benzene (p-DNB) completely inhibits the reaction of ethyl α-nitroisobutyrate with the lithium salt of 2-nitropropane.[2] Only after 4.5 hr does the reaction begin, and by this time a parallel reaction conducted in the absence of p-DNB is 98% complete.

Evidence for the involvement of free-radical intermediates has been obtained by using galvinoxyl, which is known to be an efficient scavenger for free radicals.[3] Five mole per cent of galvinoxyl completely stops the reaction of ethyl α-nitroisobutyrate with the lithium salt of 2-nitropropane for 2.5 hr, after which the reaction slowly starts up; even after 5 hr the reaction has gone only 10%. In contrast, without galvinoxyl, the reaction proceeds 84% in 2.5 hr and is complete in 5 hr.[3a]

In the same way, the reaction of α-nitroisobutyrophenone (Ib) with the salt of 2-nitropropane (eq 1) is completely inhibited for 30 min by either 5 mol % p-DNB or 5 mol % galvinoxyl; in the absence of these inhibitors the reaction proceeds 35% to completion in 30 min.[3a] We conclude that the displacement of a nitro group from the α-nitro ketone proceeds by a chain sequence completely analogous to that of eq 2–5.

The reaction of 2-cyano-2-nitropropane (Ic) with the 2-nitropropane anion exhibits the same characteristics as those employing the α-nitro ester Ia and the α-nitro ketone Ib; at the 5 mol % level the presence of p-DNB results in a dead period of 2.5 hr after which the reaction begins. With 5 mol % of galvinoxyl the reaction is completely inhibited for 1 hr. In the absence of p-DNB and galvinoxyl the reaction proceeds 23% in 1 hr and 47% in 2.5 hr.[3a] Clearly, displacement of a nitro group from the α-nitro nitrile is a chain process. A mechanism analogous to that of eq 2–5, involving the $(H_3C)_2C(CN)NO_2\cdot^-$ radical anion and the $(H_3C)_2\dot{C}CN$ radical, is easily envisioned.

When conducted in DMSO the reaction between 2,2-dinitropropane (Id) and the lithium salt of 2-nitropropane is complete in 2 min but, if 5 mol % p-DNB is present, it proceeds only 10% in this time. In DMF, galvinoxyl at the 5 mol % level completely stops the reaction for 90 min, and even after 210 min the reaction goes only 8%.[3a] In contrast, the reaction in DMF is 99% complete after 90 min. As in the preceding cases, it is apparent that we deal with a chain reaction. Here again it is reasonable to presume that a radical-anion free-radical mechanism, fully analogous to that of eq 2–5, is involved.

The idea that an aliphatic nitro group is capable of accepting one electron and that the resulting radical anion, by loss of nitrite ion, gives a free radical (eq 2 and 3) is derived from the pioneering work of Hoffmann, *et al.*[4] However, where the earlier workers employed metallic sodium, or electrochemical reduction, as the source of electrons, the present study uses nitroparaffin salts. It is quite remarkable that such a "low-pressure" source of electrons as a nitroparaffin anion is able to bring about the transformations of eq 1 and of the accompanying communication.[1]

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* Address correspondence to this author.

Nathan Kornblum,* Steven D. Boyd
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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[3] P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, **84**, 2600 (1962).

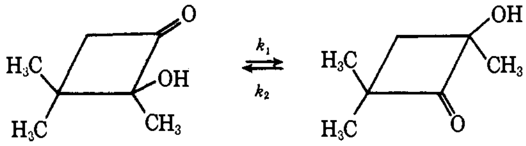
[3a] Note Added in Proof. It has now been found that 5 mol % of di-*tert*-butylnitroxide (or 5 mol % of p-benzoquinone) also inhibits these reactions.

[4] A. K. Hoffmann, W. G. Hodgson, D. L. Maricle, and W. H. Jura, *ibid.*, **86**, 631 (1964); also see H. Sayo, Y. Tsukitani, and M. Masui, *Tetrahedron*, **24**, 1717 (1968).

Ketol Rearrangements of 2-Hydroxy-2-methylcyclobutanones

Sir:

Secondary reactions have made the study of the photocyclization of 2,3-alkanediones difficult. In the presence of acids,[1a,2a] bases,[1b,c] and some metal salts,[1b,2] the product 2-hydroxy-2-methylcyclobutanones rearrange. These catalysts are so effective that as adventitious impurities they cause interconversion during photolysis and product isolation. Hence, this rearrangement is much more facile than those of cyclobutanones[3] and other tertiary ketols[1,2] previously reported. The two-component system ($\mathbf{1} \rightleftarrows \mathbf{2}$) was convenient for the study of catalysis. The compositions at equilibrium (also with four-component systems involving 3- and 4-alkyl-2-hydroxy-2-methylcyclobutanones) permit calculation of the differences in free energy between isomers.



1 **2** (1)

Irradiation (three GE sunlamps at 6 cm, 2.5 hr, 25°, N_2, in a water-cooled Pyrex cell) of 5-methyl-2,3-hexanedione (0.1 M in benzene) gave nearly pure **1** (nmr) after evaporation of the solvent. Simple distillation gave a mixture of **1** (90%, nmr) and **2** (10%, bp 38–42° (0.4 mm)). Pure **1** (mp 11–14°; ir 1786 and 3400 cm^{-1}; parent mass 128; nmr (CCl_4) δ 1.12 (s, 3), 1.27 (s, 3), 1.30 (s, 3), 2.41 and 2.69 (AB m, 2, J = 16.8 Hz), 3.5–4.3 concentration dependent (s, 1); p-nitrophenylhydrazone, mp 215–217°) was obtained by recrystallization (pentane, −78°). Slow spinning-band distillation of a mixture of **1** and **2** gave *only* pure **2**: bp 38–39° (0.4 mm); ir 1784 and 3400 cm^{-1}; nmr (CCl_4) δ 1.21 (s, 3) 1.24 (s, 3), 1.41 (s, 3), 2.00 (s, 2), 3.5–4.3 ppm concentration dependent (s, 1); in benzene, ring methylene gives δ 1.68 and 1.88 (AB, m, 2, J = 11.3 Hz); p-nitrophenylhydrazone mp 142–145°. Periodic acid oxidation of **1** gave 4-oxo-3,3-

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[2] (a) S. N. Danilov and E. Venus-Danilova, *Zh. Obshch. Khim.*, 3, 559 (1933); *Ber.*, **67**, 24 (1934); (b) L. L. Smith, M. Marx, J. J. Garbarini, T. Foell, V. E. Origoni, and J. J. Goodman, *J. Amer. Chem. Soc.*, **82**, 4616 (1960); (c) H. Köller, *Tetrahedron Lett.*, 4317 (1968); (d) C. A. Brown and C. Djerassi, *J. Chem. Soc. C*, 2550 (1969).

[3] (a) W. T. Erman, *J. Amer. Chem. Soc.*, **91**, 779 (1969); (b) P. Yates and A. G. Fallis, *Tetrahedron Lett.*, 2493 (1968).

Table I. Rates of Rearrangement **1** ⇄ **2**

		Conditions						
Expt no.	Catalysts and solvents	Initial molarity [**1**] + [**2**]	Reaction temp, °C	Time followed, hr	$\mathbf{1}_e$[a]	$\mathbf{1}_0$ →	**1**[b]	$(k_1 + k_2)$,[c] sec^{-1}
1	Water (DSS, 0.05 *M*)	0.5	25	216	0.54[d]	0.84	0.83	$<5 \times 10^{-8}$
2	NaOH (0.1 *M* in water)	0.3	38	24[h]	0.48[e]	0.95	0.48	1×10^{-2}
3	Hydrochloric acid (0.2 *M*)	0.3	25	66[g]	0.54[d]	0.74	0.62	4×10^{-6}
4	Glycine (0.05 *M*), hydrochloric acid (0.044 *M*), pH 2.2	0.3	25	258	0.51[d]	0.73	0.72	$<1 \times 10^{-7}$
5	Aluminum chloride (0.03 *M*) in acetic acid (0.05 *M*)–sodium acetate (0.05 *M*) buffer, pH 4.7	0.3	25	336[h]	0.54[e]	0.75	0.54	$>1 \times 10^{-3}$
6	Cupric chloride (0.01 *M*) in same acetate buffer as 5	0.3	38	312[h]	0.53[e]	0.78	0.53	3×10^{-4}
7	Cupric chloride (0.01 *M*) in 0.2 *M* hydrochloric acid	0.3	25	20[g]	0.54[d]	0.75	0.68	6×10^{-6}
8	Barium nitrate (0.03 *M*) in same acetate buffer as 5	0.5	25	432	0.54[d]	0.81	0.56	1.5×10^{-6}
9	Trifluoroacetic acid (1.7 *M*) in nitrobenzene	1.5	25	9[g,h]	0.45[e]	0.99	0.45	4×10^{-3}
10	Trifluoroacetic acid (0.4 *M*) in benzene	0.4	25	70[h]	0.48[e]	0.95	0.48	4×10^{-4}
11	Trifluoroacetic acid (2.7 *M*) in acetonitrile	1.5	25	72[f,g]	0.45[e]	0.95	0.45	2×10^{-4}
12	Trifluoroacetic acid (2.7 *M*) in dimethyl sulfoxide-d_6	1.6	25	2208[g]	0.50[d]	0.98	0.67	6×10^{-8}

[a] Fraction [**1**]/([**1**] + [**2**]) at equilibrium. [b] This fraction followed from $\mathbf{1}_0$ to **1** given. [c] Slope of ln $(\mathbf{1}_0 - \mathbf{1}_e)/(\mathbf{1} - \mathbf{1}_e)$ *vs.* time in seconds. [d] Estimated value. [e] Many nmr analyses made after equilibrium had been reached to determine $\mathbf{1}_e$ directly. [f] Nonlinear plot, initial slope given. [g] Competing acid-catalyzed reactions also occurred, but were so slow that they did not prevent determination of rearrangement rate. [h] Reached equilibrium in 30 min.

Table II

	Equilibrium compositions				ΔG_{38}°, kcal/mol			
R	**4E**	**4Z**	**5E**	**5Z**	**4E**-**4Z**	**5Z**-**5E**	**5E**-**4E**	**5Z**-**4Z**
CH_3-	20	15	12	53	0.2	0.9	−0.3	0.8
$(CH_3)_2CH$-	11	5	16	68	0.5	0.9	0.2	1.6
$C_6H_5(CH_3)_2C$-	<2	<2	24	76		0.7	>1.5	>2.2

dimethylpentanoic acid (mp 43–44°)[4] and **2** gave 4-oxo-2,2-dimethylpentanoic acid (mp 72–74°).[4]

Further proliferation of isomers occurs if irradiation is continued after the dione is consumed. For example, photolysis (41 hr with one sunlamp) of a mixture of 60% **1** and 40% **2** (0.01 mol in 30 ml of ether) gave 3,3-dimethyl-4-oxopentanal (36%) and 2,2-dimethyl-4-oxopentanal (29%, oxidation with hydrogen peroxide gave the corresponding acids above[4]).

The ketol rearrangement (eq 1) (nmr analysis by integration of appropriate methyl singlets of **1** and **2**) follows pseudo-first-order equilibrium kinetics, and its equilibrium constant is near unity (0.8–1.2 in various solvents, differences of free energies of **1** and **2** do not exceed 0.1 kcal/mol). In aqueous solutions, base is a powerful catalyst, but acid is a weak one (Table I, *cf.* experiments 1–4). Metal ion catalysis depends both upon the ion and the buffer system used (*cf.* experiments 5–8). In acetate-buffered aqueous solutions, the catalytic sequence (Al, Cu(II) ≫ Ag(I), Pb(II) ≫ Mg, Co(II), Ni(II) > Ba, K, Li) was observed. Rates in the presence of the latter three (experiment 8) were about the same as in the acetate buffer. Catalysis by trifluoroacetic acid is more effective in less basic solvents (*cf.* experiments 9–11 with 12). Interestingly, 2-pyridone is not a catalyst in benzene solution.[5]

Products of photocyclization of 2,3-alkanediones contain impurities that catalyze their rearrangements (most rapid with neat 2-hydroxycyclobutanones, and in their solutions in nonbasic solvents). Hence, rate data for these "uncatalyzed" reactions are unreliable. Self-catalysis (increased rearrangement rates with higher concentrations of **1** and **2** in nitrobenzene) was suspected until a sample of **1** that had been purified by recrystallization and then high vacuum sublimation gave no such results. Even with this highly purified **1**, rate constants differed too much to report, but they approach that in water (Table I, experiment 1). As a practical matter, the rearrangement is slowest in the

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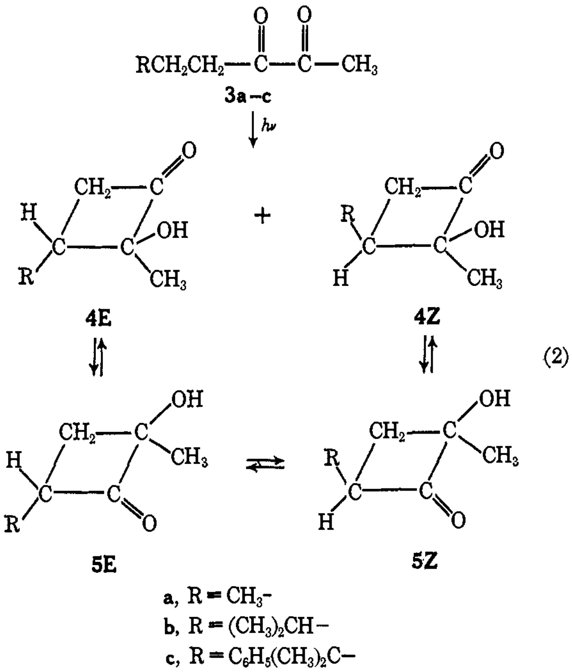
(4) C. Pascual, *et al.*, *Helv. Chim. Acta*, **47**, 213 (1964).

(5) P. R. Rony, *J. Amer. Chem. Soc.*, **91**, 6090 (1969).

more basic solvents (water, dimethyl sulfoxide, or pyridine).

In such polar solvents at low dione concentrations and temperatures and with short irradiation times, this rearrangement can be so limited that only photocyclization occurs. Then only **1** is obtained, and **3a–c** give only **4a–cE** and **4a–cZ** with little stereoselectivity (**4aE**/**4aZ** = 1.0, **4bE**/**4bZ** = 1.2, and **4cE**/**4cZ** = 0.6). Under other conditions, these ratios **4E**/**4Z** are different, and **5E** and **5Z** appear in the photolysis products.

Ketol rearrangement (**4E** $\rightleftarrows$ **5E** and **4Z** $\rightleftarrows$ **5Z**) and epimerization *via* enolization[6] (**5E** $\rightleftarrows$ **5Z**) give equilibrium between the four isomers. Their ratios permit the first direct comparison of vicinal and transannular interactions in four-membered rings. Equilibrations occurred rapidly in sodium hydroxide solutions (0.02 *M*) in 20% aqueous pyridine. The compositions of these equilibrium mixtures (nmr integration of appropriate methyl absorptions) are given in Table II. They were obtained from pure substances (**5bE**, **5bZ**, **5cE**, **5cZ**, and the bishemiketal dimers[7] from **4aE**, **4bE**, and **4cE**) and various mixtures.



(2)

a, R = CH$_3$-
b, R = (CH$_3$)$_2$CH-
c, R = C$_6$H$_5$(CH$_3$)$_2$C-

Inversion of configurational preference is seen (Table II) between sets of epimeric pairs (**4** or **5**). The differences (ΔG, 4E − 4Z, 5Z − 5E) observed are insensitive to the size of R. The relative importance of vicinal compared to transannular interactions is enhanced by groups larger than methyl, and is greater for **Z** than for E configurations. For a single methyl substituent ΔG (**5Z** − **4Z**) is positive and ΔG (**5E** − **4E**) negative, whereas, for the *gem*-dimethyl groups in **1** and **2**, 1,2 and 1,3 interactions are nearly equal. These results suggest that pseudoequatorial arrangement of both the 2-hydroxyl (here probably hydrogen bonded to solvent) and the 3 or 4 substituent is preferred. Both of these groups cannot be so placed in **4Z** and **5E**, and hence they are less stable than their epimers.

Different interactions obviously are involved in determining these equilibrium compositions and photochemical selectivities. The photocyclization of 4-methyl-2,3-pentanedione yields predominantly **5aE** (**5aE**/**5aZ** = 3.0), although **5aZ** is the most stable isomer (Table II, **5aE**/**5aZ** = 0.23). That of 6-methyl-2,3-heptanedione (**3b**) shows little selectivity (**4cE**/**4cZ** = 1.2), while **4cE** is thermodynamically preferred (Table II, **4cE**/**4cZ** = 2.2).

The degenerate rearrangement of 2-hydroxy-2-methylcyclobutanone was observed *via* its hydrogen exchange with deuterium oxide containing pyridine (0.8 *M*). The nmr absorptions of its 3- and 4-methylenes disappeared at approximately equal rates, but its methyl singlet was unchanged. Hence, its rearrangement is faster than its enolization and it does not occur by homoenolization[1c] at methyl.

A simple methyl migration is suggested by the stereospecificity of this rearrangement,[7b] and by the above lack of methyl deuteration. This evidence also makes it less likely that a ring reorganization sequence, as proposed for other cyclobutanone rearrangements,[3a] occurs. The latter mechanism deserved serious consideration since its two steps, ring contraction[8] and expansion,[9] have been observed separately.

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* Address correspondence to this author.

W. H. Urry,* J. C. Duggan, Mei-shu H. Pai
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

Received June 8, 1970

Electron Paramagnetic Resonance Spectra of Metal Complexes Oriented in Nematic Glasses

Sir:

Single-crystal electron paramagnetic resonance (epr) spectra have been exceedingly valuable in helping to interpret bonding and structural parameters in paramagnetic transition-metal compounds.[1,2] However, this technique suffers especially from two inherent experimental difficulties, the need to grow suitable single crystals and the requirement that the paramagnetic material must be magnetically dilute. This latter problem usually is alleviated by doping an ion or molecule into a diamagnetic host, a procedure that requires the availability of suitable host materials.

In principle, the use of liquid crystals to orient materials in magnetic fields can produce the same result that is obtained from oriented, magnetically dilute single-crystal epr measurements. Furthermore, data may be obtained without the drawbacks of the single-

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