Anal. Calcd. for $C_8H_6N_4O_3$: C, 46.61; H, 2.93. Found: C, 46.53; H, 3.10.

2,4-Dihydroxy-6-cyanopyrido[2,3-*d*]pyrimidine (9). Method A.—Four grams (19.4 mmoles) of **27** in 200 ml. of phosphorus oxychloride was refluxed for 8 hr. After cooling to 0° a tan solid separated which was collected and washed with acetone and ether, 2.75 g. (75%). The analytical sample was recrystallized from water, m.p. 353–355° dec. Pertinent infrared bands were at 4.51, 5.85, and 5.97 μ.

Anal. Calcd. for $C_8H_4N_4O_2$: C, 51.07; H, 2.14; N, 29.78. Found: C, 50.81; H, 2.16; N, 29.42.

Method B.—2-Amino-5-cyano-3-pyridinecarboxamide (**8**, 0.75 g., 4.6 mmoles) was added to a solution of 0.75 g. of sodium in 60 ml. of absolute ethanol and heated to reflux. Diethyl carbonate (6 ml.) was added slowly with occasional agitation. The reaction mixture was refluxed for 1 hr. and then poured into 400 ml. of water and filtered. Upon acidification with dilute acetic acid and concentration to a volume of 100 ml., 0.6 g. of a yellow solid precipitated which decomposed above 350°. The infrared spectra of samples from methods A and B were identical and a mixture melting point showed no depression.

4-Amino-6-cyanopyrido[2,3-*d*]pyrimidine (28).—One gram (7 mmoles) of **1** in 45 ml. of formamide was heated at 100 ± 5° for 30 min. under nitrogen. As the reaction proceeded, the solution became quite dark. The solution was decolorized, heated briefly to boiling, and filtered. Upon cooling to 20° a yellow-tan solid separated which was collected and washed with water, acetone, and ether (crude yield, 1.5 g., 97%). The crude solid was recrystallized several times from water to yield colorless flakes which decomposed above 335°. Pertinent infrared bands were at 3.00 and 4.47 μ.

Anal. Calcd. for $C_8H_5N_5$: C, 56.13; H, 2.94; N, 40.92. Found: C, 55.88; H, 3.20; N, 40.72.

Reduction of 2-Amino-3,5-dicarbethoxypyridine (10) with Lithium Borohydride in Diglyme.[13]—Three grams (12.3 mmoles) of **10** was added to a stirred solution of 2.1 g. of anhydrous lithium bromide and 0.92 g. of sodium borohydride in 100 ml. of anhydrous diglyme. The mixture was stirred 3 hr. at room temperature under nitrogen. The reaction mixture was then poured into a mixture of ice and 20 ml. of concentrated hydrochloric acid. The clear aqueous solution was adjusted to pH 6 with sodium bicarbonate and was extracted several times with chloroform. The chloroform was extracted once with aqueous bicarbonate. Evaporation of the dried chloroform gave a yellow oil, which upon treatment with 25 ml. of benzene gave 0.91 g. (30%) of a yellow solid. Recrystallization from toluene gave an analytical sample that melted at 145–147°: λ_{max}^{EtOH} for **29**, 251.5 mμ, and for **10**, 273.5 mμ; infrared data (Nujol mull) for carbonyl **10**, 5.83 and 5.88 μ, and carbonyl **29**, 5.94 and 5.99 μ. The analysis corresponded to a dihydro-2-amino-3,5-dicarbethoxypyridine (**29**).

Anal. Calcd. for $C_{11}H_{16}N_2O_4$: C, 54.98; H, 6.71; N, 11.66. Found: C, 54.97; H, 6.89; H, 11.82.

2-Amino-5-aminomethyl-3-pyridinecarboxamide (30).—To a mixture of 150 ml. of dimethylformamide, 40 ml. of concentrated ammonium hydroxide, and 10 ml. of water was added 7.0 g. (43 mmoles) of **8**. Approximately 25 g. of W-4 Raney nickel was added and the mixture was shaken with hydrogen at 60 p.s.i. for 25 hr. After separation of the catalyst, the filtrate was evaporated to dryness under reduced pressure giving 3.25 g. of a gummy solid. Extraction of the catalyst with boiling water gave, after evaporation, an additional 0.70 g. of solid. Recrystallization of the crude product from 2-propanol gave a colorless solid, m.p. 208–215°; total yield was 3.95 g. (55%). An analytical sample was obtained by recrystallization from ethanol–toluene and had m.p. 214–216°, λ_{max}^{water} 251 and 321.5 mμ, λ_{min}^{water} 273 mμ.

Anal. Calcd. for $C_7H_{10}N_4O$: C, 50.60; H, 6.06; N, 33.71. Found: C, 50.58; H, 6.39; N, 33.13.

The Base-Catalyzed Autoxidation of Hydrocarbons in Diphenyl Sulfoxide[1]

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The use of diphenyl sulfoxide (DPSO) as a solvent for the base-catalyzed autoxidation of weak hydrocarbon acids has been investigated. Stability studies indicate that DPSO is much more stable than DMSO in the presence of potassium *t*-butoxide and molecular oxygen. This is attributed to the different types of carbon–hydrogen bonds in the two sulfoxides. It was possible to autoxidize diphenylmethane, toluene, and *o*-xylene in potassium *t*-butoxide–DPSO at 100° at reasonable rates. The rates of oxygen consumption were dependent on the base/hydrocarbon ratio, type of base employed (KO-*t*-Bu *vs.* KOH), and the acidity of the hydrocarbons. The results are consistent with a carbanion-radical autoxidation process.

In the past few years, solvent effects in the base-catalyzed oxidation of acidic hydrocarbons,[2,3] the isomeric picolines,[4] and sulfur compounds[5–7] have been reported. These studies have been carried out in solvents such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), pyridine, and ethers which are all capable of accelerating base-catalyzed reactions.[8,9] Despite these findings, a suitable solvent medium for carrying out the low-temperature anionic oxidation of inert hydrocarbons such as toluene has not been uncovered. This is due to one of two factors: (a) inability of existing solvents to effectively ionize carbon–hydrogen bonds with pK_a values of 50–60, and (b) preferential oxidation of the solvent instead of the hydrocarbon. The present paper summarizes our studies on this problem using molten diphenyl sulfoxide (DPSO) as the solvent.

Results

In order to determine the suitability of DPSO as a solvent for the anionic oxidation of weak hydrocarbon acids, the stability of the solvent to heat, weak bases, and oxygen was determined. DPSO was heated at 80–140° for periods of 2–3 days. Temperature-programmed gas chromatographic analyses on a 2-ft. silicone rubber column indicated that diphenyl sulfide and diphenyl sulfone were not present, thus eliminating the possibility of a disproportionation reaction (eq. 1).

$$2R_2SO \longrightarrow R_2S + R_2SO_2 \qquad (1)$$

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(1) (a) Presented at the Symposium on Selective Oxidation Processes, sponsored by the Petroleum Division, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30–Sept. 4, 1964; (b) for a preliminary communication, see T. J. Wallace, A. Schriesheim, and N. Jacobson, *Chem. Ind.* (London), 1316 (1964).

(2) Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 5449 (1961).

(3) G. A. Russell, *et al.*, *ibid.*, **84**, 4154 (1962); **84**, 2652 (1962), and pertinent references therein.

(4) W. Bartok, D. D. Rosenfeld, and A. Schriesheim, *J. Org. Chem.*, **28**, 410 (1963).

(5) T. J. Wallace and A. Schriesheim, *Tetrahedron Letters*, **No. 17**, 1131 (1963).

(6) T. J. Wallace, H. Pobiner, and A. Schriesheim, *J. Org. Chem.*, **29**, 888 (1964), and pertinent references therein.

(7) T. J. Wallace, N. Jacobson, and A. Schriesheim, *Nature*, **201**, 609 (1964).

(8) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(9) D. J. Cram, *Chem. Eng. News*, **41**, No. 33, 92 (1963).

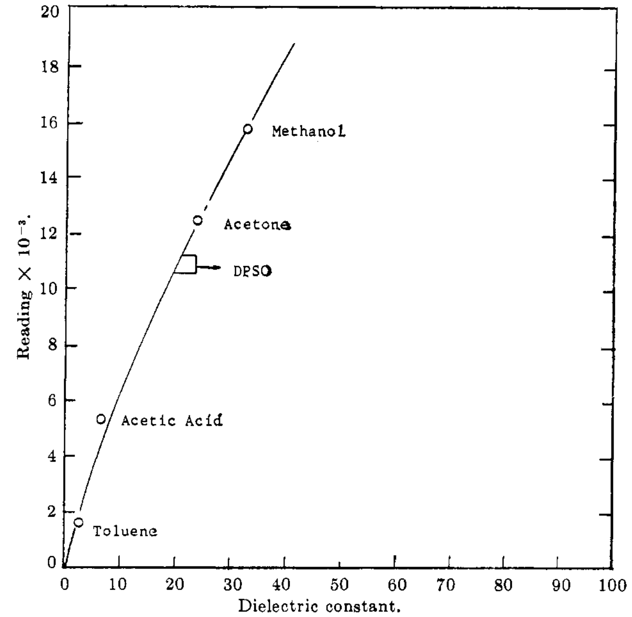


Fig. 1.—Dielectric constant (ε) of DPSO; for determination, see Table VI.

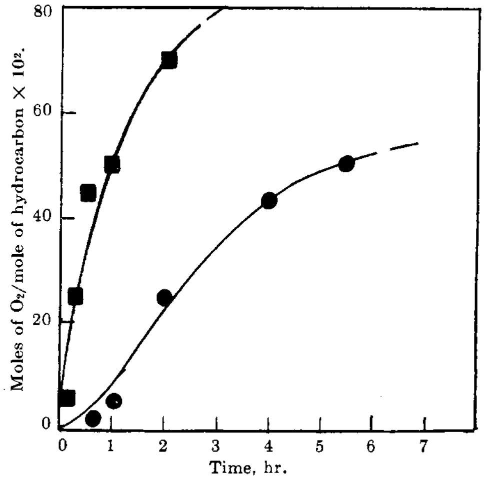
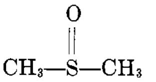
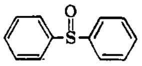


Fig. 2.—Effect of base–hydrocarbon ratio on the rate of toluene oxidation in KO-*t*-Bu–DPSO at 100°; base/hydrocarbon: ●, 3; ■, 5.

TABLE I

STABILITY STUDIES ON DPSO

Solvent	Structure	Base	Temp., °C.	O_2 consumed, mmoles	Time, hr.
DMSO	 $CH_3-\overset{\overset{O}{\|}}{S}-CH_3$	KO-*t*-Bu	80	78.9	23
DMSO		KOH	80	50.4	68
DPSO		KO-*t*-Bu	99	0.26	20
DPSO		KOH	99	0.002	17.5
DPSO		KOH	120	0	22
DPSO		KOH	140	1.7	22

Such reactions are reported to occur with aliphatic sulfoxides.[10] The stability of DPSO in the presence of potassium *t*-butoxide and potassium hydroxide was determined over the same temperature range. In these studies, a 5:1 molar ratio of DPSO/base was employed. Again, gas chromatographic analyses indicated no apparent decomposition. This was also true when the ratio of DPSO/base was decreased to 5:3 at 100°. When an equimolar mixture of potassium *t*-butoxide and DPSO was employed at 100°, some solvent decomposition was observed.[11,12] The stability of DPSO to base and oxygen was next determined at 100° and 1 atm. of oxygen. These results are summarized in Table I. Data obtained with DMSO are also listed. As indicated, DPSO was highly resistant to attack by molecular oxygen in comparison to DMSO. Thus, molten DPSO appeared to be sufficiently stable as a solvent for the base-catalyzed oxidation of weakly acidic hydrocarbons.

A reasonable dielectric constant (ε) is believed to be an essential characteristic for solvents capable of accelerating carbanion reactions.[8,9] Hence, this property of DPSO was determined. Dielectric measurements were determined on a Sargent oscillometer at 100°. A standard curve was constructed from solvents of known dielectric. Oscillometer measurements on molten DPSO were then carried out. As shown in Fig. 1, ε for DPSO between 78 and 110° varied from 15 to 17.

Toluene was selected as a model hydrocarbon for oxidation studies in DPSO. In all oxidation studies a 5:1 molar excess of DPSO/base was employed and a constant oxygen partial pressure of 1 atm. was maintained throughout the oxidation period. The results of our toluene oxidation studies in KO-*t*-Bu–DPSO at 100° are summarized in Table II. As indicated, excellent material balance between the per cent toluene converted and the mole per cent yield of benzoic acid produced was observed. Both the mole per cent yield of acid and the rate of oxygen consumption (see Fig. 2) increased as the ratio of KO-*t*-Bu/toluene was increased from 1 to 3. Oxidation studies were next carried out on *o*-xylene under the same reaction conditions and these results are summarized in Table III. Again, excellent material balance between the per cent hydrocarbon converted and the total acid produced was observed. The acidic fraction was a mixture of *o*-toluic and phthalic acids and the yield of acid was again a function of the base/hydrocarbon ratio employed. An attempt to oxidize *o*-xylene in the presence of excess potassium hydroxide was also made. As shown in Table IV, at a KOH/*o*-xylene ratio of 6, oxidation beyond the *o*-toluic acid stage was negligible. Further, induction periods of 6–8 hr. were observed under these conditions.

A brief investigation on the oxidation of more acidic hydrocarbons in the present system was also undertaken and these results are summarized in Table V. Due to insolubility, efficient oxidation of *p*-nitrotoluene could not be obtained. Only a 28% yield of *p*-nitrobenzoic acid was obtained after 40 hr. of oxidation in KO-*t*-Bu–DPSO. On the other hand, diphenylmethane was readily oxidized to benzophenone in the presence of either KO-*t*-Bu or KOH. In addition, as shown in Fig.

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[10] H. H. Szmant, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Inc., New York 22, N. Y., 1961, Chapter 16, p. 154, *et seq.*

[11] In the presence of strong bases such as benzylsodium, phenylsodium, sodamide, butyllithium, and phenyllithium complex cleavage reactions of DPSO take place; see (a) ref. 10 and (b) K. K. Andersen and S. A. Yeager, *J. Org. Chem.*, **28**, 865 (1963).

[12] The greater stability of DPSO in comparison to DMSO is also consistent with our recent studies on oxidation-reduction reactions between thiols and sulfoxides; see T. J. Wallace and J. J. Mahon, *J. Am. Chem. Soc.*, **86**, 4099 (1964).

Table II

Summary of Toluene Oxidation Studies in KO-*t*-Bu–DPSO[a]

KO-*t*-Bu/ toluene	Benzoic acid, mole %	Toluene, % conversion	O_2 consumed, mmoles	O_2 calcd., mmoles[b]	Reaction time, hr.	Material balance, %
1	25.8	...	1.82	1.56	13.5	...
1	28.3	35	2.01	1.93	17.6	94
1	33.5	42	2.20	2.39	20	92
2	49.4	34	3.52	3.48	18.5	116
3	64.2	63.5	5.06	4.66[c]	21	102

[a] Toluene, 4.73 mmoles; 100 ± 2°; 1 atm. of O_2. [b] Based on 1.5 mmoles of O_2/mmole of benzoic acid. [c] Some solvent cooxidation may occur at this base/hydrocarbon ratio.

Table III

Summary of *o*-Xylene Oxidation Studies in KO-*t*-Bu–DPSO[a]

KO-*t*-Bu/ *o*-xylene	*o*-Toluic acid, mole %	Phthalic acid, mole %	*o*-Xylene, % conversion	O_2 consumed, mmoles	O_2 Calcd., mmoles[b]	Reaction time, hr.	Material balance, %
1	...	16	...	2.37	2.02	17.5	...
1	9.6	16.6	26.4	2.17	2.64	19	99
1	2.85	5.7	13.1	0.88	0.90	2.5	107
2	35.6	17.3	53.4	4.20	4.38	21	99
3	54.1	37.5	91.6	4.50	5.60	21	100

[a] *o*-Xylene, 4.15 mmoles; 100 ± 2°; 1 atm. of O_2. [b] Based on 3 mmole of O_2/mmole of phthalic acid and 1.5 mmole of O_2/mmole of *o*-toluic acid.

Table IV

Oxidation Studies on *o*-Xylene in KOH–DPSO[a]

KOH/*o*-xylene	Time, hr.	*o*-Toluic acid, mole %	Phthalic acid, mole %
3	24	14.7	4.4
6	25	20	4.1

[a] *o*-Xylene, 4.15 mmoles; 100°; 1 atm. of O_2.

Table V

Diphenylmethane and *p*-Nitrotoluene Oxidations

Reactant (mmoles)	Base (mmoles)	Product (mole %)[a]	Temp., °C.	Time, hr.
p-$NO_2C_6H_4CH_3$ (4.08)	KO-*t*-Bu (4.3)	*p*-$NO_2C_6H_4COOH$ (28)	93	40
$C_6H_5CH_2C_6H_5$ (2.48)	KO-*t*-Bu (4.3)	$(C_6H_5)_2CO$ (68.4)	100	20
$C_6H_5CH_2C_6H_5$ (2.98)	KOH (26.8)	$(C_6H_5)_2CO$ (54)	100	23

[a] Based on the initial mmoles of reactant.

3, the rate of oxygen consumption by diphenylmethane was much greater than that observed with toluene.

Discussion

The stability of diphenyl sulfoxide under these controlled conditions is probably due to the position of the sulfoxide linkage with respect to the carbon–hydrogen bonds. In DPSO, four carbon–hydrogen bonds are β to the sulfoxide linkage. All carbon–hydrogen bonds in DMSO are α to the sulfoxide linkage and the pK_a of this carbon acid is estimated to be about 40.[13] Thus, preferential autoxidation of DMSO in the presence of base and a hydrocarbon such as toluene ($pK_a \sim 59$) would be expected. DPSO as a solvent has some obvious disadvantages. Relatively high temperatures must be employed in order to obtain a reasonable rate of reaction. This is probably due to its moderate dielectric constant. Further, product isolation can be a problem since DPSO is a solid at room temperature. However, for our specialized purpose, it has allowed us to carry out some novel carbanion autoxidations.

Several factors suggest that we are dealing with an anion-radical oxidation rather than a pure free-radical process. As indicated in Fig. 2 and 3, both toluene and diphenylmethane are oxidized without any appreciable induction period. The dependence of the rate of oxygen consumption on the base/hydrocarbon ratio employed suggests that the equilibrium (eq. 2) is indeed

$$RCH_3 + RO^- \rightleftharpoons RCH_2^- + ROH \qquad (2)$$

important. The greater ease of *o*-xylene autoxidation in the presence of KO-*t*-Bu in comparison with that observed in the presence of KOH and the greater reactivity of diphenylmethane ($pK_a \sim 42$) in comparison with toluene ($pK_a \sim 59$) are also consistent with an anionic intermediate and a rate-determining step of proton abstraction from the hydrocarbons. Thus, intermediate free radicals are most likely produced by reactions 3 and 4.[14] In the presence of excess oxygen, the

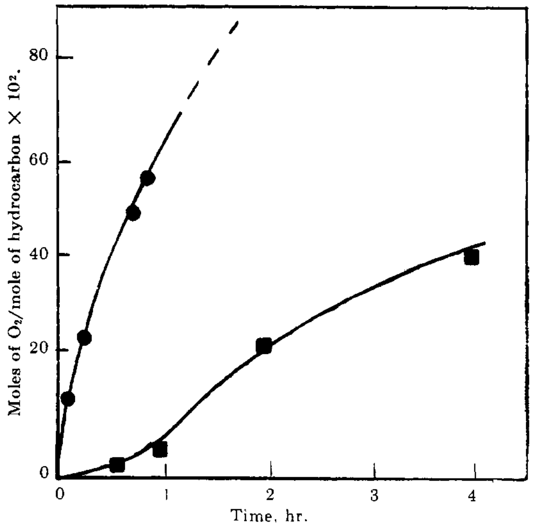

Fig. 3.—Comparison of the reactivity of diphenylmethane and toluene in KO-*t*-Bu-DPSO at 100°: ●, diphenylmethane; ■, toluene.

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[13] A summary of all pertinent pK_a values may be found in ref. 9.

[14] Peroxide ions may be destroyed by reaction with either water or alcohol which are produced during the reaction.

$$\mathrm{RCH_2^- + O_2 \longrightarrow RCH_2\cdot + \dot{O}_2^-} \quad (3)$$

$$\mathrm{RCH_2^- + O_2 \longrightarrow RCH_2\cdot + O_2^{-2}} \quad (4)$$

radical intermediate would be rapidly consumed by formation of a peroxy radical (reaction 5). The rapidity of this reaction under our experimental conditions is undoubtedly responsible for the absence of coupling products.[15] Chain transfer by hydrogen atom abstraction from the hydrocarbon would yield an intermediate hydroperoxide. This species could be destroyed by reaction with the carbanion produced in reaction 2.[16] The resulting alcohol would be unstable

$$\mathrm{RCH_2\cdot + O_2 \longrightarrow RCH_2OO\cdot} \quad (5)$$

$$\mathrm{R^- + ROOH \longrightarrow RO^- + ROH} \quad (6)$$

$$\mathrm{R^- + ROOH \longrightarrow R\cdot + RO\cdot + HO^-} \quad (7)$$

under the present conditions and rapid autoxidation to the acidic product would occur. In those reactions where excess base was employed an alternative mode of hydroperoxide decomposition is available. Proton abstraction to produce a ketone or an aldehyde could occur.[17] In the case of diphenylmethane this would

$$\mathrm{R_2CHOOH + RO^- \longrightarrow R_2CO + ROH + HO^-} \quad (8)$$
$$\mathrm{R = H \text{ or } C_6H_5}$$

give the product directly. In the toluene case, the resulting benzaldehyde would be rapidly converted to benzoic acid. For weak carbon acids the equilibrium concentration of the anion is probably small. Thus, reaction 8 is the most probable mode of intermediate hydroperoxide decomposition.

As shown in Tables II and III, essentially all oxygen consumed can be accounted for by the acidic products formed. Thus, the following stoichiometry per methyl group oxidized must be operative.

$$\mathrm{RCH_2^- + 1.5O_2 \longrightarrow RCOO + H_2O^-} \quad (9)$$

Since *o*-toluic acid was observed in all *o*-xylene oxidations the reaction probably involves a stepwise oxidation of the methyl groups to produce phthalic acid. In all reactions, the rate of oxidation decreased with time. This is probably due to the production of alcohol and water and the consumption of the base by the acidic products.

Finally, the significance of the present results in regard to previous carbanion autoxidation studies[18] should be mentioned. Russell and co-workers[3a] have shown that for highly acidic hydrocarbons, *e.g.*, nitro-substituted toluenes, where the degree of ionization is high, formation of the anion is not the rate-determining step. Rather, electron transfer between the carbanion and oxygen is the slow step and the rate of this reaction is apparently determined by the instability of the resulting anion. A similar reactivity sequence has been observed with thiolate (mercaptide) ions.[19] These compounds are roughly 10^{20} to 10^{40} times more acidic than diphenylmethane and toluene. Hence, based on the present results, a probable conclusion is that the rate-determining step in carbanion autoxidations will vary with the acidity of the hydrocarbon.

Experimental

Reagents.—Diphenyl sulfoxide was obtained from Eastman Organic Chemicals as the reagent grade material in sealed containers. The received material melted sharply at 71° and was stored in a nitrogen drybox to prevent contamination by moisture from the atmosphere. Potassium *t*-butoxide was obtained from the Mine Safety Appliance Co. as the sublimed white powder (98.5%). The base was also stored in a nitrogen drybox. Toluene, *o*-xylene, diphenylmethane, and *p*-nitrotoluene were obtained from the Matheson Co. as reagent grade materials and used without further purification. Potassium hydroxide was the usual 87% reagent grade material.

Preparation of Reaction Mixtures and Actual Oxidation Experiments.—All DPSO/base mixtures were prepared in a nitrogen drybox. A 5:1 molar ratio of DPSO/base was used in each experiment. Potassium hydroxide was ground to a fine powder before use. Each base did not dissolve completely in the molten DPSO; *i.e.*, all mixtures were heterogeneous. When the mixture was prepared, the reaction flask was sealed, transferred to the oxidation apparatus, and immersed in the constant-temperature bath. When the mixture reached thermal equilibrium, the hydrocarbon was injected into the mixture through the reaction flask side arm. In each experiment, the base/hydrocarbon ratios quoted represent mole quantities.

The reaction flask was a heavy-walled, Pyrex glass flask equipped with a ground-glass sealed side arm. The flask was attached to a water-cooled condenser which was attached to the source of oxygen. The oxygen was stored in a polyethylene gas balloon under 1 atm. of oxygen. The oxygen flowed from the balloon through a wet-test meter (10-ml. gradations) and into a large drying tube filled with indicating Drierite before entering the glass reaction vessel containing the reaction mixture. In actual operation, the system was initially purged with oxygen through the reaction flask side arm, the side arm was sealed, and an equilibrium pressure was established. The reaction was then initiated by magnetic stirring at 1300 r.p.m. The volume of oxygen consumed as a function of time was determined from the wet-test meter which allows an estimation of the volume of gas consumed to within ±1 ml. With this method, a constant oxygen partial pressure of 1 atm. was maintained above the system. All reactions were allowed to proceed to completion, *i.e.*, till no apparent oxygen consumption was observed. This oxidation technique and its applications have been described in detail previously.[20]

Quantitative Analysis for Reactants and Products.—Analyses for the acidic materials were carried out according to the methods of Pobiner, Wallace, and Hofmann.[21] Two techniques can be employed. One involves an extraction–ion-exchange–infrared procedure and the other an extraction–ultraviolet procedure. Both rely on initial homogenization with water and subsequent extraction with cyclohexane to remove the starting material and nonacidic products. This removes any spectral interference in the determination of acidic products. Acidic products remain as their acid salts in the aqueous phase and are subsequently liberated by acidification with hydrochloric acid. If the acid is aromatic, it can be quantitatively determined directly by ultraviolet spectroscopy from standard curves. If the acidic material is aliphatic or presents a weak ultraviolet absorption it is determined by the ion-exchange–infrared method. This involves treating the aqueous phase with Amberlite LA-2 anion-exchange resin. The free acid is extracted with CCl_4 and quantitatively determined by infrared spectroscopy. These methods were accurate to within 95–99% for all products identified.

Other Methods of Identification.—In addition to the ultraviolet and infrared comparison to authentic samples, further proof

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[15] This combination reaction is favorable by at least 46 kcal./mole. For a discussion see A. D. Medley and S. D. Cooley, "Advances in Petroleum Chemistry and Refining," Vol. III, J. J. McKetta, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 7.

[16] G. A. Russell, *J. Am. Chem. Soc.*, **76**, 1595 (1954).

[17] N. Kornblum and H. E. De La Mare, *ibid.*, **73**, 880 (1951).

[18] For a discussion see G. A. Russell, "Peroxide Reaction Mechanism," J. O. Edwards, Ed., John Wiley and Sons, Inc., New York 16, N. Y., 1962, p. 107, *et seq.*

[19] T. J. Wallace, A. Schriesheim, and W. Bartok, *J. Org. Chem.*, **28**, 1311 (1963).

[20] T. J. Wallace, W. Bartok, and A. Schriesheim, *J. Chem. Educ.*, **40**, 39 (1963).

[21] H. Pobiner, T. J. Wallace, and J. E. Hofmann, *Anal. Chem.*, **35**, 680 (1963).

for the formation of acidic products was obtained by isolation of the acid and the determination of its melting point. Thus, benzoic acid (m.p. 122°), p-nitrobenzoic acid (m.p. 243°), o-toluic acid (m.p. 180°), and phthalic acid (206–7°) were further substantiated. Coupling products were also formed from p-nitrotoluene but no attempt to obtain quantitative data on them was made.

Dielectric Measurements.—All dielectric measurements on molten DPSO were obtained with Sargent oscillometer between 78 and 110; all pertinent data are summarized in Table VI.

Table VI

Determination of Dielectric Constant (ϵ) of DPSO

ϵ	Temp., °C.	Oscillometer ± 150
15.0	110	10,557
15.8	100	10,612
16.0	97	10,916
16.4	91	11,035
16.8	84	11,183
17.0	78	11,326

Carbon–Carbon Bond Fission in Cyclopropanes. V. The Acid-Promoted Opening of the Three-Membered Ring in Bicyclo[5.1.0]octane

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The acid-promoted opening of bicyclo[5.1.0]octane gives 1-methylcycloheptene as the predominant olefin and a mixture of acetates which largely consists of *cis*- and *trans*-2-methylcycloheptyl acetate. The *trans* isomer is found only in slight excess of the *cis* isomer. The reactivity and extent of transannular hydride shift in the ring opening of some bicyclo[n.1.0]alkanes and epoxycycloalkanes are compared. Mechanistic implications of the results are discussed.

The acetate formation accompanying the acid-promoted opening of strained bonds in some bicyclo[n.1.0]alkanes[2] was found to be largely, though not completely, stereoselective. This result has been attributed to an S$_N$2 nucleophilic solvent attack on a protonated[3] three-membered ring prevailing over a competing carbonium ion pathway. However, S$_N$2 displacements in seven-membered and medium-sized rings, relative to aliphatic substrates, are subject to a rate retardation[4-6] attributed to the sterically induced noncollinearity of the leaving group and nucleophile.[7] These results and their interpretation suggested that a higher activation energy would possibly be involved in a nucleophilic solvent attack of a protonated, strained carbon–carbon bond in bicyclo[5.1.0]octane[8] than in the bicyclo[n.1.0]alkanes studied previously. Consequent to this higher activation energy would be the compression of transition state energies of nucleophilic solvent attack and carbonium ion processes. The anticipated, observable result would be a loss of stereoselectivity in the formation of acetate from bicyclo[5.1.0]octane.

In continuation of our studies of the acid-promoted opening of the three-membered ring in bicyclo[n.1.0]-alkanes we carried out an analysis of the products arising from bicyclo[5.1.0]octane when it was treated with 0.07 N sulfuric acid in glacial acetic acid. The product mixture obtained from a 47-hr. reaction was shown by gas chromatography to contain 40% olefin and 60% acetate. Further analysis of the product mixture demonstrated the presence of 1-methylcycloheptene (79%), 3-methylcycloheptene (15%), vinylcyclohexane (4%), cyclooctene (1%), and unconverted bicyclo[5.1.0]octane (<1%). Identification of the olefins was made through gas chromatographic retention times obtained from three different columns. The olefins present in 79 and 15% were isolated by gas chromatography and their infrared spectra confirmed their identity with 1-methylcycloheptene and 3-methylcycloheptene, respectively. The presence of 1-ethylcyclohexene, ethylidenecyclohexane, and 4- and 5-methylcycloheptene, all of which were considered possible olefinic reaction products, could not be detected in the olefin component.

After olefin analysis, the crude product mixture was treated with lithium aluminum hydride and the resulting mixture of alcohols was analyzed by gas chromatography in order to ascertain the identity and distribution of acetates in the acetate component (60%). A chromatogram obtained by employing a Castorwax column revealed that the alcohol mixture consisted of mostly (86%) 2-, 3-, and 4-methylcycloheptanols and small amounts of 1-methylcycloheptanol (4%), methylcyclohexylcarbinol (8%), and cyclooctanol (2%). A second chromatogram obtained by employing a glycerol column showed five peaks. Because the resolution of peaks was poor (see Experimental) only a rough determination of relative amounts of each component of the alcohol mixture was possible. One of two major peaks accounted for about 40% of the mixture and had a retention time identical with the retention times of 1-methylcycloheptanol, methylcyclohexylcarbinol, and *cis*-2-methylcycloheptanol. Since chromatography on Castorwax demonstrated that the sum of 1-methylcycloheptanol and methylcyclohexylcarbinol was 12%, the relative amount of *cis*-2-methylcycloheptanol in the alcohol mixture could be set at about 30%. The second major peak (also ~40%) had a retention time identical with only *trans*-2-methylcycloheptanol. Minor components were *trans*-3-

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(1) National Science Foundation Cooperative Fellow, 1963–1965.

(2) Paper IV: R. T. LaLonde and M. A. Tobias, *J. Am. Chem. Soc.*, in press, and earlier papers in this series.

(3) In this paper we arbitrarily assume that the nucleophilic solvent attack is subsequent to protonation although protonation concerted with nucleophilic attack appears equally possible.

(4) L. Schotsmans, P. J. C. Fierens, and T. Verlie, *Bull. soc. chim. Belges*, **68**, 580 (1959).

(5) P. J. C. Fierens and P. Verschelden, *ibid.*, **61**, 427, 609 (1952).

(6) S. F. Van Straten, R. V. V. Nicholls, and C. A. Winkler, *Can. J. Chem.*, **29**, 372 (1951).

(7) J. Sicher in "Progress in Stereochemistry," P. B. D. de la Mare and W. Klyne, Ed., Butterworth and Co., Washington, D. C., 1962, pp. 226, 227.

(8) An inspection of a Dreiding model of bicyclo[5.1.0]octane in the more favorable of two possible chair conformations reveals that displacement of a protonated carbon–carbon bond by the backside approach would be hindered by C-3 and -5 hydrogen atoms.