with methanol to give colorless crystals of 1-(1-naphthyl)-1-phenyl-2-propanone: mp 83–84°, lit.[29] mp 84.5–85°; nmr 2.2, 2.8 (multiplet, 12 H), 4.31 (singlet, 1 H), 7.86 (singlet, 3 H); ir 1708 cm^{-1} (C–O).

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.27; H, 6.36.

Photooxidation of 1-Naphthylphenyldiazomethane in Benzaldehyde. A solution of 2.45 g (10 mmol) of 1-naphthylphenyldiazomethane in 100 ml of benzaldehyde was photooxidized at 10–15° using an oxygen input of 100 ml/min and operating the lamp at 50 V for 50 min. After removing excess benzaldehyde under reduced pressure, the remaining liquid was chromatographed on silica gel (60 g silica gel, 3 g H_2O). Elution was carried out with benzene-hexane (20:80) and then benzene-hexane (50:50). All fractions were analyzed for ozonide using analytical tlc. Fractions containing ozonide were combined and chromatographed on preparative tlc plates using benzene-hexene (80:20) for development and benzene for recovery. The recovered ozonide (2.20 g, 5.6%) had a cis/trans ratio of 1.49. In this case the tentative stereochemical assignment is also based on the nmr spectrum. In ozonides with groups having diamagnetic anisotropies attached to the carbon containing the methine hydrogen it is found that the previously cited correlation is reversed and the trans isomer is the one with the methine hydrogen at lower field.[17,18] Both of the ozonides have a multiplet absorption at 1.8–3.0 (17 H) while the cis isomer has a singlet at 3.86 (1 H) and the trans has a singlet at 3.56 (1 H).

When the ozonide was allowed to stand for 11 months, rechromatographed by preparative tlc, and the recovered material recrystallized from benzene-hexane, colorless crystals of the pure trans compound were obtained. This material had mp 116–117° and nmr absorptions at 1.8–2.7 (multiplet, 7 H), 2.78 (singlet, 5 H), 2.96 (singlet, 5 H), and 3.56 (singlet, 1 H).

Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.31; H, 5.14.

Reduction of 1-(1-Naphthyl)-1-phenyl-1-propene and 1-(1-Naphthyl)stilbene Ozonides with Triphenylphosphine. Solutions of the ozonides in carbon tetrachloride were treated dropwise with a carbon tetrachloride solution of triphenylphosphine directly in an nmr tube. The tube contents were mixed for 1 min using a vibrator and then allowed to stand for 10 min before recording the nmr spectrum. In the case of 1-(1-naphthyl)-1-phenyl-1-propene ozonide the ozonide had an initial cis–trans ratio of 0.84 and ratios of 0.92, 1.15, and 1.32 after 8.8, 21.6, and 26.8% reaction, respectively. For 1-(1-naphthyl)stilbene ozonide the starting ozonide had a cis-trans ratio of 1.64 and ratios of 1.06, 0.91, and 0.74 after 8.8, 21.6, and 26.8% reaction, respectively.

Acknowledgment. We thank the National Science Foundation for support of this work through Grant No. GP-29373X. We also thank Dr. David Higley for assistance with the work on column chromatographic separation of the ozonide stereoisomers.

(29) C. McKenzie and H. J. Tattersall, *J. Chem. Soc.*, 127, 2528 (1925).

Enolene Rearrangements. III. Investigation of Charge Distribution in the Transition State of the Enolene Rearrangement

James M. Watson, John L. Irvine, and Royston M. Roberts*

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712.

Received October 3, 1972

Abstract: The electronic nature of the transition state of the enolene rearrangement has been probed by the determination of substituent effects on the rates of rearrangement of 4′-R-4-pentenophenone-*2*-d_2 (R = H, CH_3, CH_3O, Cl, CN), 2,2-dimethyl-1-(4′-R-benzoyl)cyclopropane (R = H, CH_3, CH_3O, Cl), and 2,2-dimethyl-1-(3′-R-benzoyl)cyclopropane (R = H, CH_3O, Cl). The effects of various substituents on the rate of rearrangement have been correlated with Hammett[1] plots.

Having previously demonstrated[2–6] that the enolene rearrangement (**1** ⇄ **3**) of homoallylic ketones (**1**) proceeds *via* a reversible 1,5-hydrogen shift concerted with ring closure to an alkylacylcyclopropane intermediate (**3**), we desired to investigate the electronic nature of the transition state leading to and from **3**. We now report the results of two separate approaches to the study of this transition state which involve Hammett correlations of rearrangement rates of appropriately substituted 2,2-dideuterio-4-pentenophenones (**1a–e**, R′ = H) and of appropriately substituted alkylacylcyclopropanes (**3a–d, f, g**, R′ = CH_3).

Results

I. Syntheses of Compounds for Rearrangement. 4-Pentenophenones. With the exception of the parent compound of the series (**1a**, R′ = H),[4] the substituted 4-pentenophenones employed have not been previously reported. 4-Pentenophenone, 4′-methyl-4-pentenophenone, 4′-methoxy-4-pentenophenone, and 4′-chloro-4-pentenophenone were prepared by the imine alkylation procedure of Stork and Dowd[7] using the appropriate para-substituted acetophenone and alkyl bromide. As acetophenones bearing a strong electron-withdrawing group (*e.g.*, NO_2, CN) on the aromatic ring are not compatible with the Grignard reagent involved in imine alkylations, other approaches to the synthesis of 4-pentenophenones bearing such

---

(1) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, pp 81–93.

(2) R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, 87, 2281 (1965).

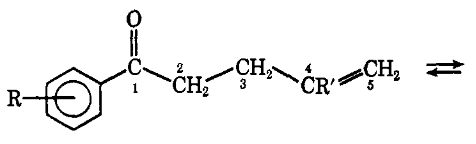
(3) R. M. Roberts, R. N. Greene, R. G. Landolt, and E. W. Heyer, *ibid.*, 87, 2282 (1965).

(4) R. M. Roberts, R. G. Landolt, R. N. Greene, and F. W. Heyer, *ibid.*, 89, 1404 (1967).

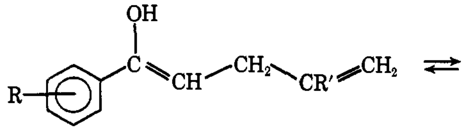
(5) R. M. Roberts and J. M. Watson, *J. Org. Chem.*, 34, 4191 (1969).

(6) H. J. Hansen, "Mechanisms of Molecular Migrations," Vol. 3, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1972, p 177.

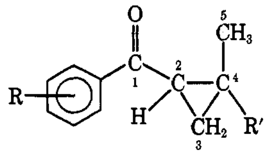
(7) G. Stork and S. R. Dowd, *J. Amer. Chem. Soc.*, 85, 2178 (1963).



1



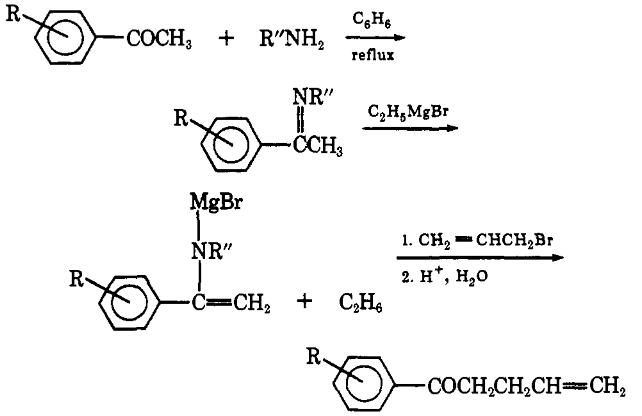
2



3

R	R
a = H	e = p-CN
b = p-CH$_3$O	f = m-CH$_3$O
c = p-CH$_3$	g = m-Cl
d = p-Cl	

R′ = H; CH$_3$



R = H, p-CH$_3$O, p-CH$_3$, p-Cl

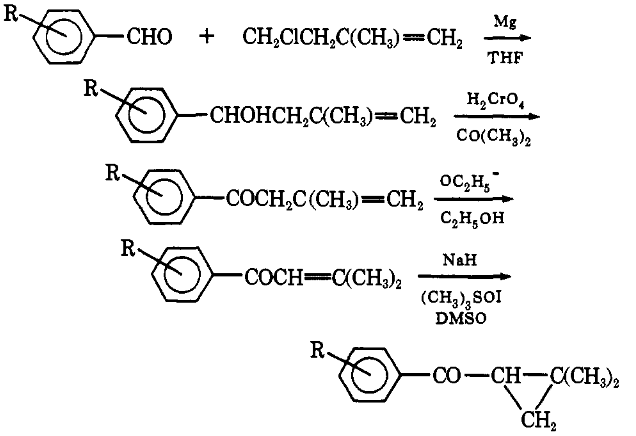
groups were necessitated. Attempts to synthesize 4′-nitro-4-pentenophenone *via* direct alkylation, enamine alkylation,[8] Kimel–Cope rearrangement,[9] and by the reaction of p-nitrobenzoyl chloride with dihomoallylcadmium[10,11] failed. As aromatic cyano groups are known to be compatible with organocadmium reagents,[12] the synthesis of 4′-cyano-4-pentenophenone by the reaction of p-cyanobenzoyl chloride with dihomoallylcadmium using a modification of the procedure of de Benneville[10] was attempted and was successful.[13]

$$CH_2BrCH_2CH{=}CH_2 + Mg \longrightarrow BrMgCH_2CH_2CH{=}CH_2 \xrightarrow{CdCl_2}$$

$$Cd(CH_2CH_2CH{=}CH_2)_2 \xrightarrow[2.\ H^+,\ H_2O]{1.\ p\text{-}CNC_6H_4COCl} p\text{-}CNC_6H_4COCH_2CH_2CH{=}CH_2$$

With the exception of 4′-cyano-4-pentenophenone, the homoallylic ketones employed were successfully deuterated in the 2 position using a mild homogeneous technique developed in this laboratory.[14] Deuterium exchange into the 2 position was in all cases ≥96.5% complete. Upon subjection to the conditions of deuteration, 4′-cyano-4-pentenophenone was found to undergo an anomalous reaction in addition to hydrogen/deuterium exchange; this is believed to be attributable to the enhancement of the reactivity of the carbonyl carbon toward nucleophilic attack (and hence reactions such as aldol condensation) because of the electron-withdrawing properties of the 4′-cyano substituent.

Alkylacylcyclopropanes. The 2,2-dimethylbenzoylcyclopropanes employed herein, none of which have been previously reported, were prepared *via* a four-step synthesis wherein the appropriately substituted benzaldehyde was first allowed to react with α-methylallyl magnesium chloride according to the procedure of Dran and Prange.[15] The resulting 1-aryl-3-methyl-3-buten-1-ol was oxidized to the corresponding ketone with Jones' reagent[16] and then allowed to isomerize in the presence of sodium ethoxide to obtain the corresponding 3-methyl-2-butenophenone. Conversion to the desired cyclopropanes was effected with trimethylsulfoxonium iodide and sodium hydride in dimethyl sulfoxide according to the procedure of Corey and Chaykovsky.[17]



R = H, p-CH$_3$O, p-CH$_3$, p-Cl, m-CH$_3$O, m-Cl

II. Thermal Rearrangements. Rearrangement of 4-Pentenophenones. Rearrangements at 217 ± 0.5° were conducted as outlined in the Experimental Section. Rate constants were calculated using eq 1; the best

$$k = \frac{-(3/2)2.3[\log(2 - \alpha - v) - \log\alpha]}{t} \qquad (1)$$

v = nmr integral of protons at C$_2$
α = initial deuterium purity at C$_2$
t = time, hr

slopes of a plot of [log (2 − α − v) − log α] *vs.* t were determined by the method of least squares.[18]

---

[8] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *ibid.*, **85**, 207 (1963).

[9] W. Kimel and A. C. Cope, *ibid.*, **65**, 1992 (1943).

[10] P. L. de Benneville, *J. Org. Chem.*, **6**, 462 (1941).

[11] Prior to this observation, the compatibility of the aromatic nitro moiety with organocadmium reagents had not been established;[12] we now wish to report that the two species are incompatible.

[12] J. Cason, *Chem. Rev.*, 40, 15 (1947).

[13] Thanks are due to Professor P. L. Stotter for his suggestion of this synthesis.

[14] J. M. Watson, A. R. Tanner, and R. M. Roberts, *J. Org. Chem.*, 37, 3743 (1972).

[15] R. Dran and T. Prange, *C. R. Acad. Sci., Ser. C*, **262**, 492 (1966).

[16] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 142.

[17] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 87, 1353 (1965).

[18] H. D. Young, "Statistical Treatment of Experimental Data," McGraw-Hill, New York, N. Y., 1962, pp 115–132.

The rate constants obtained are tabulated in Table I. 4′-Cyano-4-pentenophenone decomposed under rearrangement conditions and no rate data were obtained.

Table I. Thermal Rearrangement of 4′-R-4-Pentenophenones at 217°

R	10^2k, hr^{-1}	Correlation coeff	σ^a	$\sigma^{+\,a}$
CH_3	2.07	0.9990	−0.170	−0.778
CH_3O	1.69	0.9968	−0.268	−0.311
H	1.54	0.9994	0.000	0.000
Cl	1.45	0.9938	+0.227	+0.114

[a] From ref 1.

Rearrangements of Alkylacylcyclopropanes. Rearrangements of the dialkacyclopropanes were conducted at 125°, and rate constants were calculated using the first-order rate equation (eq 2), where A_0 = initial mole fraction of starting material, A = instantaneous mole fraction of starting material, and t = time (sec). Rate

$$k = \ln (A/A_0)/t \tag{2}$$

constants and correlation coefficients were derived from least-squares[18] treatment of a plot of $\ln A_0/A$ *vs.* t and are tabulated in Table II.

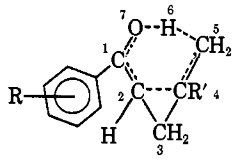
Table II. Thermal Rearrangement of 2,2-Dimethyl-1-(3′- and 4′-R-benzoyl)cyclopropanes

R	10^5k, sec^{-1}	Correlation coeff	$\sigma^{+\,a}$
p-CH_3O	1.14	0.9987	−0.778
p-CH_3	1.85	0.9974	−0.311
H	2.12	0.9995	0.000
m-CH_3O	2.65	0.9977	+0.047
p-Cl	4.15	0.9994	+0.114
m-Cl	5.61	0.9961	+0.399

[a] From H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958), solvolysis of *tert*-cumyl chloride.

Discussion

All of the evidence, to the present, regarding the enolene rearrangement points to a six-membered, cyclic transition state which can be visualized as **4**.[19]



4

This transition state can be further considered as having either a completely neutral electronic distribution in which no participating atom bears any charge, full or fractional, or a system in which alternating atoms bear either full or partial positive and negative charges. Intuitively, one might expect that some positive character is developed on atoms 1, 4, and 6, and a corresponding degree of negative character on atoms 2, 5, and 7 due to the electronegativity of oxygen compared with carbon.

It should be possible to test this idea by choosing a series of appropriately substituted compounds in which one of the possible charge centers can be either stabilized or destabilized. One such series of compounds is the 4′-substituted-4-pentenophenones (**1a–e**, R′ = H). Deuterium labeling in the 2 position is necessary for kinetic determinations, as the enolene rearrangement of these compounds is degenerate.

Inspection of the data from these rearrangements shows two significant features; electron-releasing substituents (*p*-CH_3 and *p*-CH_3O) enhance the rate, whereas electron attractors (*p*-Cl) retard the reaction. This is consistent with the idea of a charge-separated transition state in which the carbonyl carbon (C_1) assumes positive character. Secondly, the small effect indicates that the charge is small. However, the rate of the methyl compound was the fastest, not the methoxy as would be expected on the basis of electron donating ability. Hammett plots,[1] the results of which are tabulated in Table III, allow a better evaluation of these data.

Table III. Results of Hammett Plots of Kinetic Data for the Rearrangement of 4′-R-4-Pentenophenones at 217°

	Correlation with σ^b		Correlation with $\sigma^{+\,b}$	
	Slope[a]	Correlation coeff	Slope[a]	Correlation coeff
All points included	−0.22	0.7040	−0.08	0.4936
Methyl excluded	−0.14	0.9924	−0.07	0.9725
Methoxy excluded	−0.37	0.8934	−0.38	0.9926

[a] Slope of plot of $\log (k/k_0)$ *vs.* substituent constant, ρ: k = rate of substituted compound, k_0 = rate of unsubstituted compound. [b] From ref 1.

Much better correlations are obtained if either the methyl or the methoxy compound is excluded. Excluding the methyl compound, a good correlation (r = 0.9924) is obtained with σ values. When the methoxy compound is excluded another good correlation (r = 0.9926) is obtained with σ^+. Thus, it appears equally possible that the methoxy-substituted compound rearranges anomalously slow or that the methyl substituted compound rearranges anomalously fast. The former possibility is, in fact, supported by the observations of others[20–26] that in some cyclic, concerted transition states, the best correlation of substituent effect is with σ^+. This possibility is also supported by the fact that, although the elevated rate for the methyl compound cannot be explained, there is a good basis on which to expect the rearrangement of the methoxy compound to be abnormally slow.

---

[19] D. E. McGreer and N. W. K. Chiu, *Can. J. Chem.*, **46**, 2217 (1968).

[20] D. W. Emmerson and T. J. Korniski, *J. Org. Chem.*, **34**, 4115 (1969).

[21] H. L. Goering and R. R. Jacobson, *J. Amer. Chem. Soc.*, **80**, 3277 (1958).

[22] G. G. Smith, F. D. Bagley, and R. Taylor, *ibid.*, **83**, 3647 (1961).

[23] R. Tang and K. Mislow, *ibid.*, **92**, 2100 (1970).

[24] R. Taylor, G. G. Smith, and W. H. Wetzel, *ibid.*, **84**, 4817 (1962).

[25] W. N. White, *et al.*, *ibid.*, **80**, 3271 (1958).

[26] W. N. White, *et al.*, *J. Org. Chem.*, **26**, 627 (1961).

The first step in this rearrangement is enolization of the ketone.[4] After this work was completed, Tanner[27] found that enolization (**1** → **2**) was not, in all cases, faster than ring closure (**2** → **3**). While he showed that ring closure was the slow step for the unsubstituted compound (**2a**, R′ = H), he had evidence that at 217° its rate was approaching the rate of enolization. Also, base-catalyzed enolization is inhibited by electron donors, as is shown by the positive value for ρ (+0.417) in the base-catalyzed reaction of bromine with substituted acetophenones.[28] On this basis, the methoxy compound would have the slowest rate of enolization of all of the compounds of the series. Therefore, it is quite possible that in the case of the *p*-methoxy derivative, the measured rate of rearrangement was in reality the rate of enolization.

In an attempt to verify this postulate, 4′-methoxy-4-pentenophenone was heated at 217° in pyridine solution under conditions which were found to be most convenient for accelerating enolization without affecting the rate of the enolene rearrangement. As would be expected on the basis of the preceding argument, the rate of rearrangement was indeed accelerated under these conditions, thus supporting the postulate that the rate measured for the 4′-methoxy compound was actually the rate of enolization. Conversely, the rate of rearrangement of the parent 4-pentenophenone was not affected by the presence of pyridine.[27] Thus, we believe that the present data can be most meaningfully correlated by using a Hammett plot of log (k/k_0) *vs.* σ^+ wherein the rate data for the *p*-methoxy compound have been discarded (Figure 1). The value of ρ which results is -0.37; this constitutes evidence for a rather small degree of charge separation in the transition state (**4**) of the enolene rearrangement.

According to the principle of microscopic reversibility, the transition state encountered in ring closure of the enolene species is identical with that for the ring opening of the alkylacylcyclopropane. Therefore, it should also be possible to investigate the extent of charge separation of **4** by measuring the rate of ring opening of a series of substituted phenyl cyclopropyl ketones. For this purpose a series of substituted 2,2-dimethyl-1-benzoylcyclopropanes (**3a–d**, **f**, **g**, R′ = CH_3) were prepared. The 2,2-dimethylcyclopropanes were chosen as their structure ensures that there will always be a methyl group cis to the ketone group, the cis configuration being essential for rearrangement.[4]

There are several advantages to using the cyclopropyl compounds to probe the transition state (**4**). Their synthesis is less involved than that of the pentenophenones, and a larger group of suitably substituted starting materials is readily available. The problem of a prior enolization or other step which could be rate controlling is eliminated, and since the rearrangement is not degenerate, deuterium labeling techniques are not required.

Before examining the data it is helpful to digress for a discussion of possible effects of substituents on rates. Since, according to the transition state theory,[29] the rate of a reaction is a measure of the free energy difference between the ground state and the transition complex, any variation in rate will be due to an increase or decrease in this energy. Such changes in the free energy difference between ground and transition states result whenever either is raised or lowered relative to the other.

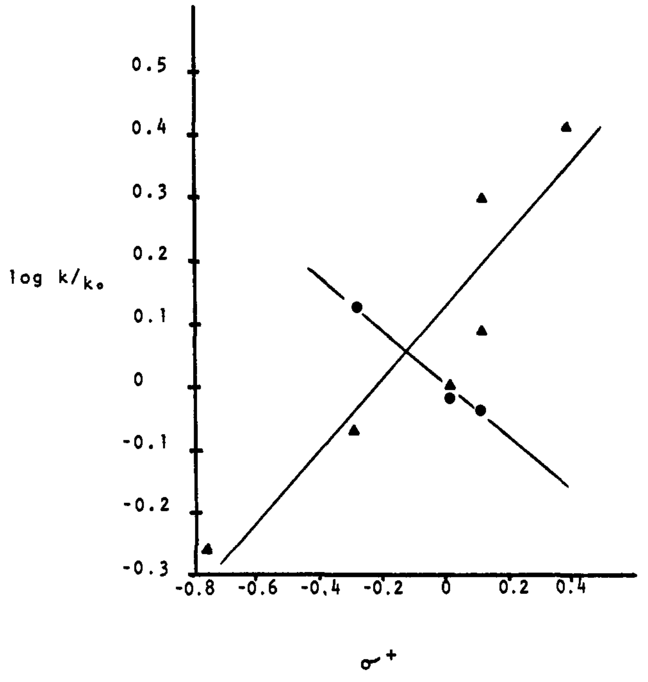


Figure 1. Hammett plots: (●) rearrangement of 4′-R-4-pentenophenones at 217°; (▲) rearrangement of 2,2-dimethyl-1-(3′- and 4′-R-benzoyl)cyclopropanes at 125°.

Inspection of the data given in Table II shows that electron releasing substituents retard the rate relative to that of the unsubstituted compound, whereas electron withdrawing substituents enhance the rate. Also, it is seen that the stronger the donating or withdrawing ability of the substituent, the greater the effect on the rate. A Hammett plot (Figure 1) of the data using σ^+ values gives a slope (ρ) of 0.57 with a correlation coefficient of 0.9256. Thus, electron-attracting substituents serve to decrease the free energy difference between the ground and transition states while the electron releasing substituents serve to increase $\Delta G^{\ddagger}$. Considering only the transition state (**4**), which can be depicted as having a degree of positive charge on C_1, an electron releasing substituent would be expected to exert a stabilizing effect thereon (by stabilizing the charge on C_1), whereas electron attracting substituents would exert a destabilizing effect. This reasoning would lead to a prediction that the rate would show an effect of substitution just opposite to that measured. However, before this depiction of the transition state is discarded as untenable, the possible effects of the substituents on the ground state must also be examined. The ground state is that of a ketone, a moiety known to be highly polarized. Thus there is the possibility of ground-state interaction between substituents on the phenyl ring and the positive carbonyl carbon. This has been demonstrated for substituted acetophenones[30]

---

(27) A. R. Tanner, Ph.D. Dissertation, The University of Texas, Austin, Tex., 1970.

(28) L. P. Hammett, "Physical Organic Chemistry," 1st ed, McGraw-Hill, New York, N. Y., 1940, p 189.

(29) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 178.

(30) R. N. Jones, W. F. Forbes, and W. A. Mueller, *Can. J. Chem.*, 35, 504 (1957).

and other ketones[31,32] by variations in the carbonyl stretching frequency of their infrared spectra. An electron donating substituent would be expected to stabilize this polarized species by inductive and/or resonance effects. The expected result would be a decrease in the double bond character of the carbonyl bond. This is seen in a lower bond energy and a decrease in the ir stretching frequency. The opposite effect would be expected for electron attracting substituents. This is the effect found experimentally. The data in Table IV show that the same effect is found in the phenyl cyclopropyl ketones used in this work, and good correlation with σ^+ ($r = 0.9869$) is seen.

Table IV. Carbonyl Stretching Frequency of Substituted 2,2-Dimethyl-1-benzoylcyclopropanes

Substituent	$\sigma^{+\,a}$	Frequency, cm^{-1}
p-CH$_3$O	−0.778	1667.4
p-CH$_3$	−0.311	1671.0
H	0	1673.5
m-CH$_3$O	0.115	1674.2
p-Cl	0.114	1674.4
m-Cl	0.373	1678.0

[a] From ref 1.

From this it is predicted that the effect on the ground state will be that electron donors will lower the ground-state energy whereas electron withdrawing substituents will raise it. Thus, the effects on the ground state and transition state are competing. The relative importance of the two effects will depend upon the amount of charge separation in the two states.

The observed effect on the rates of thermal rearrangement of the substituted cyclopropyl ketones is then reasonable if the transition state has less polar character than the ground-state ketone. This result is also consistent with results of the rearrangements of the 4-pentenophenones as interpreted earlier in this discussion. The rates measured in that case are assumed to be those for going from an enol to the same transition state. The ground state in this case should not be as polarized as that of a ketone. Thus there would be little effect on the ground-state energy but some lowering of the transition-state energy for electron donors and some elevation by electron attracting substituents. Since the overall effect in the cyclopropyl ketone ring opening is a decreased rate with electron donation, the transition state would seem to have a magnitude of charge separation more nearly like that of the enol than the ketone.

Experimental Section

I. Synthesis of 4′-Substituted-4-pentenophenones. 4-Pentenophenone-*2-d*$_2$. Acetophenone Cyclohexylimine. Acetophenone (240.0 g, 2.0 mol), cyclohexylamine (485 ml, 4.0 mol), and dry benzene (300 ml) were heated under reflux in a flask fitted with a Dean-Stark tube for 100 hr, after which time 35 ml of water (97% of the theoretical amount) had been collected. Subsequent vacuum distillation gave distillate, bp 125–135° (0.2 mm), which infrared analysis showed to be the imine (1640 cm^{-1}) uncontaminated by ketone. The yield was 290.8 g (72.2%).

Ethylmagnesium Bromide. Ethyl bromide (40 ml, 0.55 mol) was added dropwise to a stirred mixture of magnesium turnings (12.0 g, 0.50 mol) and dry tetrahydrofuran (160 ml) at room temperature over a 1-hr period, and the resulting combination was stirred overnight to complete the consumption of the magnesium.

4-Pentenophenone. Acetophenone cyclohexylimine (100.5 g, 0.50 mol) was added to a refluxing solution of ethylmagnesium bromide (0.6 mol) in tetrahydrofuran (160 ml) over a 20-min period and the resulting mixture was allowed to reflux overnight. The reaction mixture was cooled to 0° and diluted with additional tetrahydrofuran (100 ml). Allyl bromide (60.5 g, 0.50 mol) was added dropwise over a 2-hr period and the resulting mixture was stirred overnight, during which time a precipitate formed. It was then hydrolyzed with 10% hydrochloric acid (350 ml); the phases were separated and the aqueous phase was extracted with ether. The organic phases were combined, washed successively with 5% sodium bicarbonate solution and water, dried over anhydrous magnesium sulfate, and concentrated in a rotary evaporator. Vacuum distillation gave distillate, bp 102–112° (3.5 mm), which was pure to glpc analysis (10 ft × 0.125 in. 10% Carbowax 20M column), n^{25}D 1.5290. The yield was 15.7 g (19.6%). The nmr spectrum (neat) was consistent with the structure of 4-pentenophenone: δ 2.45 (split t, 2 H, –CH$_2$–), 2.9 (split t, 2 H, –COCH$_2$–), 5.0 (split t, 2 H, =CH$_2$), 5.9 (m, 1 H, –CH=), 7.4 and 7.9 ppm (2 m, 5 H, C$_6$H$_5$). The ir spectrum contained strong absorptions at 1690 (aromatic ketone), 975 and 910 cm^{-1} (terminal vinyl).

Deuterioethanol (CH$_3$CH$_2$OD).[33] Tetraethyl orthosilicate (162.0 g, 0.76 mol) and deuterium oxide (60.0 g, 3.0 mol) were stirred together in a stoppered flask until a gelatinous mass formed (48 hr), and the volatile material was then distilled from the reaction mixture. The product thus obtained was a clear liquid, bp 78–81°. Nmr analysis (neat) showed only the methyl and methylene protons; yield, 140.1 g (quantitative).

4-Pentenophenone-*2-d*$_2$. 4-Pentenophenone (8.0 g, 0.05 mol) was stirred with a tenfold amount of deuterioethanol (58.7 ml, 1.0 mol) and a catalytic amount (*ca.* 0.2 g) of sodium metal for 24 hr, after which time the deuterioethanol was removed by the application of aspirator vacuum, and a second tenfold excess of deuterioethanol and a chip of sodium were added. This process was repeated a second time, and at the conclusion of the final 24-hr period, acetyl chloride (15 drops) was added and the solution was again concentrated using aspirator vacuum. Deuterium oxide (5 ml) and ether (20 ml) were added and the resulting phases were separated. The organic phase was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. Subsequent vacuum distillation gave product, bp 58–65° (0.05 mm), n^{25}D 1.5282. The yield was 6.5 g. The nmr spectrum was identical with that of the undeuterated 4-pentenophenone except that the absorption at δ 2.9 (–COCH$_2$–) was absent and that at δ 2.45 (–CH$_2$–) had collapsed to a doublet. The ir spectrum appeared identical with that of the undeuterated material with the exception that a small absorption was present at 2200 cm^{-1} (carbon–deuterium) in the deuterated material.

Anal. Calcd for C$_{11}$H$_{10}$D$_2$O: C, 81.44; H + D, 8.69. Found: C, 81.27; H + D, 8.70.

4′-Methyl-4-pentenophenone-*2-d*$_2$. 4′-Methylacetophenone Cyclohexylimine. 4′-Methylacetophenone (100.0 g, 0.75 mol) and cyclohexylamine (149.0 g, 1.5 mol) were stirred together with refluxing dry toluene (400 ml) in a flask fitted with a Dean-Stark tube for 4 days, after which time 13.5 ml of water (100% of the theoretical amount) had been collected. The reaction mixture was cooled, then concentrated *in vacuo*. Infrared analysis showed the product thus obtained to contain a sharp absorption at 1640 cm^{-1} (imine) and to be free of both ketone and amine. This material was used without further purification. The yield was 160.5 g (quantitative).

4′-Methyl-4-pentenophenone. 4′-Methylacetophenone cyclohexylimine (160.5 g, 0.75 mol) was added to a refluxing solution of ethylmagnesium bromide (0.8 mol) in tetrahydrofuran (500 ml) over a 2-hr period. The resulting reaction mixture was heated under reflux for 4 hr, then stirred overnight. Allyl bromide (67.5 ml. 0.78 mol) was added over a 2-hr period and the resulting mixture was again stirred overnight, during which time it solidified. Hydrolysis was effected by heating this reaction mixture at reflux with 10% hydrochloric acid (350 ml) for 4 hr. The phases were subsequently separated and the aqueous phase was extracted with ether. The resulting organic phases were combined, washed successively with 5% sodium bicarbonate solution and water, dried

---

(31) N. Fuson, M. L. Joshen, and E. M. Skelton, *J. Amer. Chem. Soc.*, 76, 2526 (1954).

(32) N. L. Silver and D. W. Boykin, Jr., *J. Org. Chem.*, 35, 759 (1970).

(33) D. J. Pasto and G. R. Meyer, *J. Org. Chem.*, 33, 1257 (1968).

over anhydrous magnesium sulfate, and concentrated under vacuum. Simple vacuum distillation followed by vacuum spinning band (50 cm) fractionation gave a product which was shown by glpc analysis (10 ft × 0.125 in. 10% Carbowax 20M column) to be 96% pure. $n^{25}\text{D}$ 1.5290. The yield was 29.9 g (22.9%). The nmr spectrum (neat) was consistent with the structure of 4′-methyl-4-pentenophenone and showed no impurities: δ 2.25 and 2.4 (overlapping s and split t, 5 H, $-CH_2-$, CH_3), 2.9 (split t, 2 H, $-COCH_2-$), 5.0 (split t, 2 H, $=CH_2$), 5.8 (m, 1 H, $-CH=$), 7.1 and 7.8 ppm (2 d, 4 H, $-C_6H_4-$). The ir spectrum contained strong absorptions at 1670 (aromatic ketone), 975, and 910 cm^{-1} (terminal vinyl).

4′-Methyl-4-pentenophenone-*2-d₂*. The deuteration procedure used was identical with that employed with 4-pentenophenone; 7.0 g (0.04 mol) of 4′-methyl-4-pentenophenone was used, and vacuum distillation upon work-up gave water-clear distillate, bp 87–95° (0.2 mm), which was shown by glpc analysis (5 ft × 0.125 in. 5% SE-130 column) to be >99% pure, $n^{25}\text{D}$ 1.5290. The yield was 5.1 g. The nmr spectrum (neat) was identical with that of the undeuterated material with the exceptions that the absorption at δ 2.9 ($-COCH_2-$) was absent and that at δ 2.4 ($-CH_2-$) had collapsed to a doublet. The ir spectrum contained strong absorptions at 1675 (aromatic ketone), 970, and 915 cm^{-1} (terminal vinyl), and a weak absorption at 2150 cm^{-1} (carbon–deuterium).

Anal. Calcd for $C_{12}H_{12}D_2O$: C, 81.77; H + D, 9.15. Found: C, 81.60; H + D, 9.44.

4′-Chloro-4-pentenophenone-*2-d₂*. 4′-Chloroacetophenone Cyclohexylimine. 4′-Chloroacetophenone (150.2 g, 0.97 mol) and cyclohexylamine (178.5 g, 1.8 mol) were stirred together with refluxing dry benzene (250 ml) for 6 hr in a flask fitted with a Dean-Stark tube, after which time 17 ml of water (98% of the theoretical amount) had been collected. Concentration of the cooled reaction mixture in a rotary evaporator produced a partially crystalline product. Overnight refrigeration followed by vacuum filtration gave a white crystalline product, mp 65–66°, yield 150.4 g (65.7%). Infrared analysis indicated this product to be the imine (1640 cm^{-1}) uncontaminated by either the ketone or the amine.

4′-Chloro-4-pentenophenone. 4′-Chloroacetophenone cyclohexylimine (150.4 g, 0.64 mol) dissolved in dry tetrahydrofuran (200 ml) was added to a gently refluxing solution of ethylmagnesium bromide (0.7 mol) in tetrahydrofuran (400 ml) over a 2-hr period. The resulting reaction mixture was heated under reflux overnight, then cooled to ambient temperature. Allyl bromide (56 ml, 0.65 mol) was added over a 3-hr period and the resulting mixture was stirred overnight. Subsequent hydrolysis with 10% hydrochloric acid (450 ml) gave two phases, which were separated, and the aqueous phase was extracted with ether. The organic phases were combined, washed successively with 5% sodium bicarbonate solution and water, dried over anhydrous magnesium sulfate, and concentrated in a rotary evaporator. Simple vacuum distillation followed by vacuum spinning band fractionation gave product, bp 100–102° (1.5 mm), which was 96% pure to glpc analysis (10 ft × 0.125 in. 10% Carbowax 20 M column), $n^{25}\text{D}$ 1.5455. The yield was 30.1 g (20%). The nmr spectrum (neat) was consistent with the structure of 4′-chloro-4-pentenophenone: δ 2.1 (split t, 2 H, $-CH_2-$), 2.5 (split t, 2 H, $-COCH_2-$), 4.7 (split t, 2 H, $=CH_2$), 5.5 (m, 1 H, $-CH=$), 6.9 and 7.4 ppm (2 d, 4 H, $-C_6H_4-$). The ir spectrum possessed strong absorptions at 1680 (aromatic ketone), 990, and 915 cm^{-1} (terminal vinyl).

4′-Chloro-4-pentenophenone-*2-d₂*. The deuteration procedure used was identical with that employed with 4-pentenophenone; 5.0 g (0.026 mol) of 4′-chloro-4-pentenophenone was used, and vacuum distillation upon work-up gave water-clear distillate, bp 80–85° (0.06 mm). This product was further purified by column chromatography on silica gel (petroleum ether–benzene) followed by micro vacuum distillation. The product thus obtained was pure to glpc analysis (5 ft × 0.125 in. 5% SE-30 column), and the nmr spectrum (neat) was identical with that of the undeuterated compound with the exceptions that the absorption at δ 2.5 ($-COCH_2-$) had decreased to 0.07 proton (965.5% deuteration) and that at δ 2.1 ($-CH_2-$) had collapsed to a doublet. The ir spectrum contained strong absorptions at 1680 (aromatic ketone), 1000, and 915 cm^{-1} (terminal vinyl).

Anal. Calcd for $C_{11}H_9D_2OCl$: C, 67.17; H + D, 6.66. Found: C, 67.31; H + D, 6.64.

4′-Methoxy-4-pentenophenone-*2-d₂*. 4′-Methoxyacetophenone Cyclohexylimine. 4′-Methoxyacetophenone (100.0 g, 0.67 mol) and cyclohexylamine (139.0 g, 1.4 mol) were stirred together with refluxing dry benzene (500 ml) in a flask fitted with a Dean-Stark tube for 6 days, during which time 11.75 ml of water (97% of the theoretical amount) was collected. The solvent and excess amine were removed from the reaction mixture at 100° in a rotary evaporator, and subsequent concentration *in vacuo* followed by refrigeration gave crystalline product, mp 35–37°. The ir spectrum of this material showed it to be the imine (1630 cm^{-1}) uncontaminated by either amine or ketone. The yield was 154.7 g (quantitative).

4′-Methoxy-4-pentenophenone. 4′-Methoxyacetophenone cyclohexylimine (154.7 g, 0.67 mol) dissolved in dry tetrahydrofuran (150 ml) was added to a refluxing solution of ethylmagnesium bromide (0.7 mol) in tetrahydrofuran (450 ml) over a 4-hr period. The resulting reaction mixture was heated at reflux overnight, then cooled to ambient temperature. Allyl bromide (56 ml, 0.65 mol) was added over a 4-hr period, care being taken to prevent the temperature of the reaction mixture from exceeding 35°. This mixture solidified upon being stirred overnight and was subsequently hydrolyzed by being heated with 10% hydrochloric acid (300 ml) at reflux for 1 hr. The phases were separated and the aqueous phase was extracted with ether. The organic phases were combined, washed successively with 5% sodium bicarbonate solution and water, dried over anhydrous magnesium sulfate, and concentrated in a rotary evaporator. This material was vacuum filtered (to remove a small quantity of solid by-product, mp 153–156°), then vacuum distilled to obtain distillate, bp 120–140° (0.6 mm), which crystallized upon refrigeration. Recrystallization (three times) from petroleum ether, bp 35–60°, gave off-white crystals, mp 32–33°, the nmr spectrum (CCl_4) of which was consistent with the structure of the desired 4′-methoxy-4-pentenophenone: δ 2.4 (split t, 2 H, $-CH_2-$), 2.9 (split t, 2 H, $-COCH_2-$), 3.8 (s, 3 H, CH_3O), 5.0 (split t, 2 H, $=CH_2$), 5.9 (m, 1 H, $-CH=$), 6.7 and 7.8 ppm (two d, 4 H, $-C_6H_4-$). The ir spectrum contained strong absorptions at 1675 (aromatic ketone), 1260 (ether), 990, and 920 cm^{-1} (terminal vinyl).

4′-Methoxy-4-pentenophenone-*2-d₂*. The deuteration procedure used was identical with that employed with 4-pentenophenone; 7.0 g (0.037 mol) of 4′-methoxy-4-pentenophenone was used, and concentration of the ether phase obtained during the work-up gave white crystalline product, mp 31–32°. The yield was 3.7 g. The nmr spectrum (CCl_4) of this product was identical with that of the undeuterated compound except that the absorption at δ 2.9 ($-COCH_2-$) was absent and that at δ 2.4 ($-CH_2-$) had collapsed to a doublet. The ir spectrum possessed strong absorptions at 1675 (aromatic ketone), 1270 (ether), 1000, and 920 cm^{-1} (terminal vinyl).

Anal. Calcd for $C_{12}H_{12}D_2O$: C, 74.97; H + D, 8.39. Found: C, 74.74; H + D, 8.20.

4′-Cyano-4-pentenophenone-*2-d₂*. 3-Butenylmagnesium Bromide. Magnesium turnings (4.8 g, 0.20 mol) and anhydrous ether (250 ml) were stirred together and 4-bromo-1-butene (27.0 g, 0.20 mol) was added dropwise. The resulting reaction mixture was stirred for 4 hr to allow completion of the consumption of the magnesium.

Di(3-butenyl)cadmium. Freshly oven-dried anhydrous cadmium chloride (18.3 g, 0.095 mol) was added to the 3-butenylmagnesium bromide and the resulting mixture was stirred overnight. A negative Gilman test was obtained,[34] and the ether was removed using aspirator vacuum and replaced with dry benzene (400 ml).

4′-Cyano-4-pentenophenone. 4′-Cyanobenzoyl chloride (25.0 g, 0.15 mol) was added to the di(3-butenyl)cadmium and the resulting reaction mixture was stirred for 3 hr at ambient temperature. It was then heated at reflux for 3 additional hr and hydrolyzed with 10% sulfuric acid (250 ml). The phases were separated and the aqueous phase was extracted with ether. The organic phases were combined, washed successively with 10% sodium hydroxide solution and water, dried over anhydrous magnesium sulfate, and concentrated in a rotary evaporator to give 27.5 g of crude product. This product was combined with those from three earlier trial-scale preparations of 4′-cyano-4-pentenophenone. Simple vacuum distillation gave distillate, bp 110–150° (100 mm), before solid material began to sublime and plugged the condenser. (Subsequent recrystallization of this sublimate gave crystals, mp 197–205°, which were soluble in aqueous base and are believed to be 4′-cyanobenzoic acid.) The distillate was made to crystallize by freezing, and eight separate crops of crystals, mp 20–26°, were gathered from it. Subsequent recrystallization from ethanol and thorough washing with ice-cold petroleum ether, bp 35–60°, gave crystalline product, mp 32–33°. The yield was 3.1 g. Glpc analysis (5 × 0.125 in. 5% SE-30 column) showed this product to be

---

(34) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 417.

96% pure and to contain a single impurity (which was subsequently shown, by independent synthesis and comparison of glpc retention time, nmr, and ir, to be ethyl 4-cyanobenzoate, a common by-product in organocadmium syntheses).[12] The nmr spectrum was consistent with the structure of 4′-cyano-4-pentenophenone, the presence of the ethyl ester impurity being barely discernible: δ 2.5 (split t, 2 H, -CH_2-), 3.1 (split t, 2 H, -$COCH_2$-), 5.1 (split t, 2 H, =CH_2), 5.9 (m, 1 H, —CH=), 7.8 and 8.1 ppm (two doublets, 4 H, -C_6H_4-). The ir spectrum contained strong absorptions at 2225 (cyano), 1690 (aromatic ketone), 990, and 915 cm^{-1} (terminal vinyl) and a weak carbonyl absorption at 1720 cm^{-1} (ester, impurity).

4′-Cyano-4-pentenophenone-*2-d_2*. The procedure used was the same as that employed with 4-pentenophenone. Upon work-up with ether, a solid precipitate, mp 167–168.5°, was obtained; as this was obviously not the desired product, the organic and aqueous phases were recombined and subjected to continuous extraction with benzene for 36 hr. Concentration of the organic solution thus obtained gave a pasty material which, when washed with ether, gave a yellow supernatant plus a white solid having a high melting point (145–150°). Reconcentration of this supernatant followed by micro vacuum distillation produced approximately 0.2 ml of distillate, bp 130° (10 mm), in addition to more solid. An nmr spectrum (CCl_4) of this distillate showed it to be a mixture of approximately 85% 4′-cyano-4-pentenophenone and 15% ethyl 4-cyanobenzoate. The 4′-cyano-4-pentenophenone was 80% deuterated in the α position as shown by the decrease of the absorption at δ 3.1 (-CO-CH_2-) to 0.4 proton and by the collapse of the absorption at δ 2.5 (-CH_2-) to a doublet. No further purification of this product was attempted.

II. **Synthesis of Alkylacylcyclopropanes. 2,2-Dimethyl-1-benzoylcyclopropane. 3-Methyl-1-phenyl-3-buten-1-ol.** A 500-ml, round-bottomed flask, equipped with an addition funnel, Friedrich condenser, $CaSO_4$ drying tube, and nitrogen inlet, was charged with magnesium turnings (9.7 g, 0.4 mol) and flamed out under a fast nitrogen sweep. After the apparatus had cooled to room temperature, 75 ml of THF (distilled from CaH) was added and heated to a gentle reflux. From the addition funnel, approximately 15 ml of a solution of β-methallyl chloride (2.7 g, 0.30 mol) in 75 ml of dry THF was added in one portion. After a few minutes, formation of Grignard reagent was evidenced by darkening of the solution. To the solution in the addition funnel, benzaldehyde (21.3 g, 0.20 mol) was added and mixed with a stirring rod. The heat was removed from the flask and a gentle reflux was maintained by adjusting the rate of addition of the aldehyde–chloride mixture. After the addition was completed, the reaction mixture was stirred for 3–4 hr at room temperature. The reaction mixture was decanted from excess magnesium onto 500 g of cracked ice containing 20 ml of concentrated sulfuric acid. The aqueous mixture was extracted with ether several times to give a total of 1 l. of organic material. After drying over $CaCl_2$, the ether was removed on a rotary evaporator. The residue was distilled under vacuum through a short-path, total take-off still at 62–69° (0.5 mm). The yield was 95% and the ir spectrum showed a strong hydroxyl absorbance but no carbonyl. The nmr spectrum (neat) was consistent with the structure of 3-methyl-1-phenyl-3-buten-1-ol: δ 1.61 (d, 3 H, CH_3), 2.29 (d, 2 H, -CH_2-), 3.78 (s, 1 H, OH), 4.61 (t, 1 H, -CH-) 4.7 (m, 2 H, =CH_2), and 7.15 ppm (s, 5 H, C_6H_5).

3-Methyl-3-butenophenone. The chromic acid oxidant solution (Jones' reagent)[16] used in this procedure was prepared by careful addition of 46 ml of concentrated sulfuric acid, with cooling, to approximately 125 ml of water. Anhydrous CrO_3 (50.0 g, 0.50 mol) was dissolved in this solution. The resulting solution was diluted to 200 ml with water to obtain a solution containing 2.5 mmol of oxidizing agent/ml. A solution of 3-methyl-1-phenyl-3-buten-1-ol (38.5 g, 0.20 mol) in 300 ml of acetone was stirred with a mechanical stirrer and cooled in an ice bath while 56 ml of the Jones' reagent (0.14 mol of H_2CrO_4) was added dropwise. Each drop turned instantly from bright red to dark blue-green. A thick, black, gummy residue soon formed, making a mechanical stirrer essential. After all the H_2CrO_4 had been added (about 1 hr), the acetone solution was decanted from the residue and diluted to 1.5 l. with water. The aqueous solution was then extracted several times with ether to make a total of about 1 l. of ether solution. The ether was dried over $CaCl_2$ and removed on a rotary evaporator. The residue was not purified further but was used in the following step as obtained.

3-Methyl-2-butenophenone. The crude product from the above reaction was poured into 300 ml of anhydrous ethanol in which a small chunk of sodium had been dissolved. There was an immediate formation of a yellow color owing, presumably, to enolate formation. Reaction for longer than 30–45 min was unnecessary. After the required time, glacial acetic acid was added until the solution became acidic to pH paper. The solution turned from yellow to green as this was done. After acidification, the solution was distilled with 200 ml of water and concentrated on a rotary evaporator until a second phase separated. This mixture was then extracted several times with ether to give a total of 1 l. of organic material. After drying over $CaCl_2$ the ether was removed on a rotary evaporator and the residue was distilled *in vacuo* through a short-path, total take-off still. The yield was 52% of a liquid distilling at 63° (0.25 mm). The nmr spectrum (neat) was consistent with the structure of 3-methyl-2-butenophenone: δ 1.83 (d, 3 H, trans CH_3), 2.12 (d, 3 H, cis CH_3), 6.7 (m, 1 H, -CH=), 7.1–8.0 ppm (2 m, 5 H, C_6H_5).

Trimethylsulfoxonium Iodide.[17] To dimethyl sulfoxide (96 g, 1.23 mol) in a 500-ml flask equipped with a Friedrich condenser, mechanical stirrer, and nitrogen inlet was added, in one portion, 180 ml (2.9 mol) of methyl iodide. The mixture was heated at reflux under a nitrogen atmosphere for 3 days. The reaction mixture was allowed to cool to room temperature and was filtered. The collected solid was rinsed with chloroform and recrystallized with water. After air-drying, the product was ground in a mortar and dried *in vacuo* before use.

2,2-Dimethyl-1-benzoylcyclopropane. To an oven-dried 500-ml flask equipped with a nitrogen inlet and $CaSO_4$ drying tube was placed 5.1 g of 57% NaH/mineral oil dispersion (0.12 mol NaH). The mineral oil was removed by washing the NaH with three 100-ml portions of pentane, followed by decantation. After the last washing, the residual pentane was removed using a vigorous nitrogen sweep. The flask was equipped with a mechanical stirrer and addition funnel, and trimethylsulfoxonium iodide (27.4 g, 0.12 mol) was added in one portion. A water bath was placed around the flask and the stirrer was started to thoroughly mix the two solids. Dimethyl sulfoxide (100 ml, dried over 3 Å molecular sieves) was added in small portions with stirring. Following completion of DMSO addition, the reaction mixture was stirred for 30 min in the water bath. 3-Methyl-2-butenophenone (16.0 g, 0.10 mol) was added over a 1-hr period. The resulting light brown solution was stirred 3–4 hr at room temperature. The reaction mixture was diluted to 750 ml with water and extracted several times to give a total of 1 l. of organic material. After drying over $CaCl_2$, the ether was removed on a rotary evaporator. No further purification was carried out on the bulk of the material, as distillation would be expected to cause considerable rearrangement. Instead, sufficient material for rearrangement was obtained by preparative glpc (11 ft × 0.375 in. 20% XF-1150 column at 135–140°). The nmr spectrum (CCl_4) was consistent with the structure of 2,2-dimethyl-1-benzoylcyclopropane: δ 0.84 (2 d, 1 H, -CH_2-, trans H to CO), 1.05 (s, 3 H, cis CH_3), 1.36 (s, 3 H, trans CH_3), 1.47 (2 d, 1 H, CH_2, cis H), 2.40 (2 d, 1 H, -CH-), and 7.2–7.6 and 7.8–8.0 ppm (2 m, 5 H, C_6H_5). The infrared spectrum contained a strong carbonyl stretching band at 1673 cm^{-1}.

Anal. Calculated for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.57; H, 8.08.

2,2-Dimethyl-1-(4′-methylbenzoyl)cyclopropane. 3-Methyl-1-(4′-methylphenyl)-3-buten-1-ol. This material was prepared in the same manner as the parent compound except that *p*-tolualdehyde was used in place of benzaldehyde. Distillation at 74–75° (0.2 mm) gave a 90% yield of colorless liquid. The infrared spectrum showed a strong hydroxyl band but no carbonyl absorption. The nmr spectrum (neat) was consistent with the structure of 3-methyl-1-(4′-methylbenzoyl)-3-buten-1-ol: δ 1.58 (d, 3 H, CH_3), 2.20 (s, 3 H, CH_3Ar), 2.30 (d, 2 H, -CH_2-), 3.65 (s, 1 H, OH), 4.53 (t, 1 H, -CH-), 4.7 (m, 2 H, =CH_2), and 7.0 ppm (d, 4 H, -C_6H_4-).

3,4′-Dimethyl-3-butenophenone. This material was prepared from the product above in the same manner as the parent compound. The product was not purified, but was used as obtained from the reaction for the next step.

3,4′-Dimethyl-2-butenophenone. This material was prepared in the same manner as the parent compound; distillation at 55–60° (0.15 mm) gave a 50% yield of a clear colorless liquid. The nmr spectrum (neat) was consistent with the structure of 3,4′-dimethyl-2-butenophenone: δ 1.87 (d, 3 H, trans CH_3), 2.10 (s, 3 H, CH_3Ar), 2.17 (d, 3 H, cis CH_3), 6.7 (m, 1 H, —CH=), 7.1–7.2 and 7.5–7.8 ppm (2 d, 4 H, -C_6H_4-).

2,2-Dimethyl-1-(4′-methylbenzoyl)cyclopropane. This material was prepared from the product above in the same manner as the parent compound; purification of samples for rearrangement was by column chromatography (silica gel, 3:1 hexane–ethyl acetate). The nmr spectrum was consistent with the structure of 2,2-dimethyl-1-(4′-methylbenzoyl)cyclopropane, but chemical shifts were not determined as the product was sealed *in vacuo* for rearrangement immediately following purification. The ir spectrum contained a strong carbonyl absorption at 1671 cm^{-1}. The 2,4-dinitrophenylhydrazone (mp 172–173°) was prepared by standard procedures[35] and used for carbon, hydrogen analysis.

Anal. Calcd for $C_{19}H_{20}N_4O_4$: C, 61.95; H, 5.47. Found: C, 61.99; H, 5.35.

2,2-Dimethyl-1-(4′-methoxybenzoyl)cyclopropane. 3-Methyl-1-(4′-methoxyphenyl)-3-buten-1-ol. This material was prepared in the same manner as the parent compound except that *p*-anisaldehyde was substituted for benzaldehyde. The crude product could not be distilled because the heat caused elimination of water. Therefore, the product was used as obtained in the next step.

3-Methyl-4′-methoxy-3-butenophenone. This material was prepared in the same manner as the parent compound and was used as obtained in the next step.

3-Methyl-4′-methoxy-2-butenophenone. This material was prepared in the same manner as the parent compound; distillation at 80–90° (0.2 mm) gave a 48% yield of a clear colorless liquid. The nmr spectrum (CCl_4) was consistent with the structure of 3-methyl-4′-methoxy-2-butenophenone: δ 1.91 (d, 3 H, trans CH_3), 2.16 (d, 3 H, cis CH_3), 6.7 (m, 1 H, —CH=), 6.7–6.9 and 7.8–8.0 ppm (2 d, 4 H, $-C_6H_4-$).

2,2-Dimethyl-1-(4′-methoxyphenyl)cyclopropane. This material was prepared from the product above in the same manner as the parent compound. Purification of samples for rearrangement was by column chromatography on silica gel (hexane–ethyl acetate). The nmr spectrum was consistent with the structure of 2,2-dimethyl-1-(4′-methoxyphenyl)cyclopropane but chemical shifts were not determined as the product was sealed *in vacuo* for rearrangement immediately following purification. The ir spectrum possessed a strong carbonyl absorption at 1667 cm^{-1}. The 2,4-dinitrophenylhydrazone (mp 179–180°) was prepared by standard procedures[35] and used for carbon, hydrogen analysis.

Anal. Calcd for $C_{19}H_{20}N_4O_5$: C, 59.37; H, 5.24. Found: C, 59.05, 59.21; H, 5.39, 5.57.

2,2-Dimethyl-1-(3′-methoxybenzoyl)cyclopropane. *m*-Methoxybenzaldehyde. To a 1-gallon, screw-cap bottle was added acetone (1.2 l., dried over $MgSO_4$), *m*-hydroxybenzaldehyde (106 g, 1.0 mol), methyl iodide (213 g, 1.5 mol), and anhydrous K_2CO_3 (103 g, 0.75 mol). The bottle was capped and shaken at room temperature for 3.5 days. The solids were filtered away and the acetone was removed on a rotary evaporator. Water (200 ml) was added to the residue which was then extracted with ether to give a total of 1 l. of organic material. After drying ($CaCl_2$), the ether was removed on a rotary evaporator. The crude product was used without further purification.

3-Methyl-1-(3′-methoxyphenyl)-3-buten-1-ol. This material was prepared in the same manner as the parent compound except that *m*-methoxybenzaldehyde was substituted for benzaldehyde. Distillation at 100–105° (0.3 mm) gave a clear liquid which solidified upon standing. The solid had mp 32–34° when recrystallized from hexane. The nmr spectrum (CCl_4) was consistent with the structure of 3-methyl-1-(3′-methoxyphenyl)-3-buten-1-ol: δ 1.66 (d, 3 H, CH_3), 2.28 (d, 2 H, $-CH_2-$), 3.10 (s, 1 H, OH), 3.64 (s, 3 H, CH_3O), 4.60 (t, 1 H, -CH-), 4.70 (m, 2 H, CH_2=), 6.5–7.3 ppm (m, 4 H, $-C_6H_4-$).

3-Methyl-3′-methoxy-3-butenophenone. This material was prepared from the product above in the same manner as the parent compound and was used as obtained in the next step.

3-Methyl-3′-methoxy-2-butenophenone. This material was prepared in the same manner as the parent compound; distillation at 80–90° (0.2 mm) gave a clear colorless liquid. The nmr spectrum (CCl_4) was consistent with the structure of 3-methyl-3′-methoxy-2-butenophenone: δ 1.89 (d, 3 H, trans CH_3), 2.15 (d, 3 H, cis CH_3), 3.70 (s, 3 H, CH_3O), 6.7 (quintet, 1 H, —CH=), 6.8–7.7 ppm (m, 4 H, $-C_6H_4-$).

2,2-Dimethyl-1-(3′-methoxybenzoyl)cyclopropane. This material was prepared from the product above in the same manner as the parent compound. Purification of samples for rearrangment was by column chromatography on silica gel (hexane–ethyl acetate). The nmr spectrum was consistent with the structure of 2,2-dimethyl-1-(3′-methoxybenzoyl)cyclopropane but chemical shifts were not determined as the product was sealed *in vacuo* for rearrangement immediately following purification. The ir spectrum contained a strong carbonyl absorption at 1674 cm^{-1}. The 2,4-dinitrophenylhydrazone (mp 170–171°) was prepared by standard procedures[35] and used for carbon, hydrogen analysis.

Anal. Calcd for $C_{19}H_{20}N_4O_5$: C, 59.37; H, 5.24. Found: C, 59.32; H, 5.33.

2,2-Dimethyl-1-(4′-chlorobenzoyl)cyclopropane. 3-Methyl-1-(4′-chlorophenyl)-3-buten-1-ol. This material was prepared in the same manner as the parent compound except that *p*-chlorobenzaldehyde was employed in place of benzaldehyde. Distillation at 80–90° (0.1 mm) gave a clear colorless liquid which later crystallized. The solid had a mp of 26° when recrystallized from hexane. The ir spectrum showed a strong hydroxyl absorption but no carbonyl. The nmr spectrum (CCl_4) was consistent with the structure of 3-methyl-1-(4′-chlorophenyl)-3-buten-1-ol: δ 1.66 (d, 3 H, CH_3), 2.22 (d, 2 H, $-CH_2-$), 3.32 (d, 1 H, OH), 4.40 (split t, 1 H, -CH-), 4.7 (m, 2 H, $=CH_2$), 7.40 ppm (s, 4 H, $-C_6H_4-$).

4′-Chloro-3-methyl-3-butenophenone. This material was prepared from the product above in the same manner as the parent compound and was used as obtained in the next step.

4′-Chloro-3-methyl-2-butenophenone. This material was prepared in the same manner as the parent compound; distillation at 95–100° (0.35 mm) gave a 52% yield of a clear colorless liquid which later crystallized. The solid had a melting point of 37.5–38.5° when recrystallized from methanol. The nmr spectrum was consistent with the structure of 4′-chloro-3-methyl-2-butenophenone: δ 1.97 (d, 3 H, trans CH_3), 2.15 (d, 3 H, cis CH_3), 6.6 (m, 1 H, —CH=), 7.2–7.4 and 7.7–7.9 ppm (2 d, 4 H, $-C_6H_4-$).

1-(4′-Chlorobenzoyl)-2,2-dimethylcyclopropane. This material was prepared from the product above in the same manner as the parent compound. Purification was by column chromatography on silica gel (*n*-hexane–ethyl acetate). The nmr spectrum was consistent with the structure of 1-(4′-chlorobenzoyl)-2,2-dimethylcyclopropane but chemical shifts were not determined as the product was sealed *in vacuo* for rearrangement immediately following purification. The ir spectrum contained a carbonyl absorption at 1674 cm^{-1}. The 2,4-dinitrophenylhydrazone was prepared by standard procedures;[35] however, no pure sample of compound was available for the derivative. A sample of crude ketone gave a mixture that melted at 133–140° after repeated recrystallization. This mixture was used for carbon, hydrogen analysis.

Anal. Calcd for $C_{18}H_{17}N_4O_4Cl$: C, 55.60; H, 4.41. Found: C, 55.96, 56.26; H, 4.75, 4.58

2,2-Dimethyl-1-(3′-chlorobenzoyl)cyclopropane. 3-Methyl-1-(3′-chlorophenyl)-3-buten-1-ol. This material was prepared in the same manner as the parent compound except that *m*-chlorobenzaldehyde was employed in place of benzaldehyde. Distillation at 80–90° (0.1 mm) gave a clear colorless liquid. The ir spectrum showed a strong hydroxyl absorption and no carbonyl. The nmr spectrum (CCl_4) was consistent with the structure of 3-methyl-1-(3′-chlorophenyl)-3-buten-1-ol: δ 1.72 (d, 3 H, CH_3), 2.27 (d, 2 H, $-CH_2-$), 3.20 (s, 1 H, OH), 4.60 (t, 1 H, -CH-), 4.8 (m, 2 H, $=CH_2$), and 7.0–7.4 ppm (m, 4 H, $-C_6H_4-$).

3′-Chloro-3-methyl-3-butenophenone. This material was prepared from the product above in the same manner as the parent compound and was used as obtained in the next step.

3′-Chloro-3-methyl-2-butenophenone. This material was prepared in the same manner as the parent compound; distillation at 90–100° (0.3 mm) gave a 48% yield of a clear colorless liquid. The nmr spectrum (CCl_4) was consistent with the structure of 3′-chloro-3-methyl-2-butenophenone: δ 1.98 (d, 3 H, trans CH_3), 2.17 (d, 3 H, cis CH_3), 6.6 (complex quintet, 1 H, —CH=), and 7.1–7.9 ppm (m, 4 H, $-C_6H_4-$).

1-(3′-Chlorobenzoyl)-2,2-dimethylcyclopropane. This material was prepared from the product above in the same manner as the parent compound. Purification was by column chromatography on silica gel (hexane–ethyl acetate). The nmr spectrum was consistent with the structure of 1-(3′-chlorobenzoyl)-2,2-dimethylcyclopropane but chemical shifts were not determined as the product was sealed *in vacuo* for rearrangement immediately following purification. The ir spectrum possessed a carbonyl absorption at 1678 cm^{-1}. The 2,4-dinitrophenylhydrazone (mp 167–168°) was prepared by standard procedures[35] and used for carbon, hydrogen analysis.

Anal. Calcd for $C_{18}H_{17}N_4O_4Cl$: C, 55.60; H, 4.41. Found: C, 55.50; H, 4.40.

III. Thermal Rearrangements of 4-Pentenophenones. Rear-

---

(35) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1956, p 218.

rangements were conducted at 217 ± 0.5° by suspending the samples in the vapors of refluxing naphthalene in a flask with a long-necked air condenser. Samples for rearrangement were sealed in precision thin-walled nmr tubes, containing a sealed concentric capillary of hexamethyldisiloxane (lock signal), at $\leqslant 2\text{-}\mu$ pressure, after degassing by repeated freezing in liquid nitrogen and thawing. Deuterium incorporation into the 5 (terminal) position was monitored by a Varian associates HA-100 nmr spectrometer without opening the sealed sample tubes, and all rearrangements were carried to at least 65% completion. Relative peak areas were calculated from triple electronic integrals obtained with nonspinning samples, and the absorption of the proton at C_4 (—CH═) was in all cases taken as the standard and set at 1.00 proton.[36] With the exception of that of 4′-cyano-4-pentenophenone-*2-d*$_2$, the rearrangements were quite clean as indicated by the absence of any discernible extraneous peaks in the nmr spectra even after 110 hr at 217°. That a small amount of polymerization and/or decomposition was occurring under rearrangement conditions was, however, indicated by the increase in the aromatic resonance integrals and by an upward slope of the integral line in the region between δ 0.0 and 2.5 that was observed after prolonged heating. Multiple rearrangements of samples of 4-pentenophenone-*2-d*$_2$ showed good reproducibility of rate data (variations in $k \leqslant \pm 0.03 \times 10^{-2}$ hr^{-1}) and the absence of surface phenomena was demonstrated by rearrangements conducted in the presence of glass wool.

IV. Thermal Rearrangements of Alkylacylcyclopropanes. Rearrangements of 2,2-dimethyl-1-benzoylcyclopropane and 2,2-dimethyl-1-(*p*-methylbenzoyl)cyclopropane were performed using 25-μl samples sealed *in vacuo* in Pyrex tubes after degassing. Analyses were performed by glpc (3 ft × 0.25 in. 30% diethylene glycol succinate column at 130°). Separate samples were used for each analysis and peak areas were obtained by taking the average integral of three separate injections. The (peak height) × (width at one-half height) method of integration was used. Thermal ring opening of the less volatile acylcyclopropanes (**3b,d,f,g**, R′ = CH_3) was monitored by nmr in a manner similar to that described for the 4-pentenophenones. The absorptions used to monitor the rearrangements were the upfield methyl singlet of the acylcyclopropanes and the 4-methyl resonance of the products. Each compound was subjected to rearrangement at 125 ± 0.5° in a constant-temperature bath of refluxing 2-methoxyethanol vapors.

Infrared analyses were obtained with a Beckman IR-5A spectrophotometer; neat samples were analyzed as thin films spread between sodium chloride plates, if liquids, or as KBr pellets or Nujol mulls, if solids. Analytical glpc was performed using Beckman GC-2A and Varian Hy-Fi 600 D instruments; for preparative gas chromatography, a Wilkins A-700 (Autoprep) instrument was used. Routine nmr data were obtained using a Varian A-60 spectrometer with TMS as internal standard. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by A. Bernhardt, Mülheim, Germany.

---

(36) Results reported in an earlier publication[4] show that no deuterium is incorporated into position 4 upon enolene rearrangement of 4-pentenophenone-*2-d*$_2$.

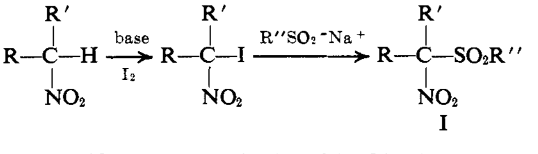
α-Nitro Sulfones

Nathan Kornblum,* Melvin M. Kestner, Steven D. Boyd, and Lawrence C. Cattran

Contribution from the Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907. *Received October 25, 1972*

Abstract: Pure α-nitro sulfones (I) are readily obtained in 85–95% yields by treating α-iodo nitroparaffins with the salts of sulfinic acids. Inasmuch as the requisite α-iodonitro compounds are rapidly and quantitatively prepared from nitroparaffins, the overall result is a facile synthesis of α-nitro sulfones. When α-bromo nitroparaffins, α-chloro nitroparaffins, and α,α-dinitro compounds react with sulfinate salts, α-nitro sulfones (I) are again produced. Evidence is presented for the view that these reactions are chain processes in which radical anions and free radicals are intermediates.

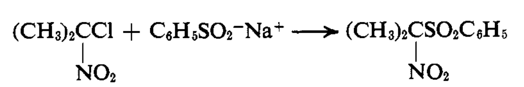
We report a new and general synthesis of α-nitro sulfones (I) in which the carbon bearing the nitro and sulfone groups is devoid of hydrogen atoms.[1] Such α-nitro sulfones are readily obtained by iodinating nitroparaffin salts and then treating the crude α-iodo nitroparaffin with the sodium salt of a sulfinic acid at −20 to 0° for several hours; the overall yields of pure products are 85–95% (Table I).



$$\mathrm{R{-}\underset{NO_2}{\overset{R'}{C}}{-}H} \xrightarrow[\mathrm{I_2}]{\text{base}} \mathrm{R{-}\underset{NO_2}{\overset{R'}{C}}{-}I} \xrightarrow{\mathrm{R''SO_2^-Na^+}} \underset{\mathrm{I}}{\mathrm{R{-}\underset{NO_2}{\overset{R'}{C}}{-}SO_2R''}} \qquad (1)$$

α-Bromo nitroparaffins also react with sulfinic acid salts to give α-nitro sulfones of the type I, but the yields are not routinely as high as when α-iodo nitroparaffins are employed, falling, instead, in the range 44–88%. Why this should be so was not investigated in view of the ready availability of the desired α-nitro sulfones *via* the sequence of eq 1.

The reaction of α-chloro nitroparaffins with sodium sulfinates at 25° is too slow to be useful. Thus, in DMF after 12 days at 25° the reaction of eq 2 is only 82% complete and a *ca.* 50% yield of the sulfone is obtained. In DMSO the reaction is faster but, even here, it is only 76% complete in 4 days.[2]



$$\mathrm{(CH_3)_2\underset{NO_2}{C}Cl + C_6H_5SO_2^-Na^+ \longrightarrow (CH_3)_2\underset{NO_2}{C}SO_2C_6H_5} \qquad (2)$$

α,α-Dinitro compounds can also be used to prepare α-nitro sulfones. For example, the displacement of a nitro group from 2,2-dinitropropane by benzenesulfinate ion takes place at room temperature and gives an 81% yield of the pure α-nitro sulfone after 3 days (eq

---

(1) Only one such compound has been prepared previously and the yield was 19%. In that preparation *p*-tolyl isopropyl sulfone was treated with *n*-butyllithium and then with ethyl nitrate: W. E. Truce, T. C. Klingler, J. E. Parr, H. Feuer, and D. K. Wu, *J. Org. Chem.*, 34, 3104 (1969).

(2) N. Kharasch and J. L. Cameron, *J. Amer. Chem. Soc.*, 73, 3864 (1951), found that 1-chloro-1-nitroethane and sodium *p*-toluenesulfinate in refluxing methanol (3 hr) give a 71% yield of α-nitroethyl *p*-tolyl sulfone; this, unlike our reactions, is presumably an S_N2 displacement.