TABLE IV

RATES OF SOLVOLYSIS AND PER CENT ELIMINATION AT 25° FOR HEXYL TOSYLATES IN TRIFLUOROACETIC ACID[a]

Reactant	$k \times 10^4$ sec.$^{-1}$	Elimination, %
2-Hexyl tosylate	1.92 (2.2)	87.5 (83.5)
3-Hexyl tosylate	8.54 (7.5)	80.9 (84)

[a] Values were determined by hydrogenation; the values in parentheses were previously determined (gas chromatographic) from ref. 9.

constant (zero order in alkene concentration) until hydrogenation was almost complete, suggesting that, if the solvolysis of a tosylate in trifluoroacetic acid were carried out under hydrogenation conditions, the alkene product might be reduced essentially as fast as it was formed. Hydrogenation did, in fact, occur as expected provided freshly prepared tosylates were used. A first-order plot of the hydrogen uptake is shown in Fig. 2 for the hydrogenation of 3-hexyl tosylate. A single experiment yields both the rate constant for tosylate solvolysis and the per cent elimination. Results for the hexyl tosylates are given in Table IV. These reasonably precise results are in agreement with approximate values previously determined by a gas chromatographic method.

It is noteworthy that the sulfur-containing tosylates do not poison the catalyst. A slightly discolored tosylate which had stood at room temperature for several days did poison the catalyst, however, probably because traces of polymer were present as a result of an elimination reaction followed by acid-catalyzed polymerization. Traces of pyridine in the tosylate samples were also suspected of causing anomalous hydrogenation behavior.[10]

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[10] P. E. Peterson and R. E. Kelly, Jr., unpublished work.

Terminal Benzoylation of Certain β-Keto Sulfones to Form Diketo Sulfones by Means of Sodium Hydride. Dibenzoylation of Dimethyl Sulfone[1]

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Benzoylations at the methyl groups of benzenesulfonylacetone and methyl phenacyl sulfone were effected with methyl benzoate by means of sodium hydride to form the corresponding terminal derivatives. The twofold terminal benzoylation of dimethyl sulfone to form the corresponding diketo sulfone was accomplished similarly. Sodium hydride appears not to produce initially the dicarbanion of the β-keto sulfone, which is the reactive intermediate in the analogous reaction employing potassium amide.

Benzoylation at the methyl group of benzenesulfonylacetone (I) has previously been accomplished through dicarbanion II, which was prepared by means of two molecular equivalents of potassium amide in liquid ammonia. Thus II condensed with methyl benzoate to form the terminal derivative III.[2]

$C_6H_5SO_2CH_2COCH_3$ I

$C_6H_5SO_2\bar{C}HCO\bar{C}H_2$ II

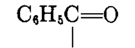
$C_5H_5SO_2CH_2COCH_2COC_6H_5$ III

Benzoylations at the methyl groups of keto sulfones I and IV have now been realized by means of sodium hydride in refluxing 1,2-dimethoxyethane (monoglyme) even though this reagent may not produce dicarbanions as intermediates.

$C_6H_5COCH_2SO_2CH_3$ IV

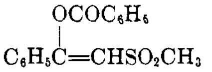
$C_6H_5COCH_2SO_2CH_2COC_6H_5$ V

The product from I was identified as methyl derivative III by comparison with an authentic sample prepared through II.[2] By analogy, the product from the benzoylation of IV was expected to be its methyl derivative V, not the possible methylene derivative VI or VII. In agreement with this, the product failed to give a positive enol test with ethanolic ferric chloride indicating that it was not VI, and its infrared spectrum was consistent with V, not VII. Its spectrum showed a band at 1690 cm.$^{-1}$ for the carbonyl group[3] and bands at 1330 and 1145 cm.$^{-1}$ for the sulfonyl group.[4] Had the product been the possible methylene derivatives VI, it should have given a positive enol test since VI is a β-diketone having an α-hydrogen; had the product been enol benzoate VII, it should have shown an infrared spectrum somewhat different from that observed.



$$\begin{array}{c} C_6H_5C{=}O \\ | \\ C_6H_5COCHSO_2CH_3 \end{array}$$

VI



$$\begin{array}{c} OCOC_6H_5 \\ | \\ C_6H_5C{=}CHSO_2CH_3 \end{array}$$

VII

Structure V was confirmed by its n.m.r. spectrum, which showed besides the aromatic proton resonance (intensity = 10) only a single peak located at τ 5.02 (intensity = 4), indicative of two identical methylene groups. No peak was observed in the region that may be ascribed to a terminal methyl group as in structure VI or VII. The n.m.r. spectrum of the parent compound IV showed peaks at τ 5.37 and 6.89, which were assigned to the methylene and methyl groups, respectively.[5]

The yields of diketo sulfones III and V from keto sulfones I and IV were 55 and 78%, respectively. The yield of III by the earlier potassium amide method was 60% based on the ester but the per cent conversion of I to III was only 30%.[2]

Since sodium hydride was found to effect the benzoylation of not only keto sulfone IV to form V but also of

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[1] Supported by the National Institutes of Health.

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

[3] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 134.

[4] See ref. 3, p. 360.

[5] H.-D. Becker and G. B. Russell, *J. Org. Chem.*, **28**, 1896 (1963).

TABLE I

BENZOYLATIONS OF KETO SULFONES AND DIMETHYL SULFONE WITH METHYL BENZOATE BY MEANS OF SODIUM HYDRIDE IN MONOGLYME

Starting sulfone	Mole	Ester, mole	NaH, mole	Monoglyme, ml.	Time, hr.	Product, number	M.p., °C.	Yield, %
Benzenesulfonylacetone	0.05	0.075	0.25	200	5	III	144–146[a]	low
	0.05	0.075	0.25	200	17	III	144–146[a]	55
Methyl phenacyl sulfone	0.02	0.03	0.08	100	5	V	124–125	78
Dimethyl sulfone	0.1	0.1	0.2	300	4	IV	107–108.5[b]	67
	0.2	0.2	0.4	300	9	IV	107–108.5[b]	83
Dimethyl sulfone	0.05	0.15	0.3	200	5	V	124–125	66
	0.1	0.25	0.5	200	19	V	124–125	87

[a] Lit.[2] m.p. 145–146.5°. [b] Lit. m.p. 106–107°[5] and 107.5–108°.[6]

TABLE II

HYDROGEN EVOLVED ON ADDITION OF KETO SULFONES TO SODIUM HYDRIDE IN MONOGLYME AND ON SUBSEQUENT ADDITION OF METHYL BENZOATE

	H_2 from addition of keto sulfone			H_2 on subsequent addition of ester				
							Reaction period	
Keto sulfone	Calcd. for 1 mol. equiv., ml.	Found, ml.	% of theory	Calcd. for 2 molecular equiv., ml.	Found, ml.	% of theory	Time,[a] hr.	Half-time,[b] min.
Benzenesulfonylacetone	1121	979	87	2242	2160	97	44	420
Methyl phenacyl sulfone	1121	1080	96	2242	2116	94	17	45

[a] This is the period of hydrogen evolution after ester had been added. [b] This period has been approximated from the periodic readings.

dimethyl sulfone to give IV, this reagent was expected to bring about twofold benzoylation of dimethyl sulfone to afford V in a single experiment. Dibenzoylation was realized to produce V in 87% yield (eq. 1); this method is recommended for the synthesis of V (see Table I).

$$CH_3SO_2CH_3 + 2C_6H_5COOCH_3 \xrightarrow[\text{2. acid}]{\text{1. NaH (excess)}} \mathrm{V} \qquad (1)$$

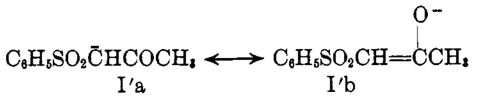
Dimethyl sulfone has previously been benzoylated with methyl benzoate by sodium in benzene[6] and by potassium *t*-butoxide in dimethyl sulfoxide[5] to form IV in yields of 44 and 90%, respectively. Our yield of IV with sodium hydride was 83%.

The terminal benzoylations of keto sulfones I and IV by sodium hydride are rather remarkable since excess of this reagent appears to effect ionization of only a methylene hydrogen of I or IV, not both a methylene and methyl hydrogen as observed with excess potassium amide.[2] Thus, only one molecular equivalent of hydrogen was evolved from I or IV in the presence of four molecular equivalents of sodium hydride in refluxing monoglyme. However, two more equivalents of hydrogen were evolved when methyl benzoate was subsequently added (see Table II). These results indicate that I or IV is converted initially only to its monocarbanion, for example, IV′, and that a methyl hydrogen of IV′ is gradually removed as a proton[7] as the condensation proceeds with the ester; a methylene hydrogen of the resulting monocarbanion of the condensation product is evidently ionized to form the dicarbanion of the product (Scheme A).

SCHEME A

$$\begin{tikzcd} \mathrm{IV} \arrow[r, "\mathrm{NaH}", "\mathrm{excess}"'] & C_6H_5CO\bar{C}HSO_2CH_3 + H_2 \\ & \mathrm{IV}' \arrow[d, "C_6H_5COOCH_3"] \\ \mathrm{V} & C_6H_5CO\bar{C}HSO_2\bar{C}HCOC_6H_5 + 2H_2 \arrow[l, "\mathrm{acid}"'] \end{tikzcd}$$

The fact that monocarbanion IV′ undergoes benzoylation more readily than monocarbanion I′a–b (see Tables I and II) is not surprising since, whereas the methyl hydrogens of IV′ are activated by the sulfone group, the methyl hydrogens of I′a–b should be deactivated somewhat by resonance form I′b.



$$\underset{\mathrm{I'a}}{C_6H_5SO_2\bar{C}HCOCH_3} \longleftrightarrow \underset{\mathrm{I'b}}{C_6H_5SO_2CH{=}\overset{O^-}{\overset{|}{C}}CH_3}$$

Experimental[8]

Benzoylations of Keto Sulfones and Dimethyl Sulfone.—To a stirred slurry of sodium hydride[9] in monoglyme at reflux, under dry nitrogen, was added a solution of the appropriate sulfone and methyl benzoate in 1,2-dimethoxyethane (monoglyme) over a period of *ca.* 20 min. Refluxing was continued for an appropriate period, and most of the solvent was then removed under reduced pressure. The resulting paste was cooled in an ice–water bath, and 150 ml. of ether was added. After stirring the mixture, 150 ml. of cold water was added; initially, the water was added dropwise until the excess sodium hydride was destroyed. The layers were separated. The ethereal layer was extracted with three 100-ml. portions of cold water, and these extracts were combined with the original aqueous layer. To the resulting aqueous solution was added 100 g. of crushed ice followed by 50 ml. of 12 *N* hydrochloric acid. The resulting precipitate was removed by filtration, washed with water, and recrystallized from 95% ethanol. The results are summarized in Table I.

Diketo sulfone III was identified by the mixture melting point method and by comparison of its infrared spectrum with that of an authentic sample of III prepared as described previously.[2]

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(6) W. E. Truce and R. H. Knospe, *J. Am. Chem. Soc.*, **77**, 5063 (1955).

(7) The dicarbanion is not necessarily formed since removal of the proton might be accompanied by simultaneous condensation with the ester in a termolecular mechanism.

(8) Melting points were taken on a Thomas-Hoover "Uni-Melt" which had been calibrated with melting point standards. Infrared spectra were determined with a Perkin-Elmer Infracord, Model 137, by the potassium bromide pellet method. N.m.r. were determined with a Varian A-60 high resolution spectrometer. Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(9) Sodium hydride was obtained from Metal Hydrides, Inc., as an approximately 50% dispersion in mineral oil and was used as received.

A sample of diketo sulfone V (m.p. 124–125°) was analyzed.

Anal. Calcd. for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67; S, 10.61. Found: C, 63.52; H, 4.76; S, 10.54.

Although diketo sulfone IV was known,[4,5] a sample of it (m.p. 107–108.5°) was analyzed.

Anal. Calcd. for $C_9H_{10}O_3S$: C, 54.52; H, 5.08; S, 16.18. Found: C, 54.32; H, 5.04; S, 15.97.

Measurement of Hydrogen Evolution.—In a 500-ml. two-necked flask equipped with a tightly fitting addition funnel (with a pressure equalizing side arm) and an efficient reflux condenser was placed 50 ml. of purified monoglyme and 0.25 mole of sodium hydride.[9] The upper end of the condenser was fitted with a gas take-off which was connected to an American Meter Company wet test meter filled with water. The system was flushed with dry nitrogen, and a solution of 0.05 mole of a β-keto sulfone in 100 ml. of monoglyme was placed in the addition funnel. The system was closed, and the flask was placed on the steam bath. When thermal equilibrium was established, an initial reading was taken on the test meter. The solution in the funnel was then added during 10–12 min. After the solution had been added, readings were taken periodically until the hydrogen evolution ceased. This required 30–40 min. The system was opened, and a solution of 0.075 mole of methyl benzoate in 50 ml. of monoglyme was placed in the addition funnel. The apparatus was closed, equilibrium was established, an initial reading was taken, and the ester solution was added during a period of 5–7 min. Readings were then taken periodically until gas evolution was no longer detectable. The values were corrected for temperature, pressure, and water vapor pressure. The results were summarized in Table II.

Diphenylcyclobutadienoquinone. III.[1] Attempted Synthesis of 1,2-Diphenylcyclobutadiene[2]

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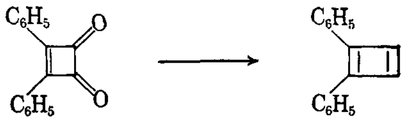
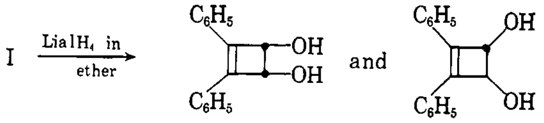
With the object of realizing a synthesis of 1,2-diphenylcyclobutadiene, further study has been made of diphenylcyclobutadienoquinone as a suitable precursor. Lithium aluminum hydride reduction of this diketone in ether gives mainly *cis*-1,2-diphenylcyclobutene-3,4-diol (23%) as well as some (3%) of the corresponding *trans*-diol. Reaction of the *cis*-diol with phosphorus tribromide affords smoothly (73%) *cis*-3,4-dibromo-1,2-diphenylcyclobutene. All efforts to prepare and isolate (or trap) the desired cyclobutadiene *via* debromination of the *cis*-dibromide with lithium amalgam, zinc dust, or nickel carbonyl have given only intractable polymeric organic products. Infrared studies of the *cis* and *trans* isomers of 1,2-diphenylcyclobutene-3,4-diol suggest that in the *cis*-1,2-diol there is intramolecular OH · · · π-electron hydrogen bonding with the cyclobutene double bond. Evidence that similar hydrogen bonding obtains for the *trans*-diol as well is not conclusive.

A considerable effort has been made in recent years by many investigators to prepare and isolate, or trap, *bona fide* cyclobutadienes. With diphenylcyclobutadienoquinone (I) readily available in the Cornell Laboratories,[1b] studies of this diketone as a precursor for the possible synthesis of 1,2-diphenylcyclobutadiene (II) were encouraged. The present report presents results of these investigations that supplement those presented earlier.[1b] In particular, this article describes efforts to realize the diene II *via* debromination of 3,4-dibromo-1,2-diphenylcyclobutene. Since this approach to a cyclobutadiene, *i.e.*, dehalogenation of 3,4-dihalo-1-cyclobutenes, has been widely and successfully used by many investigators to prepare cyclobutadienes *transiently*,[4] the method merited consideration for specific application to the 1,2-diphenyl-1-cyclobutene system.



I II

Lithium aluminum hydride reduction of the dione I in solvent ether gave *cis*-1,2-diphenylcyclobutene-3,4-diol (III), m.p. 135.5–136.5°, in 23% yield, and the corresponding *trans*-diol IV (3%), as well as products from expected ring-opening side reactions.[5] Only the *trans*-diol IV (5.5%), m.p. 183–184.5°, was formed upon $LiAlH_4$ reduction in tetrahydrofuran.[7] The two diols showed the following ultraviolet absorption maxima: the *cis*-diol III at 227 (ε 16,500) and 292 mμ (12,000); the *trans*-diol IV at 228 (ε 15,800) and 292 mμ (12,500). Unlike *cis*-tetramethylcyclobutenediol,[8]



III (23%)
m.p. 135.5–136.5°

IV (3%)
m.p. 183–184.5°

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[1] (a) For the preceding paper in this series, see A. T. Blomquist and P. R. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962). (b) For papers closely related to this study, *i.e.*, "Diphenylcyclobutadienoquinone I and II," see A. T. Blomquist and E. A. LaLancette, *ibid.*, **83**, 1387 (1961), and **84**, 220 (1962).

[2] For preliminary portions of this study, see (a) Abstracts of Papers, the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 54-0; (b) Abstracts of Papers, presented at the 16th National Organic Chemical Symposium of the American Chemical Society, Seattle, Wash., June 15-17, 1959, p. 11.

[3] Supported by funds from the Sage Fellowship, summer, 1957; Procter and Gamble Fellow, summer, 1958; American Cyanamid Fellow, summer, 1959; Allied Chemical and Dye Fellow, 1959-1960.

[4] R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959); M. Avram, E. Marica, and C. D. Nenitzescu, *Chem. Ber.*, **92**, 1088 (1959); M. Avram, E. Marica, J. Pogany, and C. D. Nenitzescu, *Angew. Chem.*, **71**, 626 (1959); C. D. Nenitzescu and M. Avram, *ibid.*, **72**, 39 (1960); M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957); C. D. Nenitzescu, M. Avram, and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957); M. Avram, D. Dinu, and C. D. Nenitzescu, *Chem. Ind.* (London), 257 (1959); M. Avram, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **93**, 1789 (1960).

[5] Reaction of the compound I with aqueous methanolic sodium hydroxide results in cleavage of the cyclobutene ring to give, as isolable products, benzaldehyde and α-keto-βγ-diphenyl-γ-butyrolactone. Similarly, ring cleavage occurs in the reaction of the diketone I with *o*-phenylenediamine to produce 3-phenylacetyl-2-phenylquinoxaline.[1b] The reduction of the related phenylcyclobutadienoquinone with either sodium borohydride or lithium aluminum hydride is reported[6] to yield intractable products. See also M. P. Cava, D. R. Napier, and R. J. Pohl, *J. Am. Chem. Soc.*, **85**, 2076 (1963).

[6] J. D. Roberts, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **17**, 104 (1956).

[7] Oily products obtained in the reductions were not characterized. However, both reductions afforded a solid crystalline accessory product of m.p. 196-197°, having λ_{max}^{KBr} 5.95 μ and indicative of the occurrence of ring opening.

[8] R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957).