Alkyl–Oxygen Bond Cleavage in Trityl Acetate-^{18}O during Reaction with Phenyl Grignard Reagent[1a]

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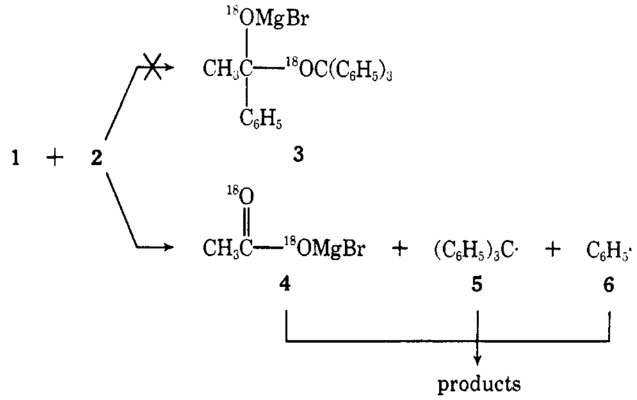
Triphenylmethyl (trityl) acetate-^{18}O and phenylmagnesium bromide (1:1.3 molar ratio) react in ether at room temperature. Trityl peroxide and acetic acid are the major products detected in the reaction mixture after hydrolysis in the presence of air. Acetophenone, triphenylmethane, benzophenone, triphenylmethanol, tetraphenylmethane, and very small quantities of several other compounds were also identified by glpc and mass spectral analysis. Since trityl peroxide did not contain ^{18}O, a classical acyl–oxygen [C(=O)O] bond cleavage was considered untenable. The acetic acid examined contained ^{18}O in the amount essentially identical with that determined in trityl acetate-^{18}O used as starting material. A mechanism is postulated to involve electron transfer by the Grignard reagent to trityl cation to give trityl radical.

In a continuing study,[2] it was observed[3] that several carboxylic esters of triphenylmethanol behave in an anomalous fashion toward aryl Grignard reagents.[4] Unequivocal evidence is now available by the use of trityl acetate-^{18}O (**1**) to substantiate a mechanism in which alkyl–oxygen bond cleavage[5a] occurs in the ester prior to or during attack by phenylmagnesium bromide (**2**). A classical intermediate[5b] **3** resulting from addition of the Grignard reagent to the carbonyl group is untenable, but a different mechanism tentatively postulated[3] is supported. (See Scheme I.)

SCHEME I



The distribution of ^{18}O in the final products is found in Table I. It is clear that decomposition by the intermediate **3** in a classical manner would be expected to give triphenylmethanol containing ^{18}O. In two separate experiments with labeled **1**, glpc and mass spectral analyses confirmed the presence of triphenylmethanol, but with only 1–2% ^{18}O, which most likely results from hydrolysis of a small amount of unreacted **1**.

TABLE I

QUANTITATIVE ANALYSIS OF PER CENT YIELDS AND PER CENT ^{18}O IN THE PRODUCTS RESULTING FROM THE REACTION OF TRITYL ACETATE-^{18}O (**1**) AND PHENYLMAGNESIUM BROMIDE (**2**), 1:1.3 MOLAR RATIO

Product	Typical yield, %[a]	% ^{18}O[b]	% ^{18}O[c]
Trityl Peroxide (**7**)	60	0	0
Acetic Acid	80[d]	0[e]	50
Acetophenone (**9**)	14	15	20.6
Triphenylmethane	23	. .	. . .
Benzophenone	12	0	0
Triphenylmethanol	~5	3	0
Biphenyl	23	. .	. . .
1,1-Diphenylethanol (**9**)	~2	. .[f]	. . .[f]
Tetraphenylmethane	~2	. .	. . .
1,1-Diphenylethene (**10**)	~2	. .	. . .
Bromobenzene	. . .[g]	. .	. . .
Phenol	. . .	. .	. . .[h]

[a] Yields based on trityl acetate. The yield of **7** is that obtained by actual isolation of the material. It was inadvertently implied in the preliminary communication[3] of our data that this yield was determined by glpc analysis. The yield of **7** varied from a minimum of 60% to a maximum of 72% of isolated pure product. This situation was created owing to the lack of a good purification solvent for **7**, since hot benzene proved to be only a fair solvent and no other solvent proved superior. [b] Started with trityl acetate-^{18}O (47%) and mixture hydrolyzed with 6 *N* HCl. [c] Started with trityl acetate-^{18}O (50%) and mixture decomposed with anhydrous H_2SO_4. [d] Yield of acetic acid was obtained by an nmr study of the water layer, using dimethyl sulfoxide as an internal standard. A deviation of ±2% of the actual yield under controlled conditions was observed for acetic acid. [e] ^{18}O exchanged with H_2O in water layer. [f] Mass spectrum of the oxygen-containing molecular ion could not be obtained owing to ease of dehydration of the alcohol. [g] Not determined. [h] Found in all reaction mixtures (<2%) but did not contain ^{18}O as determined within the limits of mass spectral analysis.

Electron transfer from the Grignard reagent **2** to trityl cation to give **4**, **5**, and **6** permits a prediction as to

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[1] (a) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967. (b) To whom inquiries should be addressed at the Department of Chemistry, Oklahoma State University, Stillwater, Okla. 74074. (c) Predoctoral NASA Trainee, 1965–1968.

[2] K. D. Berlin and B. S. Rathore, *J. Org. Chem.*, **29**, 993 (1964), contains reference to prior work.

[3] K. D. Berlin, R. D. Shupe, N. L. Doss, W. J. Leivo, M. D. Bell, R. D. Grigsby, E. D. Mitchell, Jr., and G. R. Waller, *Chem. Commun.*, 624 (1968).

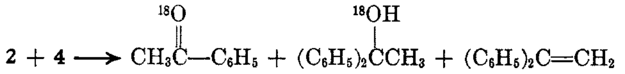
[4] Facile reduction of trityl cations at the dropping mercury cathode was observed recently; see M. I. James and P. H. Plesch, *Chem. Commun.*, 508 (1967). Trityl cation is reported to undergo an electron exchange with trityl radical; see J. W. Lown, *Proc. Chem. Soc.*, 283 (1963).

[5] (a) Ion-pair formation in trityl esters is well documented. Much of the data has been summarized; see S. Winstein and B. R. Appel, *J. Amer. Chem. Soc.*, **86**, 2718 (1964), **86**, 2720 (1964). Ion-pair formation by **1** could yield trityl cation, which could then be reduced. (b) It is recognized that esters of triphenylmethanol undergo heterolytic bond cleavage to give trityl cation in alcohols in the synthesis of trityl ethers. For a discussion of this, see E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt & Co., New York, N. Y., p 344.

distribution of ^{18}O in the products.[6] First, trityl peroxide (**7**), a major product (see Table I), did not contain ^{18}O, a fact which does not support heterolytic or homolytic acyl–oxygen bond cleavage for [C(=^{18}O)^{18}O] in **1** or **3**. Trityl peroxide must arise by reaction of trityl radical with oxygen during the workup. Trityl radicals probably exist in equilibrium with hexaphenylethane in solution; during work-up, reaction with oxygen occurs to give tritylperoxy radicals.[7]

$$(C_6H_5)_3C\cdot + O_2 \rightleftharpoons (C_6H_5)_3COO\cdot \xrightarrow{(C_6H_5)_3C\cdot} \mathbf{7}$$

With a molar ratio of 1.3:1 for **2**:**1**, only a slight excess (maximum 0.3 equiv) of **2** would be available to react with any intermediates, assuming 1 equiv would be consumed in the reduction step. This means that further reaction of **2** with **4** should be small and therefore the amount of acetophenone produced would be low. This low yield was substantiated by careful glpc analysis using standards (see Table I).[8] Mass spectral analysis of the ^{18}O content of **8** revealed an incorporation of 20.6% in the experiment starting with **1** (50 atom % ^{18}O). The cause of this isotopic dilution is difficult to assess, but one tentative explanation may rest in an unusual reaction involving formation of acetophenone from ethyl ether and **2** or radical fragments therefrom. As a model experiment to evaluate this question, trityl bromide and **2** were allowed to react in anhydrous ethyl ether by Gomberg's method.[9] Glpc analysis revealed *acetophenone* and *benzophenone* as important products along with those compounds already reported,[9] in addition to several others previously unreported. Participation of ethyl ether in the reaction leading to acetophenone appears likely, but no direct evidence is available from which to support a mechanism.



$$2 + 4 \longrightarrow CH_3\overset{^{18}O}{\overset{\|}{C}}-C_6H_5 + (C_6H_5)_2\overset{^{18}OH}{\overset{|}{C}}CH_3 + (C_6H_5)_2C{=}CH_2$$

8 **9** **10**

In a second experiment (see Table I) with a separately prepared sample of labeled **1** (47 atom % ^{18}O), the incorporation of ^{18}O in **8** was 15%. We have noted in this laboratory that decomposition of commercial phenylmagnesium bromide in ether or freshly prepared reagent with dilute aqueous hydrochloric acid leads to only 1–2% acetophenone.

Decomposition of the reaction mixture of **2** and **1** (50 atom %) with a few drops of concentrated sulfuric acid (previously treated with fuming sulfuric acid to minimize the water content) gave a heterogeneous mixture in which the acetic acid remained in solution while trityl peroxide and the magnesium salts precipitated. The acetic acid was 50 atom % ^{18}O (±2%). Thus, it appears that essentially all of the acetic acid derived from **1** does not experience an exchange of ^{18}O. This is reasonable if the mechanism postulated is applicable, in which **4** is formed and is decomposed by concentrated sulfuric acid without ^{18}O exchange.

Trityl radicals may abstract hydrogen from ether in addition to reacting with oxygen. From the former situation, triphenylmethane is expected, except that the source of the hydrogen is somewhat speculative, but two observations are pertinent. First, the yield of acetic acid was 80% or greater in experiments with a 1:1.3 ratio of **1**:**2**. This implies that removal of hydrogen from **1** or **4** is probably not important; this is tenable since the concentrations of **1** or **4** are small. Additional support is provided for this by the detection of 1–2% of ^{18}O in triphenylmethanol which is thought to arise from hydrolysis of unreacted **1**. Moreover, the dilution effect on the ^{18}O content of acetophenone is more easily understood if ether participates at some stage of the over-all reaction by furnishing hydrogen to the trityl radical. In total, labeled acetic acid, acetophenone, and triphenylmethanol account for the bulk of ^{18}O in the products.

A solution of **1** in anhydrous ether was treated with dried oxygen for 8 hr. The ester **1** was recovered unchanged. Although the degree of ionization of **1** is unknown, if a reaction occurred between trityl cation and O_2, even trace amounts of the cation should give some detectable **7** (at least this should be a detectable quantity within the period used for the general reaction). After 1 hr of reaction, a mixture of **1** and **2** was subjected to a stream of dried oxygen for 6 hr. Trityl peroxide began to precipitate immediately. This was taken as additional evidence for the presence of trityl radical. A special experiment was conducted in a drybox in which deoxygenated N_2 was used to degas the ether prior to use, the reaction mixture during reaction, and the water used to decompose the mixture. The resulting organic layer appeared clear, but, upon exposure to the atmosphere, immediate precipitation of **7** occurred. Thus, in the absence of oxygen, trityl radical reacts principally (although very slowly) by abstracting hydrogen as suggested previously.[3,10] The assumption that trityl bromide, like **1**, can form trityl cations in solution is not without precedence.[11]

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(6) It is important to note that an electron transfer from potassium heptaphenylcycloheptatrienide to heptaphenyltropylium cation to give heptaphenylcycloheptatrienyl radical in dimethoxyethane has been recorded recently; see R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **87**, 2200 (1965). A free-radical mechanism has been suggested in the reaction of methylmagnesium bromide with 7,7-dibromobicyclo[4.1.0]heptane; see D. Seyferth and B. Prokai, *J. Org. Chem.*, **31**, 1702 (1966). A very recent report presents strong evidence for fleeting radical intermediates in reactions of certain Grignard reagents with allylic bromides; see R. G. Gough and J. A. Dixon, *J. Org. Chem.*, **33**, 2148 (1968). A paper just published contains a summary of many electron transfer reactions involving cations, carbanions, metals, Lewis bases, etc.; see K. A. Bilevitch, N. N. Bubnov, and O. Yu. Okhlobystin, *Tetrahedron Lett.*, 3465 (1968). An example which appears to be related to our study is that of Shilov and coworkers who found trityl radicals in the reaction of $(C_6H_5)_3CCl$ with C_2H_5Li; see F. S. Dyachkovskii, N. N. Pubnov, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **123**, 870 (1958); *Chem. Abstr.*, **55**, 7996 (1961).

(7) This equilibrium appears to be well substantiated now; see C. L. Ayers, E. G. Janzen, and F. J. Johnston, *J. Amer. Chem. Soc.*, **88**, 2610 (1966); **89**, 1176 (1967).

(8) Unfortunately, the peak for **9** was buried under that of benzophenone in the glpc analysis. Extensive dehydration of **9** to **10** occurred during the reaction and on the glpc columns used, and prevented any quantitative estimate of ^{18}O in **9** by mass spectral examination.

(9) M. Gomberg and D. Kamm, *J. Amer. Chem. Soc.*, **39**, 2009 (1917). These workers found trityl peroxide and other triaryl-substituted hydrocarbons by extremely careful distillations. Acetophenone was not reported however. See also C. S. Schoepfle and S. G. Trepp, *ibid.*, **58**, 791 (1936).

(10) It has been suggested by a referee that products from reaction of O_2 with C_6H_5MgBr [these react at −78°; *cf.* C. Walling and F. A. Buckler, *J. Amer. Chem. Soc.*, **77**, 6039 (1955)] could be involved in the mechanism of reaction of **1** and **2**. If this were true to an appreciable extent, it is reasonable to expect considerable dilution effect in the ^{18}O content in the products. The ^{18}O balance is near 90% in analysis of acetic acid, acetophenone, and triphenylmethanol from the labeling experiment. This does not include the 1,1-diphenylethanol, which must arise from attack of **2** on **4**, nor does the loss of ^{18}O in dehydration to 1,1-diphenylethene. In addition, since in the experiments with deoxygenated N_2 no **7** was detectable in the organic layer (after decomposition) until air was admitted, trityl radical is relatively unreactive toward other radicals in solution.

(11) A. G. Evans, I. H. McEwan, A. Price, and J. H. Thomas, *J. Chem. Soc.*, 3098 (1955); P. B. D. De La Mare and E. D. Hughes, *ibid.*, 1059 (1949); F. Fairbrother and B. Wright, *ibid.*, 1059 (1949).

Dry oxygen was bubbled into a solution of trityl bromide in anhydrous ether for 6 hr. The solution remained clear and no **7** precipitated. Thus, oxygen does not appear to be an effective electron-transfer agent for trityl cation as expected.

Phenyl radical could abstract hydrogen to give benzene or couple to give biphenyl, both of which are present in the reaction mixture. However, the yields of these materials from reaction of **1** and **2** cannot be evaluated simply, since both compounds are formed in solutions of phenylmagnesium bromide in ether. Since analysis of the phenol for ^{18}O content did not reveal any incorporation of the isotope, it is surmised that the compound does not arise from any reaction in which **1** furnishes the oxygen.

In the mass spectrum of **1**, the base peak occurs at *m/e* 243 [$(C_6H_5)_3C^+$]; masses of 302, 304, and 306 (relative ratios are 1:0.4:0.86, respectively) confirm the presence of the ^{18}O (47 atom %) in **1**. Additional ions occur at *m/e* 259 [$(C_6H_5)_3CO^+$] and 261 [$(C_6H_5)_3C^{18}O^+$].

In the mass spectrum of **7**, the base peak at *m/e* 105 [$C_6H_5C^+{=}O$] is likely formed by decomposition of the fragment at *m/e* 259 [$(C_6H_5)_3CO^+$]. It was not possible to obtain a molecular ion of trityl peroxide (placed as a solid directly into the source), as the O—O bond cleaved upon electron bombardment.

Experimental Section

Apparatus and Procedure.—Mass spectral analyses were performed on two instruments: a Bendix time-of-flight and a LKB-9000 prototype magnetic sector. Solid samples were placed in the ionization chamber with the aid of a direct probe. The ethereal reaction mixtures were analyzed *via* a glpc inlet system to the ionization chamber. The ionization voltage was 70 eV.

The nuclear magnetic resonance spectra were determined using a Varian Model A-60 high resolution spectrometer with a field-sensing stabilizer ("Super-Stabilizer").

Gas chromatographic analyses were performed using a Varian-Aerograph Model 1520 with a hydrogen flame ionization detector and a disk integrator. Acetic acid was determined with a 6 ft × $^1/_4$ in. glass column of 6% FFAP on A/W Chromosorb W, 80–100 mesh and DMCS treated. All other glpc analyses of the ether solutions were performed using a 6 ft × $^1/_8$ in. column of 6% SE-30 on A/W Chromosorb G, 60–80 mesh and DMCS treated.

Nitrogen gas used for this work was carefully dried by passing it through concentrated sulfuric acid and then through three Linde 3A Molecular Sieve traps. The N_2 was deoxygenated to a low level according to the method reported.[12] Trityl bromide was prepared according to the method in the literature.[2] Anhydrous ether[13] was degassed with the deoxygenated N_2 in the special experiment before use in the reaction; during the reaction, the mixture was also degassed with deoxygenated N_2.

Silver acetate (82% ^{18}O-labeled) was obtained from the Weizmann Institute of Science, Rehovoth, Israel.

Small-Scale Preparation of 1.—The procedure was slightly modified from that originally developed in this laboratory.[2] This description is typical of all preparations attempted for **1** in this work. All glassware was carefully dried for several hours in a drying oven above 105°. Nitrogen, dried by passing through three 3A molecular sieve containing drying towers, was passed through the system for 2 hr before any reagents were added. To the reaction vessel was added 1.00 g (0.0031 mol) of trityl bromide followed by 40 ml of reagent grade benzene dried over 3A molecular sieve. The solution was then brought to reflux, and 0.30 g (0.0018 mol) of regular silver acetate and 0.40 g (0.0024 mol) of 82% ^{18}O-labeled anhydrous silver acetate were added all at once. The resulting heterogeneous reaction mixture was stirred at near reflux for 8 hr, after which time the silver bromide and any unreacted silver acetate were filtered from the hot benzene solution. Again, all glassware used in the filtration process was carefully oven dried, as the ester is easily hydrolyzed. The benzene was immediately stripped from the dissolved trityl acetate (by using a flash evaporator) to leave a viscous oil. This oil was allowed to stand under nitrogen for 1 hr, and then cold, anhydrous petroleum ether was added. White crystals of trityl acetate formed in about 2 hr. The crystals were powdered with a mortar and pestle and then placed under high vacuum for about 1 hr. No recrystallization was necessary. Trityl acetate (0.51 g, 0.00169 mol, 47 atom % ^{18}O) was obtained in 55% yield, mp 82.5–83° (lit.[14] mp 82–84°). Nmr and infrared spectra were superimposable on those of an authentic sample.

Reaction of Trityl Acetate (1) with Phenylmagnesium Bromide (2) (1:1.3 Molar Ratio).—Trityl acetate (0.45 g, 0.00147 mol, 47 atom % ^{18}O) dissolved in ether was added dropwise to 0.00191 mol of Grignard solution over a period of 1 hr. The reaction mixture was then allowed to stir at room temperature for 12 hr while ether was added as necessary to keep the volume near 50 ml. The mixture was cooled in an ice bath and 50 ml of ice-cold 6 *N* hydrochloric acid was added very slowly to destroy any excess Grignard reagent. The organic layer was washed successively with water and 10% sodium bicarbonate solution, and again with water. A pale yellow solid, trityl peroxide (**7**), was filtered from the organic layer, after which the organic layer was dried ($MgSO_4$). Glpc analysis of the organic layer revealed many products (Table I) which were identified by mixed injections of known standards. Per cent yields of the products were calculated by using standard solutions of the reaction products and comparing peak areas with the aid of the disk integrator on the Aerograph 1520 unit. One of the products, acetic acid, was present in both the aqueous and the organic layers. The identification and determination of yield of acetic acid was accomplished by a nmr study of the aqueous layer. The methyl protons of acetic acid were identified by examination of the nmr spectrum of the aqueous layer of the reaction mixture. After determination of the partition coefficient of acetic acid between 6 *N* hydrochloric acid and ether (equal volumes) under the conditions of the reaction as described above, the per cent yield of acetic acid could be determined as follows. A known amount of dimethyl sulfoxide (DMSO) was added to the aqueous layer, and then the area under the nmr peaks due to the methyl protons in DMSO was compared with that due to the methyl protons in acetic acid. Then the per cent yield of acetic acid based on trityl acetate (**1**) was calculated by using the partition coefficient so determined. For this particular determination, the organic layer was not washed with water and sodium bicarbonate solution, as described above; instead, the aqueous layer was analyzed directly for acetic acid. This procedure was checked against a standard solution of acetic acid.

Peak integration gave the DMSO/acetic acid ratio as 1.25:1. Since 0.0356 g (0.000456 mol) of DMSO had been added, and since DMSO has six protons to every three for acetic acid, the number of moles of acetic acid present in the aqueous layer was given by (0.000456/1.25) × 2, or 0.00073 mol, but, since the partition coefficient, organic/aqueous, is 0.61, there remained (0.38/0.62) × (0.00073) = 0.00045 mol of acetic acid in the ether layer. Thus the total yield of acetic acid obtained was 0.00118 mol (80%).

In the special experiment with deoxygenated N_2, the procedure was identical with that described, except for the increased precautions to remove O_2. After decomposition with the aqueous acid (previously degassed with the deoxygenated N_2), the organic layer was carefully separated and dried ($MgSO_4$) all under N_2. Upon exposure of the clear solution to the atmosphere, trityl peroxide (**7**) precipitated at once. The remainder of the work-up was as described previously.

Determination of the Partition Coefficient of Acetic Acid between Ether and 6 *N* Hydrochloric Acid.—The general procedure was to make up equal-volume solutions of 6 *N* hydrochloric acid and ether, each presaturated with the other component, and then add to these immiscible liquids the materials that would be present after hydrolysis of a reaction mixture obtained from trityl acetate (**1**) and phenylmagnesium bromide. For example, in one experiment, based on 0.0066 mol of **1** as starting material, the mixture contained 60 ml of 6 *N* hydrochloric acid and 60 ml of ether. To these liquids were added acetophenone, biphenyl,

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(12) P. Arthur, *Anal. Chem.*, **36**, 701 (1964).

(13) Peroxides could not be detected in the ether by the method reported; see L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., Boston, Mass., 1957, p 287.

(14) K. D. Berlin, L. H. Gower, J. W. White, D. E. Gibbs, and G. P. Sturm, *J. Org. Chem.*, **27**, 3595 (1962).

benzophenone, triphenylmethane, triphenylmethanol, and magnesium bromide hexahydrate in amounts corresponding to their per cent yields given in Table I. To this mixture was added 1.00 g (0.0167 mol) of acetic acid and 0.508 g (0.0065 mol) of DMSO. Nmr peak area integration gave an average DMSO/acetic acid ratio of 23:18. Thus, only 62.4% of the acetic acid remained in the aqueous layer. An average of three different determinations, each of slightly different volumes of two liquids, resulted in an average partition coefficient (ether/aqueous) of 0.38/0.62 = 0.61, which indicates that acetic acid preferentially remains in the aqueous layer by a factor of 0.62/0.38 = 1.63.

Reaction of Acetic Acid with Phenylmagnesium Bromide (1:2:3 Molar Ratio).—Acetic acid (1.0 g, 0.0167 mol) was slowly added to 0.035 mol of phenylmagnesium bromide (**2**) in 50 ml of anhydrous ether. The reaction mixture was stirred for 3 hr, cooled, and hydrolyzed with cold 6 *N* hydrochloric acid. Analysis of the organic layer was accomplished by glpc analysis. The following products were found: benzene, phenol, acetophenone, biphenyl, 1,1-diphenylethanol, and 1,1-diphenylethene. The alkene is apparently formed by dehydration of part of the tertiary alcohol. Acetophenone was found to be present (15 ± 1% yield based on the acid), and the combined quantities of the tertiary alcohol and 1,1-diphenylethene amounted to about 40 ± 1% (based on the acid). Standard solutions were used to check each of these compounds. These yields are not unreasonably low when one considers that 1 mol of the Grignard reagent was destroyed by the acidic proton of acetic acid.

Reaction of Trityl Bromide with Phenylmagnesium Bromide (2) and Oxygen.—Phenylmagnesium bromide (0.0121 mol) was added to a reaction vessel along with 50 ml of anhydrous ether. Then 3.0 g (0.0093 mol) of trityl bromide dissolved in anhydrous ether was added dropwise. After 1 hr, the reaction mixture was dark orange-red color, but no solid material had formed. At this time, oxygen was introduced into the reaction mixture and a solid began to form. After 6 hr, the reaction mixture had assumed a pale yellow color and trityl peroxide (**7**) was readily visible. The reaction mixture was cooled in an ice bath and then hydrolyzed with 40 ml of ice-cold 6 *N* hydrochloric acid; yield of trityl peroxide was 47% (1.10 g, 0.00212 mol). Other products observed by glpc analysis were benzene, phenol, acetophenone (11%), biphenyl, benzophenone (17%), triphenylmethane (26%), triphenylmethanol (7%), and tetraphenylmethane (3%). A solution of trityl bromide in ether was bubbled with dry O_2 for 6 hr. The solution remained unchanged and no trityl peroxide precipitated.

Registry No.—Trityl acetate-^{18}O, 20449-05-2; phenylmagnesium bromide, 100-58-3.

Acknowledgment.—We are grateful to Keith Kinneberg for aid in the determination and interpretation of the mass spectra. Grateful acknowledgment is extended to the National Science Foundation, Grant GB-3482, for funds provided to Oklahoma State University for purchase of the LKB-9000 mass spectrometer–glpc unit. We thank Professor Glen Russell for helpful discussions.

The Thermal Decomposition of Dimsyl Ion in Dimethyl Sulfoxide

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The decomposition of sodium dimsyl in dimethyl sulfoxide at temperatures above 80° produces a mixture of methylated butadienes and a white precipitate which, by titration and reaction with benzyl chloride, is evidently a mixture of sodium methanesulfenate, sodium methanesulfinate, and sodium methylmercaptide.

One of the useful strong bases in dimethyl sulfoxide (DMSO) is its anion, first prepared by Corey and Chaykovsky.[2] These authors mentioned the thermal decomposition of this reagent and it was the purpose of this investigation to establish the nature of the reactions involved.

When *ca.* 1 *M* solutions of sodium dimsyl are heated to 80° for several hours, the solutions turn dark red-brown, a voluminous white precipitate separates, and a volatile product and an extremely foul odor are evolved. The initial reaction can become violent at temperatures above 100°.

The volatile products have been collected by trapping at −78° and separated by gas chromatography. Many of the fractions were identified unequivocally by comparison of their nmr and mass spectra with those reported for methylated butadienes. Typical examples are summarized in Table I.

The nmr spectrum of peak 1 indicates that it is *not* butadiene; it shows mainly paraffinic proton resonance in four major peaks between δ 1.3 and 1.85 with only very weak absorbance in the olefinic proton 5–6 region. This material is probably from residual petroleum ether used to wash sodium hydride free of mineral oil. The other peaks identified as methylated butadienes gave excellent nmr spectra with chemical shifts, splitting constants, and peak heights identical with authentic spectra.

TABLE I

IDENTIFICATION OF GLPC FRACTIONS FROM VOLATILE LIQUID FROM SODIUM DIMSYL DECOMPOSITION

	Wt %			
Peak No.	A[a]	B[b]	Mass	Identity
1	6.4	0.9	. . .	. . .
2	8.4	1.9	C_5H_8	Isoprene
3	11.0	15.2	C_5H_8	*trans*-1,3-Pentadiene
4	0.3	4.2	. . .	. . .
5	0.2	1.6	C_2H_6S	Dimethyl sulfide
6	11.8	16.3	C_6H_{10}	*trans*-2-Methyl-1,3-pentadiene
7	6.6	12.5	C_6H_{10}	4-Methyl-1,3-pentadiene
8	11.0	16.6	C_6H_{10}	*trans*-2,4-Hexadiene
9	40.0	28.2	C_7H_{12}	2,4-Dimethyl-1,3-pentadiene

[a] Decomposed for 5 hr at 85°, 33% total yield of hydrocarbons.
[b] Decomposed for 7.5 hr at 78°, 27% total yield of hydrocarbons.

A number of sulfur ylides have been reported to be sources of ethylene and/or polymethylene, although the exact mechanism of the conversions and whether they involve methylene as an intermediate are matters of controversy.[3] The formation of dienes from a methylene donor, however, appears to be a unique reaction for

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(1) Supported in part by National Science Foundation Grant GP-5269. From the Ph.D. Dissertation of T. Yukuta, University of Pennsylvania, 1968.

(2) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962).

(3) A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, p 304.