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.

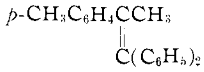
We are studying the mechanism of stilbene and azobenzene formation by the use of appropriately labeled intermediates to ascertain whether these materials result from a base-catalyzed condensation involving aldehyde or the nitroso compound. Alternately, they may result from the dehydrogenation of the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

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

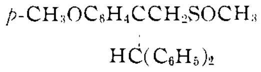
Phenyl p-tolyl sulfone (2.5 mmole) in 18 ml. of DMSO–t-BuOH containing 5 mmole of potassium t-butoxide was allowed to react with an excess of benzaldehyde (10 mmole) for 30 minutes. Addition of water yielded 1.0 mmole of II (X = H, Y = p-$C_6H_5SO_2$) (40%), m.p. 184–185°.[6] In a similar manner the 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°.



$$p\text{-}CH_3C_6H_4C(CH_3){=}C(C_6H_5)_2$$

III



$$p\text{-}CH_3OC_6H_4CH(CH_2SOCH_3)CH(C_6H_5)_2$$

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

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

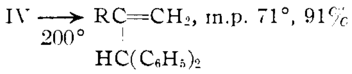
(2) Dehydration of the adduct to an unsaturated sulfoxide

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

(3) Michael addition of diphenylmethane

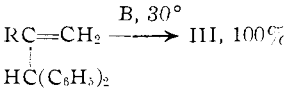
$$(C_6H_5)_2CH_2 + RCH{=}CHSOCH_3 \xrightarrow[1\text{ hr.}]{30°,\ B} \text{IV},\ 23\%$$

(4) Elimination of CH_3SOH from IV[7]



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

(5) Rearrangement of the terminal olefin[8]



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

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).

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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}-

$H_{34-6}O_4$,[1] but attempts to prepare derivatives led to complex mixtures of products.

Good single crystals of harunganin were grown by slow crystallization from methylene chloride-cyclohexane. These were monoclinic needles, cell dimensions: a = 32.90 Å., b = 9.30 Å., c = 17.80 Å., β = 101° 17′; and from the systematic extinctions belonged to one of the space groups Cc or C2/c. The density (1.150) indicated the presence of eight molecules of molecular weight 464, definitely favoring the formula $C_{30}H_{36}O_4$ (460.6).

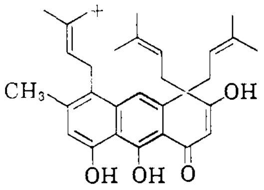
Data were collected on a G.E. counter diffractometer, 5821 reflections being scanned with 3086 measurably above background, and a three-dimensional sharpened Patterson function was calculated.

Patterson superpositions were at first based on C2/c symmetry and revealed the presence of several six-membered rings in harunganin, but the apparent molecules consistently approached each other too closely. Since the symmetry operations of Cc form a subset of those of C2/c, later superpositions were therefore based on Cc in the expectation that any higher symmetry would be revealed in the final structure. However, two molecules (68 non-hydrogen atoms) instead of only one had then to be located in the asymmetric unit of the superposition map.

Repeated superpositions and extensive testing of individual atoms revealed first one and then a second anthracene-like skeleton of six-membered rings, together with some of the atoms joined directly to the rings, 36 atoms in all. Structure factors were calculated using these and examination of a three-dimensional Fourier synthesis based on the calculated phases showed the location of thirty more side chain atoms. One more round of structure factor calculations and Fourier synthesis revealed the last two atoms of the 68. At this point, the asymmetric unit appeared to consist of two identical molecules related by the additional symmetry of C2/c, and subsequent calculations were therefore performed in this space group. Refinement by full-matrix least squares,[2] identified the oxygen atoms through the behavior of their individual temperature factors, and showed the molecular structure to be I.

When anisotropic temperature factors were introduced, it was found that one of the side chain methyl groups (starred in I) showed excessive anisotropy (r.m.s. amplitudes of vibration along the principal axes, 0.76, 0.28, and 0.42 Å.). Such behavior was found to be consistent with a crystal structure in which the side chain may lie in two slightly different positions in the cell. Despite extensive investigation, it is not yet possible to say whether this represents a slight randomization of a C2/c structure or whether harunganin in fact crystallizes in a very nearly centrosymmetric Cc form.

At the present stage of refinement, the residual index R is 11.9% on the observed reflections. The bond lengths found indicate that the predominant direction of enolization of the β-diketone system is as shown in I, but it appears possible from the packing that it is not the same in all molecules.



I

The structure of harunganin, although highly unusual, is not without analogy. *gem*-Diisopentenyl substitution on phenolic precursors also has been found in the hop principle lupulon.[3] Furthermore, in view of the close botanical relationship of *Harungana* and the genus *Hypericum*, it is of interest that both harunganin and hypericin[4] are based on emodin related skeletons.

Acknowledgments.—This work was supported in part by grants from the National Institutes of Health and by generous gifts of computer time from the Research Computer Laboratory of the University of Washington.

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(1) Harunganin has been isolated independently by Dr. Walter C. Taylor, University of Sydney, who kindly communicated his findings to us.

(2) A Crystallographic Least Squares Refinement Program for the IBM 704. W. R. Busing and H. A. Levy, Oak Ridge National Laboratory, 1959.

(3) M. Verezele and F. Govaert, *Bull. soc. chim. Belg.*, **58**, 432 (1949).

(4) H. Brockmann, E. H. F. v. Falkenhausen, R. Neeff, A. Dorlars and G. Budde, *Ber.*, **84**, 865 (1951).

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RECEIVED MAY 14, 1962

A NEW SYSTEM OF STABLE FREE RADICALS[1]

Sir:

We wish to report the first members in a series of complex free radicals, stable at ambient temperatures, containing only boron and chlorine. The first has been completely characterized by analysis, molecular weight determinations and the electron spin resonance spectrum as $B_{12}Cl_{11}$. The second has been obtained so far in quantities too small for adequate characterization but has a composition in the range $(B_{1.0}Cl_{0.9-1.1})_x$ and a molecular weight in the range from 650–750.

Both of the new radicals are formed in the spontaneous disproportionation of diboron tetrachloride.

Other volatile materials formed in this disproportionation are boron trichloride, tetraboron tetrachloride in trace quantities, and a moderate amount of a clear yellow solid slightly volatile at room temperature *in vacuo*. A refractory white solid having the composition $(B_{1.0}Cl_{0.6})_x$ also is formed.

The radical $(B_1Cl_{0.9-1.1})_x$ is a dark purple crystalline solid, volatile at 45° *in vacuo*, melting sharply at 185°. It exhibits a broad paramagnetic resonance absorption resolved into four lines centered at a g value of 2.034 with a breadth of approximately 50 gauss between outermost points of extreme slope.

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(1) The research herein reported was supported by the Public Health Service under a National Institutes of Health grant.