olefinic absorption at 1613 cm.$^{-1}$ and gave a positive qualitative test for unsaturation. The p.m.r. spectrum of this fraction indicated it to be a mixture containing *ca.* 90% of **12**, the presumed precursor of **9**, and *ca.* 10% of a trisubstituted olefin. The identity of these products could not be confirmed since the components of the mixture could not be separated.

The high reactivity observed in this reaction is consistent with the nucleophilic nature of the attack of trialkyl phosphites on acetylenes. The corresponding reaction with the less electrophilic acetylene, phenylacetylene, requires a reaction temperature of 120° for a period of 4 to 6 days. By contrast, the reaction leading to the formation of **9** requires a reaction period of 2 to 3 hr. at 35°.

An attempted study of the reaction of triethyl phosphite with both dimethyl acetylenedicarboxylate and ethyl propiolate led to inconclusive results. The reactions were extremely exothermic and led to the formation of inseparable mixtures and large amounts of nondistillable tars. The p.m.r. spectra of distillable fractions indicated the extensive formation of C-ethyl groups.

This study confirms the initial postulate regarding the reactivity of quasi-phosphonium dipoles (**2**). In the absence of extensive anionic stabilization by electron-attracting groups (**2**, R = aryl, alkyl), protonative decomposition occurs, while oxygen to carbon alkyl transfers predominate in more highly stabilized anions [**2**, R = COOR′, P(O)(OR′)$_2$].

Experimental[7]

Reaction of Trimethyl Phosphite with Dimethyl Acetylenedicarboxylate.—Dimethyl acetylenedicarboxylate (14.2 g., 0.100 mole) was added dropwise at 5–10° to a solution of 25.3 g. (0.204 mole) of trimethyl phosphite in 200 ml. of anhydrous ether. After addition was completed, the reaction mixture was stirred for 1 hr. at room temperature and then refluxed for 1 hr.; all of these operations were carried out under an atmosphere of nitrogen. Upon cooling, a thick oil separated from the reaction mixture; the ethereal layer was reduced in volume to afford additional quantities of the oil. The combined oils were distilled under reduced pressure to give dimethyl acetylenedicarboxylate (8.7% recovery) and 14.7 g. (37.7%) of **2,3-bis(carbomethoxy)-2,3-bis(dimethylphosphono)butane** (**9**), b.p. 190° (0.50 mm.). This material crystallized on standing for a few days at room temperature; recrystallization from carbon tetrachloride gave material of m.p. 164.5–165.5°.

Anal. Calcd. for $C_{12}H_{24}O_{10}P_2$: C, 36.93; H, 6.19; P, 15.88; mol. wt., 390. Found: C, 37.15, 37.19; H, 5.93, 6.02; P, 16.05, 16.03; mol. wt., 368, 377.[8]

The infrared spectrum of **9** (in $CHCl_3$) showed bands at 2985 s, 2950 s, 2899 w, 2841 s, 1718 s, 1449 s, 1429 s, 1385 s, 1227 s, 1087 m, 1036 s, 980 m, and 960 m cm.$^{-1}$.

A lower boiling fraction, b.p. 126–126.5° (0.50 mm.), was also obtained during the isolation of **9**. The infrared spectrum of this material (film) showed absorptions at 1721 s (ester C=O), 1613 w (C=C), 1252 s (P—O), 1179 m (P—O—CH_3), 1024 s [P—O—C-(alkyl)], and 830 m cm.$^{-1}$ (C—H out-of-plane deformation, trisubstituted olefins). The p.m.r. spectrum showed C-methyl signals at τ = 7.7–8.0 p.p.m., an O-methyl complex centered at τ = 6.3 p.p.m., and vinyl absorptions at τ = 3.1–4.0 p.p.m. Attempted purification of this fraction by distillation and silicic acid chromatography was unsuccessful.

Benzylation and Benzoylation of Methyl Phenacyl Sulfone

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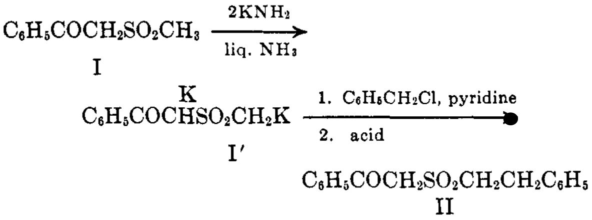
Benzylation at the terminal methyl group of benzenesulfonylacetone by means of its dipotassio salt has previously[1] been described. We now report the benzylation at the terminal methyl group of keto sulfone I by means of its dipotassio salt (I′) in pyridine (eq. 1).



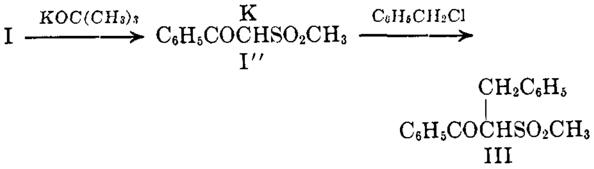
$$\underset{\text{I}}{C_6H_5COCH_2SO_2CH_3} \xrightarrow[\text{liq. } NH_3]{2KNH_2} \underset{\text{I}'}{C_6H_5CO\overset{K}{C}HSO_2CH_2K} \xrightarrow[2.\ \text{acid}]{1.\ C_6H_5CH_2Cl,\ \text{pyridine}} \underset{\text{II}}{C_6H_5COCH_2SO_2CH_2CH_2C_6H_5} \quad (1)$$

The structure of the alkylation product was established by independent synthesis of II from phenacyl bromide and sodium 2-phenylethylsulfinate (eq. 2).

$$C_6H_5COCH_2Br + C_6H_5CH_2CH_2SO_2Na \longrightarrow \text{II} \qquad (2)$$

When the benzylation reaction was attempted in liquid ammonia, a high yield of stilbene and no benzoyl product was obtained. This may indicate that an appreciable amount of potassium amide was present in equilibrium with I′, since benzyl chloride is known to be converted to stilbene by the amide ion.[2]

Benzylation of the monopotassio salt (I″) of I, prepared by means of potassium *t*-butoxide in *t*-butyl alcohol gave 1,3-diphenyl-2-methylsulfonylpropan-1-one (III) in 81% yield (eq. 3).



$$\text{I} \xrightarrow{KOC(CH_3)_3} \underset{\text{I}''}{C_6H_5CO\overset{K}{C}HSO_2CH_3} \xrightarrow{C_6H_5CH_2Cl} \underset{\text{III}}{C_6H_5CO\overset{CH_2C_6H_5}{\overset{|}{C}}HSO_2CH_3} \quad (3)$$

That the product was the expected C-benzyl derivative III and not the possible O-benzyl derivative was shown by its infrared spectrum which had a strong carbonyl peak at 1695 cm.$^{-1}$. It was shown not to be the only other possible C-benzyl derivative II by comparison of infrared spectra and by the mixture melting point method. When the reaction was carried out in dimethyl sulfoxide, the same product (III) was obtained in lower yield. It is interesting to note that carbon alkylation only was obtained in this solvent which favors oxygen alkylation in some other ambident anions.[3]

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[7] Infrared spectra were determined on a Beckman IR-8 spectrophotometer. P.m.r. spectra were determined with a Varian Associates A-60 spectrometer on 20–30% solutions in deuteriochloroform using tetramethylsilane as an internal standard. Microanalyses were performed by Galbraith Microanalytical Laboratories.

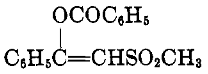
[8] Molecular weight determinations were carried out with a Mechrolab Model 301A vapor pressure osmometer using dilute solutions in benzene at 37°.

[1] W. I. O'Sullivan, D. F. Tavares, and C. R. Hauser, *J. Am. Chem. Soc.*, **83**, 3453 (1961).

[2] C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *ibid.*, **78**, 1653 (1956).

[3] See N. Kornblum, R. Seltzer, and P. Haberfield, *ibid.*, **85**, 1148 (1963).

Keto sulfone I was converted by means of a number of bases into its monopotassio salt which was benzoylated with benzoyl chloride in a variety of solvents (see Table I) to produce the O-benzoyl derivative IV and not the C-benzoyl derivative V.


$$C_6H_5C(OCOC_6H_5)=CHSO_2CH_3$$
IV

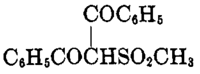

$$C_6H_5COCH(COC_6H_5)SO_2CH_3$$
V

TABLE I

BENZOYLATION OF I'' AT REFLUX TEMPERATURES

Base	Solvent	Reaction time, hr.	% yield of IV	% of I recovered
Potassium amide	Ether	6	14	45
Potassium ethoxide	Ethanol	3	26	61
Potassium *t*-butoxide	*t*-Butyl alcohol	5	70	..

The product failed to give an enol test with ethanolic ferric chloride or to form a copper chelate with copper acetate, tests which should have been expected to be positive had the product been the β-diketone V. The product was shown not to be the only possible benzoyl derivative VI by comparison of infrared spectra. In the infrared spectrum of the product, the strong peak at 1735 cm.$^{-1}$, which is indicative of an α-unsaturated benzoate,[4] supported structure IV.

Finally, when I was treated with 2 equiv. of potassium amide in liquid ammonia and then with methyl benzoate, no benzoyl product was isolated. However, when the reaction was carried out in pyridine at 70°, benzoyl products IV and VI were obtained in 10 and 2% yields, respectively. When the reaction was effected in toluene at 60° by means of phenylsodium, the yield of VI was 20% (eq. 4).

$$\text{I} \xrightarrow[C_6H_5COOMe]{\text{excess } C_6H_5Na} \underset{\text{VI}}{C_6H_5COCH_2SO_2CH_2COC_6H_5} \qquad (4)$$

Diketo sulfone VI was identified by microanalytical and spectral analyses. This compound (VI) has recently been characterised by Miles and Hauser[5] who effected its synthesis in 78% yield from I with methyl benzoate by use of sodium hydride.

Experimental[6]

Benzylation of Monopotassio Salt I''.—To a stirred solution (0.025 mole) of potassium *t*-butoxide in 20 ml. of *t*-butyl alcohol was slowly added 4.95 g. (0.025 mole) of methyl phenacyl sulfone[7] (I), and the mixture was heated under reflux for 0.5 hr. Benzyl chloride (3.16 g., 0.025 mole) and, after 1 hr., 0.3 g. of potassium iodide were added; heating and stirring were continued for a further 8 hr. The alcohol was removed by distillation and cold water (17 ml.) was added to the cooled residue. The crude product was recrystallized from methanol to give 5.85 g. (81%) of 1,3-diphenyl-2-methylsulfonylpropan-1-one (III), m.p. 137–138°.

Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.39; H, 5.34; S, 11.2.

Its melting point was depressed by admixture with a sample of keto sulfone II.

When the reaction was carried out in dimethyl sulfoxide for 3 hr., the yield of III was 29%; unchanged keto sulfone I (44%) was recovered.

Benzylation of I to Form Keto Sulfone II.—Powdered keto sulfone I (4.95 g., 0.025 mole) was added to a stirred suspension of potassium amide (0.05 mole) in 60 ml. of anhydrous liquid ammonia. After 0.5 hr. the liquid ammonia was replaced by an equal volume of ether,[8] the latter was then replaced by an equal volume of pyridine, and the resulting solution was heated at 50° for 1 hr. Benzyl chloride (3.15 g., 0.025 mole) was then added slowly and heating was continued for a further 3 hr. On cooling, the mixture was neutralized with hydrochloric acid (6 *N*) and extracted with methylene chloride. The methylene chloride solution was extracted with 5% sodium hydroxide. The brown oil obtained on acidification of the sodium hydroxide solution was crystallized from methanol and then recrystallized from ethanol to give 3.02 g. (61%) of starting keto sulfone I and a yellow solid, m.p. 78–82°. Repeated crystallizations of the latter from methanol yielded 0.7 g. (10%) of colorless prisms of phenacyl 2-phenylethyl sulfone (II), m.p. 82–83°. A mixture melting point determination with a sample of II prepared by independent synthesis (below) showed no depression.

Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59; S, 11.12. Found: C, 66.43; H, 5.31; S, 11.27.

Independent Synthesis of Keto Sulfone II.—Equimolar quantities of sodium 2-phenylethylsulfinate[9] (1.7 g.) and phenacyl bromide (1.7 g.) were heated in absolute ethanol at reflux temperature for 5 hr. The reaction mixture was cooled, diluted with water, and extracted with methylene chloride. The methylene chloride solution was extracted with 5% sodium hydroxide; the extract, on acidification, yielded a colorless, crystalline solid, m.p. 80–81°, which on recrystallization from methanol gave 1.98 g. (58.8%) of phenacyl 2-phenylethyl sulfone, m.p. 82°.

Benzoylation of the Monopotassio Salt I''. A. In Ether.—Methyl phenacyl sulfone (4.95 g., 0.025 mole) was added to potassium amide (0.025 mole) in 100 ml. of liquid ammonia. After 0.5 hr. the liquid ammonia was replaced by an equal volume of ether.[8] Benzoyl chloride (3.52 g., 0.025 mole) was then added, and the reaction mixture was heated, with stirring, for 6 hr. The residue obtained on removal of the ether was carefully neutralized in the presence of ice with hydrochloric acid and then extracted with methylene chloride. The methylene chloride solution was extracted with a saturated solution of sodium bicarbonate and then with 10% sodium hydroxide. Acidification of the bicarbonate extract yielded benzoic acid (0.73 g., 41.3%), m.p. and m.m.p. 122°, while acidification of the sodium hydroxide extract afforded 2.21 g. (45.6%) of unchanged keto sulfone I. The methylene chloride solution was dried ($CaSO_4$), and the solvent was removed to give 1.1 g. (14%) of α-benzoyloxy-β-methylsulfonylstyrene (IV), m.p. 150–151°.

Anal. Calcd. for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67; S, 10.6. Found: C, 63.6; H, 4.75; S, 10.41.

B. In *t*-Butyl Alcohol.—To a solution of potassium *t*-butoxide (0.015 mole) in 20 ml. of *t*-butyl alcohol was added 3.0 g. (0.015 mole) of I, and the mixture was heated under reflux for 1 hr. Benzoyl chloride (2.1 g., 0.015 mole) was added very slowly, and the resulting suspension was heated for a further 5 hr. The *t*-butyl alcohol was removed by distillation, and the product was worked up as in the previous experiment. The yield of α-benzoyloxy-β-methylsulfonylstyrene was 3.39 g. (70%).

C. In Ethanol.—When a similar reaction was carried out in ethanol with potassium ethoxide, α-benzoyloxy-β-methylsulfonylstyrene was obtained in 26% yield and unchanged starting keto sulfone in 61% yield.

Benzoylation of I to Form Diketo Sulfone VI. A. With Potassium Amide in Pyridine.—Methyl phenacyl sulfone (4.95 g., 0.025 mole) was added to potassium amide (0.05 mole) in 60 ml. of liquid ammonia. When the ammonia had evaporated, 60 ml. of dry pyridine was added, and the reaction mixture was heated for 1 hr. at 70°. Methyl benzoate (1.7 g., 0.0125 mole) was added and, after stirring for 3 hr.

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(4) See L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 179.

(5) M. L. Miles and C. R. Hauser, *J. Org. Chem.*, **29**, 2329 (1964).

(6) Melting points are uncorrected. Infrared spectra were determined with a Beckman IR-5 spectrometer. Ultraviolet spectra were measured in 95% ethanol on a Bausch and Lomb Spectronic 505 spectrometer. Elemental analyses were by University College, Dublin, Microanalytical Laboratory.

(7) H. D. Becker and G. B. Russell, *J. Org. Chem.*, **28**, 1896 (1963).

(8) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

(9) P. Rumpf and J. Sadet, *Bull. soc. chim. France*, 448 (1958).

at 70°, the reaction mixture was cooled, neutralized, and extracted with methylene chloride. The methylene chloride solution was extracted with a saturated solution of sodium bicarbonate and then with 5% sodium hydroxide. The O-benzoyl derivative IV (0.8 g., 10%), m.p. and m.m.p. 150–151°, was obtained from the methylene chloride solution. Acidification of the sodium hydroxide extract yielded a yellow solid which, on fractional crystallization from methanol, afforded 3.65 g. (69.4%) of unchanged I, m.p. and m.m.p. 108–109°, and 0.07 g. (2%) of diphenacyl sulfone (VI), m.p. 122–123° (lit.[5] m.p. 124–125°).

Anal. Calcd. for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67; S, 10.6. Found: C, 63.78; H, 4.11; S, 10.9.

It failed to produce a color with ethanolic ferric chloride or to form a derivative with copper acetate. Its infrared spectrum showed a sharp benzoyl carbonyl group peak at 1695 cm.$^{-1}$ (lit.[6] ν 1690 cm.$^{-1}$). Its ultraviolet spectrum had λ_{max} 253 mμ (ϵ 38,600), compared with λ_{max} 251 mμ (ϵ 15,300) for I. Its n.m.r.[10] spectrum had a singlet at τ 4.9 and a multiplet at 1.9–2.74 (ten protons).

B. With Phenylsodium in Toluene.—A hot solution of 4.95 g. (0.025 mole) of I in toluene was added to a stirred hot suspension of phenylsodium[11] in toluene, and the mixture was stirred at 60° for 2.5 hr. and then 1.7 g. (0.0125 mole) of methyl benzoate in 3 ml. of toluene was added and stirring at 60° was continued for a further 5 hr. The reaction mixture was cooled, treated with ethanol (to destroy excess of sodium), and then poured onto a slight excess of hydrochloric acid in the presence of ice. The product on working up as in the previous experiment gave 0.75 g. (20%) of diketo sulfone VI, m.p. 122°, and 3.71 g. (75%) of unchanged keto sulfone I.

Acknowledgment.—The authors thank Professor E. M. Philbin of this Department and Professor C. R. Hauser of Duke University, Durham, North Carolina, for advice.

[10] We are indebted to Dr. G. R. Bedford of Imperial Chemical Industries Ltd., Pharmaceuticals Division, Macclesfield, Cheshire, England, for this determination.

[11] See "Sodium Dispersions," U. S. Industrial Chemical Co., Division of National Distillers Production Corp., New York, N. Y., 1957, p. 36.

Azo-Hydrazone Conversion. III. The Autoxidation of Benzaldehyde Phenylhydrazones

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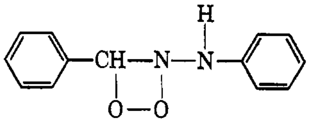
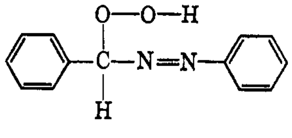
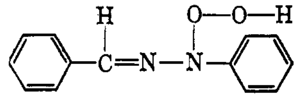
Busch and Dietz[2] reported that certain benzaldehyde phenylhydrazones can take up oxygen to form peroxides and assigned the structure I to these peroxides. Pausacker[3] determined the rate of oxidation by measuring the oxygen consumption. He suggested two other possible structures, II and III, for the oxidation product. Pausacker could not unequivocally distinguish between these two structures but favored structure II. Criegee and Lohans[4] compared the rates of oxidation of several series of substituted benzaldehyde phenylhydrazones. They found that although benzaldehyde phenylhydrazones take up oxygen readily, under the same conditions N-substituted benzaldehyde phenylhydrazones are not reactive with oxygen. On these bases, they also favored structure II for the autoxidation product and suggested a possible tautomerization (eq. 1). Structure IV comes close to Busch's formulation I.



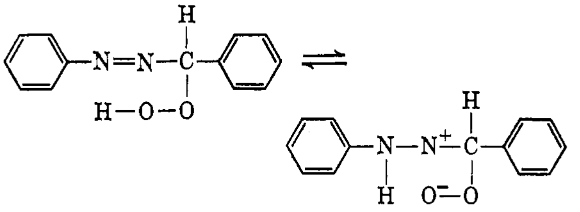
I



II



III



(1)

IV

However, no evidence other than the rate measurements has been given to distinguish among the above formulations, I, II, and III. This is possibly due to the instability of such oxidation products, which readily decompose at room temperature in the solid state as well as in solution.

Recently, spectral properties of phenylhydrazones have been shown to be quite different from those of the tautomeric azo compounds.[5-9] It is interesting, therefore, to re-examine the structures of the products from the autoxidation of phenylhydrazones by spectral methods. In the present work, the autoxidation of several benzaldehyde phenylhydrazones has been carried out at room temperature and in an atmosphere of oxygen. The stability of these products depends largely on the *para* substituents of the benzaldehyde moiety and increases in the following order: $Cl < H \leq CH_3 < OCH_3$. While the *p*-chloro-substituted product often decomposes readily in the process of crystallization, the *p*-methyl-substituted product can be recrystallized from benzene and stored at 0° for several hours. The *p*-methoxy-substituted product decomposes very slowly at room temperature; it can be stored at about 0° for several weeks without decomposition. These products have been taken for the spectral study of their chemical structures.

Yao and Resnick[5] reported that the ultraviolet absorption spectra of phenylhydrazones differ from those of the phenylazo compounds obtained from the coupling of benzenediazonium ion to α-substituted acetoacetanilides and acetoacetic acid esters. The former have a weak band at 285 to 295 mμ and a stronger band at wave length longer than about 320 mμ. The latter, which have a phenylazo group attached to an aliphatic carbon, show a characteristic band at 270 to 280 mμ.[5,7]

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[1] To whom communications should be sent: Scientific Laboratory, Ford Motor Co., Dearborn, Mich.

[2] M. Busch and N. Dietz, *Ber.*, **47**, 3281 (1914).

[3] K. H. Pausacker, *J. Chem. Soc.*, 3478 (1950).

[4] R. Criegee and G. Lohans, *Ber.*, **84**, 219 (1951).

[5] H. C. Yao and P. Resnick, *J. Am. Chem. Soc.*, **84**, 3514 (1962).

[6] H. H. Szmant and H. J. Planinsek, *ibid.*, **72**, 4042 (1950); E. E. Lockhart, M. C. Merritt, and C. D. Mead, *ibid.*, **73**, 858 (1951).

[7] D. C. Iffland, L. Salisbury, and W. R. Schafer, *ibid.*, **83**, 747 (1961).

[8] D. L. Ross and J. J. Chang, *J. Org. Chem.*, **29**, 2024 (1964).

[9] H. C. Yao, *ibid.*, **29**, 2959 (1964).