) (eq 2). The results of photolysis of some organomercury compounds in THF are shown in Table I.



(2)

In the photolysis of carbomethoxymercury compounds, the formation of the esters may be evidence for the carbomethoxy radical and successful carbomethoxyl-

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(1) P. Gray and J. C. J. Thynne, *Nature*, **191**, 1357 (1962).

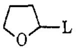
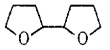
(2) T. Sakakibara, Y. Odaira, and S. Tsutsumi, *Tetrahedron Lett.*, 503 (1968).

(3) Unpublished result.

(4) G. F. Fanta, *J. Org. Chem.*, **29**, 1610 (1964).

TABLE I

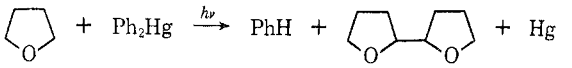
PHOTOCHEMICAL REACTION OF ORGANOMERCURY COMPOUNDS WITH TETRAHYDROFURAN

	Products, %[a]						
Reactant L-Hg-L′	Hg	Hg$_2$Cl$_2$			L-H (L′-H)	L-L	Evolved gas, ml
L = L′ = COOCH$_3$ (I)	100		21	43	50	5.3	230[b]
L = COOCH$_3$; L′ = Ph (II)	100		6	36	35 (96)	0.6	200
L = COOCH$_3$; L′ = Cl (III)		92	6	10	37	Trace	200
L = Ph; L′ = Cl (IV)		59	Trace	8	94	None	
L = L′ = Ph (V)	97		None	92	97	None	

[a] Yields of orgnic products were based on reacted organomercury compound. [b] Gaseous products consisted of CO (55%), CO$_2$ (22%), and CH$_4$ (24%).

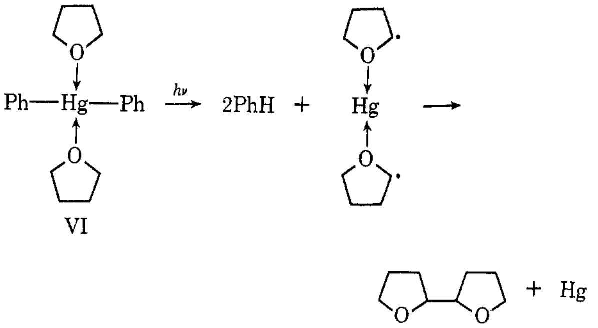
ation of an aliphatic compound. In photodecomposition of the mercury compounds II and III, the formed carbomethoxy radicals mainly decomposed to give carbon monoxide or carbon dioxide, etc., and the esters were obtained in lower yields, while in photodecomposition of I the esters were given in better yields. This shows that the carbomethoxy radicals produced in photolysis of I and of II (or III) do not necessarily have the same stability or reaction behavior.

In the photochemical reaction of diphenylmercury (V) in THF, the products, α,α'-bistetrahydrofuranyl and benzene, were obtained in nearly quantitative yields (eq 3). This apparently shows that the phenyl radicals



(3)

produced by photolysis of V may abstract the α hydrogen of THF to give benzene and α-tetrahydrofuranyl radicals, which may dimerize exclusively to form α,α'-bistetrahydrofuranyl. However, when THF was gradually diluted by cyclohexane, the formation of α,α'-bistetrahydrofuranyl sharply decreased relatively to that of bicyclohexyl (Table II). That is, the increasing dilution of THF may decrease the formation of the α-tetrahydrofuranyl radical while increasing that of cyclohexyl radical. We have already suggested that certain organomercury compounds may form the complexes with THF.[2] The present result also suggests the formation of a ground-state complex of THF with diphenylmercury, such as VI. If this is the case, the dilution of THF may cause the dissociation of the complex into V and THF to decrease the formation of the α-tetrahydrofuranyl radical in the photoreaction (eq 4).



VI

(4)

Concerning the formation of α,α'-bistetrahydrofuranyl, the photochemical reaction of diphenylmercury and phenylmercuric chloride (IV) gave conflicting results. Although both IV and V gave benzene in nearly quantitative yields, α,α'-bistetrahydrofuranyl was predominantly formed only in the reaction of V (Table I). In IV, high-boiling carbonyl compounds were the principal products. The α-tetrahydrofuranyl radical is known to isomerize thermally to the corresponding carbonyl radical.[5] Thus, the radical produced in the reaction of V favorably dimerized with little isomerization. Moreover, the absence of cross-coupling products from the reaction of V and THF contrasted sharply with their presence from the reaction of I and THF. Consequently, the results in Table I show that the carbomethoxy radical and the α-tetrahydrofuranyl radical produced from I or V (VI) are sufficiently stable to couple with each other under the conditions of this reaction.

TABLE II

FORMATION RATIO OF α,α'-BISTETRAHYDROFURANYL TO BICYCLOHEXYL BY PHOTOLYSIS OF Ph$_2$Hg IN THE MIXED SOLVENT OF TETRAHYDROFURAN AND CYCLOHEXANE

Reactants (molar ratio), Tetrahydrofuran/cyclohexane	Products (molar ratio), α,α'-Bistetrahydrofuranyl/ bicyclohexyl
1.00	10
0.70	3.8
0.25	0.48
0.057	0.056

All these results suggest that the abnormal reaction behavior of α-tetrahydrofuranyl radicals of carbomethoxy radicals may be owing to an effect of the mercury atom on the radical coupling. Namely, two α-tetrahydrofuranyl radicals formed in photolysis of VI may rapidly react with each other around the mercury atom before isomerization (eq 4), while, in the photochemical reaction of I in THF, the nonfree carbomethoxy radicals and α-tetrahydrofuranyl radicals trapped on the mercury atom may rapidly react with each other, with comparatively little decomposition, to give the esters in moderate yields. This apparent *mercury template* effect may be significant and play an important role in homo coupling or cross coupling of unstable radicals.

Experimental Section

Mercury Compounds.—Carbomethoxymercury compounds and diphenylmercury were prepared by the methods of Dessy, *et al.*,[6] and Calvery,[7] respectively. Phenylmercuric chloride was obtained in quantitative yield from equimolar mixtures of V and mercuric chloride in methanol. The uv spectra of carbomethoxymercury compounds are shown in Figure 1.

Solvents.—Tetrahydrofuran was refluxed over sodium hydroxide for 6 hr and distilled and then distilled from sodium before use. Cyclohexane was purified by the method described in "Organic Solvents."[8]

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(5) T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, **27**, 3067 (1962); *Tetrahedron*, **19**, 657 (1963).

(6) F. E. Paulik and R. E. Dessy, *Chem. Ind.* (*London*), 1650 (1962).

(7) H. O. Calvery, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1967, p 228.

(8) J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," 2nd ed Wiley, New York, N. Y., 1955, p 307.

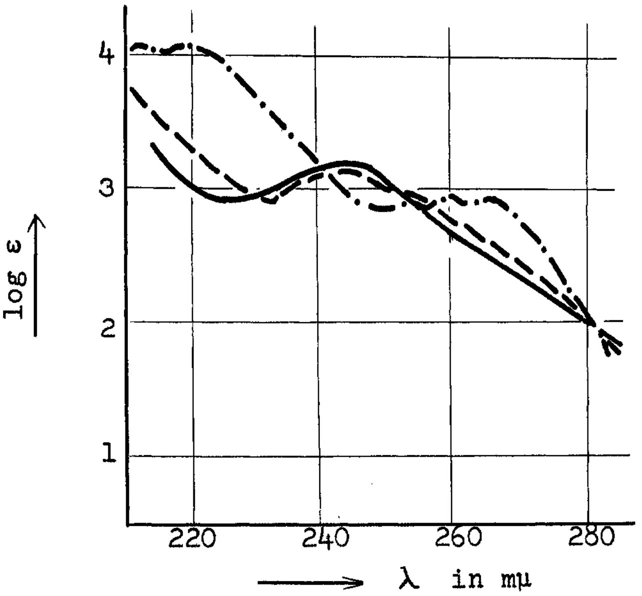

Figure 1.—Uv spectra of carbomethoxymercury compounds I (——), II (–·–·–), and III (– – –) in ethanol.

Authentic Materials.—Methyl tetrahydrofuroate, α-phenyltetrahydrofuran, and α,α′-bistetrahydrofuranyl were prepared by catalytic hydrogenation of methyl furoate,[9] by the methods of Shima, *et al.*,[10] and Mitsui, *et al.*,[11] respectively. Methyl formate, dimethyl oxalate, and bicyclohexyl were commercially availabel (from Wako Pure Chemical Industries, Ltd.).

Photochemical Reaction of Bis(carbomethoxy)mercury in THF.—Bis(carbomethoxy)mercury (4.8 g, 0.015 mol) was irradiated in THF (82 ml) for 12 hr by a 120-W low-pressure mercury lamp under nitrogen at room temperature. During the reaction, metallic mercury precipitated. Evolved gas was introduced into a cylindrical gas holder filled with a saturated aqueous solution of sodium chloride. The gaseous products (230 ml) consisted of carbon monoxide (55%), methane (24%), and carbon dioxide (22%) by glpc, using a 3-m, activated carbon column (80°, He carrier). After distillation of the reaction mixture, a lower boiling fraction, bp 30–68°, contained 0.9 g of methyl formate, which was identified by comparison with authentic material on glpc, using a 1.5-m, tricresyl phosphate on Celite 545 column (80°, He carrier gas flow rate of 46 ml/min). The glpc retention time was 1.2 min. The higher boiling fraction (1.75 g), bp 40–124° (24 mm), consisted of α,α′-bistetrahydrofuranyl (0.92 g), methyl tetrahydrofuroate (0.42 g), and dimethyl oxalate (0.10 g), which were identified by comparison with authentic materials on glpc, using a 1.5-m, silicone DC 550 on Celite 545 column (147°, H_2 carrier gas flow rate of 65 ml/min). The glpc retention times were 11.7, 6.5, and 2.4 min, respectively. Further identification by glpc using another column, 1.5 m, polyethylene glycol 6000 on Celite 545 (200°, H_2 carrier) supported the above results. The products, methyl formate, methyl tetrahydrofuroate, and α,α′-bistetrahydrofuranyl, were isolated by further distillation and preparative glpc, although dimethyl oxalate could not be isolated due to the small amount. The infrared spectra of products isolated were identical with those of authentic materials. The distillation residue was 0.2 g.

The photochemical reactions of carbomethoxymercuric chloride and phenyl(carbomethoxy)mercury were carried out under the same conditions and the reaction mixture was similarly treated.

Photolysis of Diphenylmercury in THF and Cyclohexane.—Diphenylmercury (3.5 g, 0.01 mol) was photolyzed in the mixed solvents (100 ml) at various molar ratios of THF and cyclohexane for 5 hr by a 120-W low-pressure mercury lamp. The reaction mixtures were treated as described above, and the yields of THF dimer and bicyclohexyl in higher boiling fractions were determined by glpc analysis.

Registry No.—I, 10507-39-8; II, 19638-01-8; III, 17261-26-6; IV, 100-56-1; V, 587-85-9; THF, 109-99-9.

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[9] B. H. Wojcik, *Ind. Eng. Chem.*, **40**, 210 (1948).

[10] K. Shima and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **36**, 121 (1963).

[11] S. Mitsui and H. Saito, *Nippon Kagaku Zasshi*, **81**, 289 (1960).

Reaction of Diethyl Bromomalonate with Sodium Phenoxide

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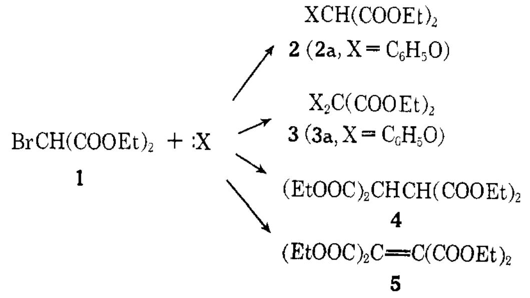
The major product(s) of the reaction of diethyl bromomalonate (**1**) with nucleophiles has been found to be dependent upon the base employed (Scheme I). Thus, the diazido compound **3** (X = N_3) is formed in the reaction with sodium azide,[2] and tetraethyl 1,1,2,2-ethanetetracarboxylate (**4**) is obtained with the sodium salts of diethyl phosphite,[3] diethyl thiophosphite,[4] and thiophenol.[5] Reagents which give the unsaturated ester, tetraethyl ethenetetracarboxylate (**5**), have been summarized.[6] Both monoaroxy- and diaroxymalonates (**2** and **3**, X=ArO) are produced when bromo ester **1** is treated with phenoxide, 3-methylphenoxide, or 4-nitrophenoxide ion.[7] The ratio of these two products formed in the reaction was reported to be solvent-dependent.

Scheme I



The purpose of the present work was to establish a reaction path for the formation of diphenoxymalonate (**3a**) in the reaction of **1** with sodium phenoxide. In addition, it was of interest to investigate further the effect of solvent on the course of the reaction.

Results and Discussion

The reaction of **1** with sodium phenoxide was carried out in the following solvents: absolute alcohol, 85% alcohol, tetrahydrofuran, benzene, and ether.

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[1] Abstracted in part from the M.S. Theses, Creighton University, of (a) S. M. P., 1968; (b) F. O. H., 1969.

[2] H. Bretschneider and N. Karpitschka, *Monatsh. Chem.*, **84**, 1091 (1953).

[3] A. E. Arbuzov and V. S. Abramov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 223 (1946).

[4] A. N. Pudovik and R. I. Tarasova, *Zh. Obshch. Khim.*, **34**, 293 (1964); *Chem. Abstr.*, **60**, 10579 (1964).

[5] K. H. Takemura and D. J. Tuma, *J. Org. Chem.*, **34**, 252 (1969).

[6] A. H. Blatt, Ed., "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 273.

[7] J. B. Niederl and R. T. Roth, *J. Amer. Chem. Soc.*, **62**, 1154 (1940).