use of the *changes* in moments of inertia[6] with substitution of ^{15}N for ^{14}N gives $d_{NN} = 1.228$ Å. The assignments of Table I are thus strikingly consistent with the assumption of a cyclic structure for diazirine. Interatomic distances and angles as derived from the data in Table II are given in Table III.

TABLE III

MOLECULAR PARAMETERS OF DIAZIRINE[a]

$d_{NN} = 1.228 \pm 0.003$ Å.	$d_{CH} = 1.09 \pm 0.02$ Å.
$d_{CN} = 1.482 \pm 0.003$ Å.	$\angle HCH = 117° \pm 2°$
$\chi_{CC} - \chi_{BB} = 6.2 \pm 0.3$ Mc.	$\lvert\chi_{AA}\rvert < 1.0$ Mc.
$\mu = 1.59 \pm 0.06$ Debye	

[a] The structural parameters d_{CN} and d_{NN} are so-called r_s parameters[7] since they were obtained by using only *isotopic shifts* in the *moments* of *inertia*.

The small quadrupole moment of the nitrogen (^{14}N) nucleus makes difficult the task of resolving hyperfine structure in the rotational spectrum of H_2CN_2 and $H_2{}^{13}CN_2$. The problem is much simpler for $H_2C^{14}N^{15}N$ which contains only one quadrupolar nucleus. From the observed Q-branch splittings for this species, we find $\chi_{CC} - \chi_{BB} = 6.2 \pm 0.3$ Mc. The $1_{01} \leftarrow 0_{00}$ transition depends only on the quadrupole coupling parameter χ_{AA}. We found it impossible to resolve any hyperfine structure in the $1_{01} \leftarrow 0_{00}$ transition for any of the three isotopic species. From observed line widths (0.5 Mc.) we conclude that $\lvert\chi_{AA}\rvert < 1$ Mc.

From Stark effect measurements on the $M = 4$ and $M = 3$ Stark components of the $4_{22} \leftarrow 4_{23}$ transitions of the common isotopic species of diazirine, we find the dipole moment to be 1.59 ± 0.06 *D*. The rather large error assigned to the dipole moment is a result of the fact that quadrupole coupling effects make difficult the measurement of Stark shifts.

Acknowledgments.—We are very grateful to Dr. W. H. Graham for providing the sample of diazirine used in this work, and to Bro. C. R. Nelson and Fr. Cyprian Flanagan for their valuable assistance in certain aspects of the experimental work. Support for this research was provided by the National Science Foundation.

(6) The rotational isotope effect is fully discussed for asymmetric rotor molecules in the rigid rotor approximation by J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).

(7) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

(8) Alfred P. Sloan Foundation Fellow.

(9) Recipient, DuPont Teaching Assistant Award 1961–1962.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA
LOUIS PIERCE[8]
SR. VICTOR DOBYNS[9]

RECEIVED MAY 14, 1962

AUTOXIDATION AND CONDENSATION REACTIONS OF CARBANIONS IN DIMETHYL SULFOXIDE SOLUTION[1]

Sir:

A recent communication by Corey and Chaykovsky,[2] concerning the methylsulfinyl carbanion and its reactions, prompts us to report some results concerning the autoxidation of carbanions in dimethyl sulfoxide solution—a study which has led to an investigation of condensation and addition reactions involving dimethyl sulfoxide. Although solutions of alkoxides in dimethyl sulfoxide react with oxygen yielding dimethyl sulfone and methanesulfonic acid, mixtures of dimethyl sulfoxide and *t*-butyl alcohol are stable to oxygen at room temperature in the presence of potassium *t*-butoxide. In these solutions (DMSO–*t*-BuOH–*t*-BuO^-) a number of hydrocarbons can be oxidized easily. In many cases similar oxidations in alcohol or pyridine solutions are not observed.

TABLE I

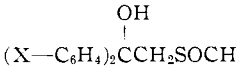
AUTOXIDATION OF DIARYLMETHANES IN DMSO–*t*-BuOH–*t*-BuO^- SOLUTION AT 25°

Diarylmethane, mmole	*t*-BuOK, mmole	Time, min.	mmole O_2	Product, mmole
Diphenylmethane, 3.0	6.3[a]	10	5.1	Benzhydrol, 1.8
Diphenylmethane, 3.0	15[a]	120	9.6	I, X = H, 1.9
Fluorene, 3.2	6.0[b]	0.5	3.0	I,[c] 2.4
Xanthene, 3.1	6.0[b]	2.5	4.2	Xanthone, 3.1
9,10-Dihydroanthracene, 3.2	9.0[d]	5	6.5	Anthracene, 2.35

[a] 35 ml. of 80–20 DMSO–*t*-BuOH. [b] 25 ml. of solvent. [c] M.p. 155.5–156.5°. [d] 50 ml. of solvent.

Triphenylmethane reacts with oxygen under these conditions to form triphenylcarbinol. Triphenylmethane (3.14 mmole) in 25 ml. of vigorously shaken 80–20 DMSO–*t*-BuOH solution containing 6 mmole of potassium *t*-butoxide absorbed 3.2 mmole of oxygen (740 mm.) in 20 minutes (2.6 mmole in two minutes) to yield 3.0 mmole of triphenylcarbinol. In the absence of oxygen, triphenylmethane-*d* lost 53% of its deuterium in five minutes at 25° even though the color of the triphenylmethide ion could not be detected as it can be in the absence of the *t*-butyl alcohol.

Diarylmethanes are oxidized readily under similar conditions to either the alcohol, the ketone or the dimethyl sulfoxide adduct of the ketone (I).



$$(X{-}C_6H_4)_2\overset{\displaystyle OH}{\overset{|}{C}}CH_2SOCH_3 \quad \text{I}$$

The oxidation of fluorene in *t*-butyl alcohol–*t*-butoxide solution is strongly catalyzed by nitrobenzene or 1,3-dinitrobenzene (3 mole %). In the absence of oxygen the nitrobenzene radical anion[3] can be detected by e.s.r. These results strongly support the concept that the oxidation of fluorene and the other arylmethanes is a radical process.[4]

Substituted toluenes ($CH_3{-}C_6H_4{-}X$, X = $SO_2C_6H_5$, CO_2CH_3, COC_6H_5, $COOCH_3$, CN, $N{=}NC_6H_5$, SOC_6H_5, NO_2) and a variety of *o*-, *m*- and *p*-substituted anilines readily undergo base-promoted autoxidation in dimethyl sulfoxide solution at room temperature whereas, with the exception of *p*-nitrotoluene, these compounds are stable to oxygen in *t*-butyl alcohol–*t*-butoxide solutions. The oxidations of phenyl *p*-tolyl sulfone and methyl *p*-toluate have been studied in more detail and are considered as representative of the other substituted toluenes except for *p*-nitrotoluene.[5]

(1) Reactions of Resonance Stabilized Anions. II.

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

(3) D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960); R. L. Ward, *ibid.*, **83**, 1296 (1961).

(4) See, however, Y. Sprinzak, *ibid.*, **80**, 5449 (1958).

(5) See G. A. Russell, Abstracts of Papers, 17th National Organic Chemistry Symposium, Bloomington, Ind., 1961, p. 71.

In DMSO–*t*-BuOH–*t*-BuO⁻ solutions these compounds are oxidized to mixtures of the carboxylic acid and stilbene. Representative data for phenyl *p*-tolyl sulfone are given in Table II.

TABLE II

AUTOXIDATION OF PHENYL *p*-TOLYL SULFONE IN 80–20 DIMETHYL SULFOXIDE–*t*-BUTYL ALCOHOL SOLUTIONS AT 25°[a]

O_2 absorbed,[b] mmole	Time, min.	$C_6H_5SO_2$-$C_6H_4CO_2H$, mmole	($C_6H_5SO_2$-C_6H_4CH=)$_2$, mmole	Dimer/acid
11.8	230	2.96 (60%)	0.87 (33%)	0.55
9.0	120[c]	2.40 (48%)	1.18 (48%)	1.0
[d]	120	3.74 (75%)	0.30 (12%)	0.16
11.2[e]	278	3.14 (62%)	0.70 (28%)	0.45

[a] 5.0 mmole sulfone, 10 mmole potassium *t*-butoxide in 30 ml. of solvent. [b] 740 mm. [c] Base added slowly over 25 min. to the oxidizing solution. [d] 3 atm. of oxygen pressure. [e] Slow stirring in an oxygen atmosphere, all other experiments were performed with good agitation.

Aniline (3.0 mmole) in 25 ml. of 80–20 DMSO–*t*-BuOH containing 6 mmole potassium *t*-butoxide absorbed 3.0 mmole of oxygen in 1 hour to give azobenzene, m.p. 67–68° in 87% yield. Similarly, these anilines gave good yields of azobenzenes, isolated by chromatography: *o*-chloroaniline, *m*-chloroaniline, *p*-chloroaniline, *o*-aminobiphenyl, *p*-aminodiphenyl sulfide and *p*-bromoaniline.

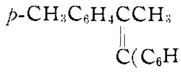
We are studying the mechanism of stilbene and azobenzene formation by the use of appropriately labeled intermediates to ascertain whether these materials result from a base-catalyzed condensation involving aldehyde or the nitroso compound. Alternately, they may result from the dehydrogenation of the bibenzyls and hydrazobenzenes arising from the coupling of benzyl or anilino radicals.

Under the reaction conditions in DMSO–*t*-BuOH–*t*-BuO⁻ a wide variety of condensation reactions readily occur. Nitrosobenzene and aniline rapidly form azobenzene and stilbenes are formed by condensation of benzaldehydes with toluenes containing acid-strengthening substituents.

$$Y{-}C_6H_4CH_3 + X{-}C_6H_4CHO \longrightarrow Y{-}C_6H_4CH{=}CHC_6H_4X \quad (II)$$

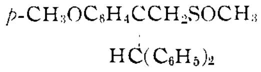
Phenyl *p*-tolyl sulfone (2.5 mmole) in 18 ml. of DMSO–*t*-BuOH containing 5 mmole of potassium *t*-butoxide was allowed to react with an excess of benzaldehyde (10 mmole) for 30 minutes. Addition of water yielded 1.0 mmole of II (X = H, Y = *p*-$C_6H_5SO_2$) (40%), m.p. 184–185°.[6] In a similar manner the stilbenes also have been prepared from phenyl *p*-tolyl sulfone and *p*-anisaldehyde, m.p. 202–203°, 32% yield; *p*-dimethylaminobenzaldehyde, m.p. 250–251°, yellow crystals, 11% yield and piperonal, m.p. 188°, 6% yield.

Attempts to condense diphenylmethane with benzaldehydes under similar conditions gave mainly recovered diphenylmethane. However, at 60° in the absence of *t*-butyl alcohol, *p*-anisaldehyde (5 mmole) and diphenylmethane (5 mmole) in 20 ml. of DMSO containing 10 mmole of potassium *t*-butoxide (sublimed) under a nitrogen atmosphere gave after 1.5 hours 62% of III, m.p. 103–104°, and 22% of IV, m.p. 178°.



$$p\text{-}CH_3C_6H_4\overset{\displaystyle CCH_3}{\underset{\displaystyle C(C_6H_5)_2}{\|}}$$

III



$$p\text{-}CH_3OC_6H_4\underset{\displaystyle HC(C_6H_5)_2}{C}CH_2SOCH_3$$

IV

The formation of III, a novel olefin synthesis involving an asymmetric three carbon condensation, proceeds by the steps 1–5, each of which has been observed separately (R = *p*-$CH_3OC_6H_4$-, B = *t*-BuOK in dimethyl sulfoxide).

(1) Addition of dimethyl sulfoxide to the aldehyde

$$RCHO + CH_3SOCH_3 \xrightarrow[10\text{ min.}]{30°,\ B} RCHOHCH_2SOCH_3\text{, m.p. 126–127°, 25\%}$$

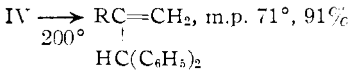
(2) Dehydration of the adduct to an unsaturated sulfoxide

$$RCHO + CH_3SOCH_3 \xrightarrow[1.5\text{ hr.}]{60°,\ B} RCH{=}CHSOCH_3\text{, m.p. 67–68°, 47\%}$$

(3) Michael addition of diphenylmethane

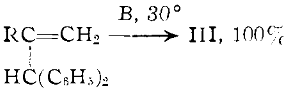
$$(C_6H_5)_2CH_2 + RCH{=}CHSOCH_3 \xrightarrow[1\text{ hr.}]{30°,\ B} \text{IV, 23\%}$$

(4) Elimination of CH_3SOH from IV[7]



$$\text{IV} \xrightarrow[200°]{} \underset{\displaystyle HC(C_6H_5)_2}{RC}{=}CH_2\text{, m.p. 71°, 91\%}$$

(5) Rearrangement of the terminal olefin[8]



$$\underset{\displaystyle HC(C_6H_5)_2}{RC}{=}CH_2 \xrightarrow{B,\ 30°} \text{III, 100\%}$$

Our results indicate that the reaction of an active methylene compound with an aldehyde in *t*-BuOK–DMSO solution will proceed *via* the aldehyde–dimethyl sulfoxide adduct if the acidic methylene compound is a very weak acid, but when a more acidic methylene compound is used direct condensation between the aldehyde and the active methylene compound occurs. Attempts to bring about similar condensations using diaryl ketones in place of benzaldehydes have so far given only I, regardless of the nature of the methylene group.

This study was supported by the Air Force Office of Scientific Research and by a Grant from the Petroleum Research Fund, administered by the American Chemical Society.

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(6) Satisfactory elemental analyses and consistent n.m.r. and infrared spectra have been obtained for all new compounds mentioned.

(7) See C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).

(8) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961); A. Schriesheim, J. E. Hofmann and C. E. Rowe, *ibid.*, **83**, 3731 (1961).

(9) Alfred P. Sloan Foundation Fellow.

DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY
AMES, IOWA

GLEN A. RUSSELL[9]
EDWARD G. JANZEN
HANS-DIETER BECKER
FRANK J. SMENTOWSKI

RECEIVED JUNE 8, 1962

HARUNGANIN: A CRYSTALLOGRAPHIC DETERMINATION OF AN UNKNOWN STRUCTURE

Sir:

We have isolated from the bark of *Harungana madagascariensis* (Guttiferae) a new orange phenolic pigment which we have named harunganin. Combustion analyses pointed to the formula C_{29-30}-