from a small amount of insoluble oil, there resulted a solution which when chilled to 6° gave 1.23 g of I as white, fluffy needles, mp 110.5–113°. Recrystallization from hexane gave I, mp 121.5–122.5°, with 70% recovery. The infrared spectrum showed absorption at 3545, 3420, 1674, 1597 (medium intensity), and 1580 (weak) cm^{-1}. The nmr spectrum showed complex aromatic absorption at τ 2.13–3.17 and complex absorption at 6.1–6.8 which was simplified to an AB quartet centered at 6.39 (J = 13 cps) by shaking the solution with deuterium oxide to remove the absorption due to the O*H*. The mass spectrum at 15 ev showed peaks corresponding to M, M + 1, and M + 2 of the group $C_6H_5CH_2COHC_6H_4Cl$ at *m/e* 231 (100), 232 (20), 233 (35). At 40 and 70 ev the ratios of the peaks at 231 ($C_6H_5CH_2COHC_6H_4Cl$) and 197 ($C_6H_5CH_2COHC_6H_5$) were 61/1 and 117/1. Only a trace peak for the parent ion could be seen.

Anal. Calcd for $C_{21}H_{17}ClO_2$: C, 74.9; H, 5.1. Found: C, 74.7; H, 5.1.

Reaction of 4-Chlorobenzil with Benzylmagnesium Chloride. Mixture of 4- and 4′-Chloro-α-benzylbenzoin.—To 4-chlorobenzil,[10] mp 76–76.5°, in 75 ml of diethyl ether cooled in an ice–water bath was added 27 ml of 0.1 *M* benzylmagnesium chloride[11] over a period of 45 min in an adaptation of the procedure for the unsubstituted compound employed by Banus and Vila.[7] After neutralization and evaporation of the solvent there was obtained 8.9 g of a yellow-white, oily solid. Recrystallization from hexane gave a 46% yield of a mixture of I and II, mp 101–105°, as shown by the near identity of the infrared spectrum with that of I prepared above; the nmr showed a complex multiplet at τ 2.1–3.2 and complex absorption at 6.0–6.8 resembling two AB quartets not resolved from each other and with the further complication of the O*H* absorption. The mass spectrum at 15 ev showed a parent mass peak at 336 *m/e* of less than 1%. Peaks at *m/e* 231 (97), 233 (33.4), and 197 (100) corresponded to the cleavage products of the two isomers with the ratio of the sum of intensities of peaks at 231 and 233 to that at 197 = 1.3 at both 40 and 70 ev. Cleavage with periodic acid and gas phase chromatographic analysis of the neutral fraction as described below gave an average value of 1.9 for I/II.

Anal. Calcd for $C_{21}H_{17}ClO_2$: C, 74.9; H, 5.1. Found: C, 75.1; H, 5.2.

4′-Chloro-α-methylbenzoin (IV) was prepared by the method employed for I by addition of methylmagnesium iodide to α-oximino-4-chlorodesoxybenzoin and hydrolysis of the oxime group. Removal of the solvent gave a yellow oil which crystallized, and recrystallization from hexane gave 50% of the theoretical amount of IV, mp 97.5–98.5°. The infrared spectrum showed absorption at 1673, 3445, and 3605 cm^{-1}. The nmr spectrum showed a complex aromatic absorption at τ 2.1–2.9 (area 9) and singlets at 5.48 (area 1) and 8.15 (area 3). A mass spectrum at 15 ev showed peaks (*m/e*) (and relative intensities) at 260 (11) (parent mass), 155 (100), 156 (10), 157 (37) ($ClC_6H_4COHCH_3$). At 15, 40, or 70 ev the ratio of peaks at *m/e* 217 or 121 to 155 was less than 0.01.

Anal. Calcd for $C_{15}H_{13}ClO_2$: C, 69.1; H, 5.0. Found: C, 69.2; H, 4.9.

Reactions of Benzoins I and IV with Methanolic Potassium Hydroxide.—In a typical reaction 4.55 mmoles (0.1 *m* solution) of benzylbenzoin I was heated with titrated 0.88 *M* methanolic potassium hydroxide for 23 hr at 56° in a tightly stoppered tube. Addition of water, extraction of the neutral portion into ether, and evaporation of the ether after drying gave 0.145 g of solid with an infrared spectrum superimposable on that of the mixture of I and II prepared from *p*-chlorobenzil and benzylmagnesium chloride except for a shoulder in the region 1710–20 cm^{-1} attributed to the presence of unconjugated ketone III. In a typical cleavage experiment 0.0098 g of product mixture was treated with 0.77 ml of 0.195 *M* solution of periodic acid dihydrate in absolute ethanol. The tube was shaken until solution was complete and allowed to stand at room temperature for 13 hr. Water was added and the mixture was extracted with 0.25 ml of chloroform.

Gas phase analysis was carried out at 240° with a 15-ft column packed with Apiezon-L, 20% on acid-washed silanized Chromasorb-W and with a flow rate of about 100 ml/min. Examination of known materials showed the retention times under these conditions to be for the product ketones as follows: benzophenone, 20.2 min; desoxybenzoin, 27.7 min; *p*-chlorobenzophenone, 38.1 min; and 4-chlorodesoxybenzoin, 52.4 min. Analysis of known mixtures (employing the products of peak height *x* width at half-height as measures of peak areas) showed that known mixtures of these substances could be analyzed to give relative amounts with an error of not more than ±5%. In one run the gas phase chromatography fractions were separated and their infrared spectra were shown to be identical with those of known samples.

Qualitative confirmation was provided by the mass spectrum of the neutral fraction at 15 ev which was used to determine the relative intensities of peaks at *m/e* 231 and 233 ($C_6H_5CH_2COHC_6H_4Cl$ from I) and 197 ($C_6H_5CH_2COHC_6H_5$ from II). Additional evidence for the presence of the benzyl ketone III in the reactions carried out for 23 hr was obtained by the observation of the nmr spectrum of the reaction mixture which showed a singlet at τ 6.15 instead of the $C_6H_5CH_2$ quartet characteristic of I and II by virtue of the fact that the benzyl group is attached directly to an asymmetric carbon atom. The relative areas of the quartet (I + II) and the singlet (III) were 4.5 ± 0.4 in the products of a reaction carrier out for 23 hr. The results are summarized in Table I.

Rearrangement of the α-methyl ketol (IV), mp 97.5–98.5°, for 23 hr under the same conditions used for the benzyl compound I gave 68% of a neutral fraction, mp 97.5–99°, with an infrared spectrum superimposable on the spectrum of IV. The mass spectrum showed, in addition to peaks at *m/e* 260 (16) and 263 (6) owing to the parent ion of IV, peaks at *m/e* 155 (100) and 157 (36) owing to the fragment $CH_3COHC_6H_4Cl$ from IV and finally a low peak at *m/e* 217 (1.4) attributable to the unit $ClC_6H_4COHC_6H_5$ formed from VI, the product of *p*-chlorophenyl migration. Nmr examination of the crude reaction mixture showed in addition to the C*CH*$_3$ singlet at τ 8.16 a new singlet at 7.74 attributed to the rearranged product VI. The ratio of the areas at 8.16 and 7.74 was 13.5 ± 1. Periodic oxidation and gas phase chromatography of the neutral fraction showed no *p*-chlorobenzophenone. The mass spectrum of the reaction mixture at 15, 40, and 70 ev showed peaks at *m/e* 121 (corresponding to the unit $C_6H_5COHCH_3$ of the product of methyl migration V) with intensities relative to the peak at 155 of less than 1/69, 1/54, and 1/60, respectively.

Registry No.—I, 7540-92-3; α-benzylbenzoin, 7540-93-4; I oxime, 7540-94-5; IV, 7540-95-6; II, 7548-10-9; III, 7540-96-7.

(10) H. H. Hatt, A. Pilgrim, and W. J. Hurran, *J. Chem. Soc.*, 93 (1936).

(11) H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p 471.

cis-α-Methyl-β-acetylacrylic Acid

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Several publications have appeared in recent years concerning the ring–chain tautomerism of *cis*-α-methyl-β-acetylacrylic acid. Although the cyclic structure (1) has been advanced,[1] less than definitive evidence has been cited in its support. Structural interpretations based on the chemistry of this substance are also partially in error.

We prepared *cis*-α-methyl-β-acetylacrylic acid according to the method of Buchta and Satzinger[2] *via* the condensation of acetone with pyruvic acid. This substance exhibited a strong band in the infrared at 5.68 μ diagnostic of the five-membered hydroxy lactone structure (1). In the ultraviolet 1 exhibited only end absorption down to 210 mμ, whereas in aqueous alkali,

(1) Compare (a) E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, **48** (1951); (b) N. Hellstrom, *Nature*, **187**, 146 (1960); (c) E. Buchta and G. Satzinger, *Chem. Ber.*, **92**, 468 (1959).

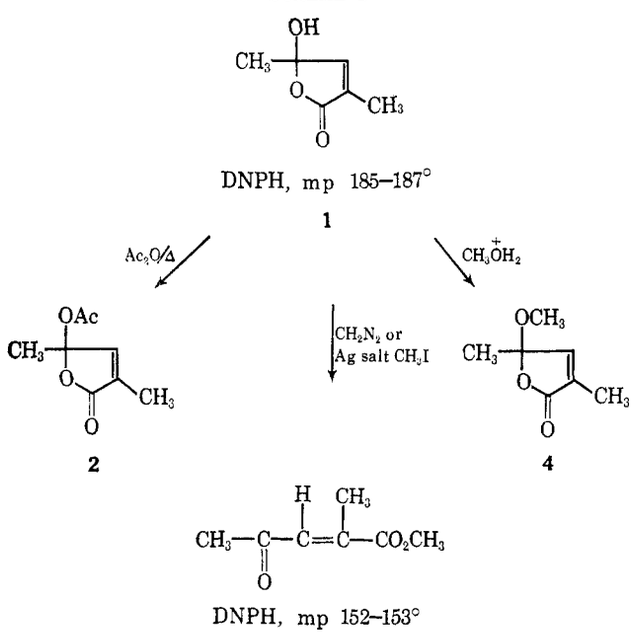
(2) E. Buchta and G. Satzinger, *ibid.*, **92**, 449 (1959).

as the salt of the acyclic acid, a well-defined maximum at 247 mμ (ε 8150) appeared. The nmr of 1 in deuteriochloroform was in conformity with the cyclic pseudo-acid structure (1) displaying a singlet methyl at τ 8.36 and a doublet methyl at 8.14 (J = 2 cps). The hydroxy lactone (1) formed a highly crystalline, yellow 2,4-dinitrophenylhydrazone derivative, mp 185–187°.

Buchta and Satzinger[1c] described the preparation of the acetoxy lactone (2) in low yield by treatment of 1 with acetyl chloride. In our experience 2 was formed quantitatively from 1 by heating the latter for several hours at 100° with acetic anhydride.[3] The acetate derivative (2) exhibited bands in the infrared at 5.6 and 5.72 μ and afforded the same 2,4-dinitrophenylhydrazone derivative as that derived from 1 itself.

The methoxy lactone structure (4) has been assigned[1c] to the product obtained from 1 with diazomethane. This assignment was based principally on the low-band position in the ultraviolet at 222 mμ. This substance actually possesses the acyclic ester structure (3) as evidenced by bands in the carbonyl region of the infrared at 5.78 and 5.88 μ together with the complete absence of a band at 5.68 μ characteristic of the cyclic system. This same ester (3), furthermore, was obtained by treatment of the silver salt of 1 with methyl iodide. The esters obtained from both preparations were identical in the infrared as well as the nmr and gave the same 2,4-dinitrophenylhydrazone derivative, mp 152–153°, distinct from the 2,4-dinitrophenylhydrazone derivative obtained from 1, 2, and 4. In this connection the ester obtained by Shaw in the desmethyl series quite probably also has the acyclic structure contrary to its original formulation.[4] Authentic methoxy lactone 4 on the other hand was obtained by treating 1 with methanolic hydrogen chloride. This substance exhibited a strong band in the carbonyl region at 5.68 μ and gave the same 2,4-dinitrophenylhydrazone as that derived from 1 and 2 (see Scheme I).

SCHEME I



(3) Compare J. Bredt, *Ann.*, **256**, 314 (1890).

(4) E. Shaw, *J. Am. Chem. Soc.*, **68**, 2510 (1946).

Experimental Section[5]

cis-α-**Methyl**-β-**acetylacrylic acid** (1) was prepared according to Buchta and Satzinger:[2] mp 100–101°; ultraviolet (CH_3OH or CH_3CN) end absorption; λ_{max}^{NaOH} 247 mμ (ε 8150); $\lambda_{max}^{CHCl_3}$ 5.68 μ; nmr bands at τ 8.36, doublet 8.36 (J = 2 cps).

Anal. Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29; neut equiv, 128.1. Found: C, 56.50; H, 6.05; neut equiv, 121.

2,4-Dinitrophenylhydrazone prepared in aqueous acetic acid, yellow prism, had mp 185–187°; $\lambda_{max}^{CH_3OH}$ 257 mμ (ε 10,600), 356 mμ (ε 15,200).

Anal. Calcd for $C_{12}H_{12}N_4O_6$: C, 46.75; H, 3.90; N, 18.15. Found: C, 46.89; H, 4.01; N, 18.31.

3,5-Dimethyl-5-acetoxy-3-butenolactone (2).—A solution of 500 mg of 1 in 5 cc of acetic anhydride was heated on a steam bath for 18 hr. At the end of this period the excess acetic anhydride was evaporated *in vacuo* and flushed several times with heptane. The residue was evaporatively distilled at 120° (18 mm) to give an equal weight of 2: $\lambda_{max}^{CHCl_3}$ 5.6 and 5.72 μ; nmr bands at τ 7.99, doublet 8.1 (J = 2 cps), and 8.22.

Anal. Calcd for $C_8H_{10}O_4$: C, 56.45; H, 5.72. Found: C, 56.48; H, 6.01.

Treatment of 2 with 2,4-dinitrophenylhydrazine in warm aqueous 50% H_2SO_4–HOAc afforded the 2,4-dinitrophenylhydrazone derivative of 1, mp 182–185°; the mixture melting point was not depressed.

cis-α-**Methyl**-β-**acetylacrylic Acid Methyl Ester** (3). **A. Diazomethane.**—A solution of 700 mg of 1 in 25 cc of ether was treated over a period of 1 hr with small amounts of an ethereal solution of diazomethane until a yellow color persisted for 15 min. The ether was evaporated and replaced with hexane and separated from unreacted 1. The hexane solution was washed several times with aqueous potassium bicarbonate, dried over magnesium sulfate, and evaporated to dryness at room temperature. The residue was evaporatively distilled at 95° (18 mm): $\lambda_{max}^{CHCl_3}$ 5.8 and 5.9 μ. This material was spectroscopically identical with 3 prepared in part B (see below).

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 58.89; H, 7.09.

The **2,4-dinitrophenylhydrazone derivative** of 3 was prepared in 50% aqueous H_2SO_4–HOAc and crystallized from ethyl acetate–methanol as orange needles, mp 152–153°. This derivative showed no melting point depression on admixture with the corresponding derivative prepared in part B (see below).

B. Silver Salt–Methyl Iodide.—A solution of 1 g of 1 in 25 cc of water was titrated with 1 equiv of 0.5 N sodium hydroxide solution. The aqueous solution of the sodium salt of 1 was subsequently treated with 1 equiv of silver nitrate and evaporated to dryness *in vacuo* at room temperature. The residue was dried by azeotropic distillation with benzene. The residue of dry salts was suspended in 50 cc of benzene, treated with an excess of methyl iodide, and refluxed for 10–12 hr. At the end of this period the benzene solution was filtered from the precipitated silver iodide, washed with aqueous bicarbonate, evaporated to dryness, and evaporatively distilled at 95° (18 mm) to afford 3: $\lambda_{max}^{CHCl_3}$ 5.8 and 5.9 μ; $\lambda_{max}^{CH_3OH}$ 221 mμ (ε 7100); nmr bands at τ 6.21, 7.78, doublet 8.00 (J = 2 cps).

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.34; H, 6.87.

The 2,4-dinitrophenylhydrazone derivative was prepared in 50% aqueous sulfuric–acetic acid and crystallized from ethyl acetate–methanol: mp 152–153°; $\lambda_{max}^{CH_3OH}$ 210 mμ (ε 17,500), 370 mμ (ε 24,000).

Anal. Calcd for $C_{13}H_{14}N_4O_6$: C, 48.45; H, 4.35; N, 17.39. Found: C, 48.57; H, 4.43; N, 17.28.

3,5-Dimethyl-5-methoxy-3-butenolactone (4).—A solution of 500 mg of 1 in 70 cc of methanol containing 7% hydrogen chloride was allowed to stand for 16–18 hr. The reaction mixture was concentrated *in vacuo*, flushed several times with benzene, and evaporatively distilled at 110° (20 mm): $\lambda_{max}^{CHCl_3}$ 5.68 μ; nmr bands at τ 6.80, doublet 8.04 (J = 2 cps), 8.40.

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.43; H, 7.33.

Treatment of 4 with 2,4-dinitrophenylhydrazine in warm, aqueous 50% H_2SO_4–HOAc afforded the 2,4-dinitrophenylhydrazone derivative of 1, mp 182–185°, not depressed on admixture with the derivative obtained from 1.

(5) All nmr spectra were measured in deuteriochloroform with a Varian A-60A spectrometer. Melting points were determined on a micro hot stage.

Registry No.—1, 7541-63-1; 1 DNPH, 7541-64-2; 2, 7541-65-3; 3, 7541-66-4; 3 DNPH, 7541-67-5; 4, 7541-68-6.

Hindered Rotation in N,N-Dimethylcarbamates

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Hindered rotation about the >N–C bond of various molecules was discovered and studied mostly by nmr methods.[1,2] In carbamates (R'R'') NCOOX hindered rotation has not been reported. In fact, Rogers and Woodbrey[2] observed no hindered rotation in two carbamates, $(CH_3)_2NCO_2CH_2CH_3$ and $(CF_3)_2NCO_2CH_3$, both as neat liquids at 25°. However, these authors did observe hindered rotation for carbamoyl chloride $(CH_3)_2NCOCl$.

The determination of the kinetic parameters of hindered rotation by nmr has been a controversial subject.[3] For instance, Whittaker and Siegel observed that the apparent activation energies (E_a) for hindered rotation in N,N-dimethylformamide[4] and in other amides[5] could be affected by a factor of up to 5, depending on the solvent used.

We studied a series of N,N-dimethylcarbamates in order to determine (a) whether hindered rotation is present in these molecules, (b) whether "true" kinetic parameters can be determined, and (c) whether these parameters can be correlated with carbamate structure and solvent interactions.

The results and conclusions of these studies are given below. The further application of these data to the calculation of the energy of activation (E_a) is now considered of doubtful value. Therefore, we are discontinuing these studies, but wished to report the findings which led us to this conclusion.

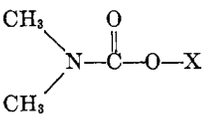
1. *All carbamates shown in the table exhibit hindered rotation about the carbonyl carbon–nitrogen bond,* as evidenced by doubling and/or broadening of the $(CH_3)_2N$ or $(CH_3CH_2)_2N$ signal at low temperatures and the coalescence of this signal at high temperatures.[6]

We also find that hindered rotation is present in $(CH_3)_2NCOF$, N,N-dimethylcarbamoyl fluoride; the $(CH_3)_2N$ proton pattern is complicated by the fact that the fluorine couples unequally to the *cis*- and *trans*-methyl protons.

2. *The parameters in the table show a strong dependence on solvent;* however, this dependence is unpredictable. For example, note that at 233°K, and for 10% solutions, $\Delta\omega$ increases in the sequence CS_2, $CHCl_3$, and $PhCH_3$ for ethyl N,N-diethylcarbamate, but increases in the sequence $CHCl_3$, CS_2, and $PhCH_3$ for cyclohexyl N,N-dimethylcarbamate.

3. *These parameters are also dependent on concentration;* note the data, for instance, in $CHCl_3$ solutions, for methyl N,N-dimethylcarbamate and cyclohexyl N,N-dimethylcarbamate (see Table I). Dipolar broadening owing to viscosity may also play a role.

TABLE I
NMR OF N,N-DIMETHYLCARBAMATES



Compd	X groups Aliphatic	Solvent	Parameters[a] t_s, °K	$\Delta\omega$	t_c, °K	t_m, °K
1	CH_3	60% in $CHCl_3$	248	0.75	260	303
		7% in $CHCl_3$	233	1.9		
2	$(CH_3)_3C$	40% in $CHCl_3$	233	B[b]		
		7% in $CHCl_3$	233	B		
3	CH_3CH_2	10% in CS_2	233	B		
	(N,N-Diethyl)[c]	10% in $CHCl_3$	233	3.4[c]		
		10% in $PhCH_3$	233	5.0		
4	Cyclohexyl	50% $CHCl_3$	233	B		313
		10% $CHCl_3$	233	0.7		
		10% CS_2	233	2.9	280	
		10% $PhCH_3$	233	5.9		
	p-(Y-Phenyl)					
5	Y = F	$CDCl_3$	281	3.05	304	336
6	Y = CH_3O[d]	$CDCl_3$	261	4.6	291	346
7	Y = NO_2	$CDCl_3$	281	5.3	312	357
8	Y = H	$CDCl_3$	260	3.0	292	333
9	Y = CH_3[d]	$CDCl_3$	260	2.2	278	348
	Others					
10	Naphthyl		281	11.35	315	373
11	6-Methyl-2-*n*-propyl-pyrimidin-4-yl (pyramat)		281	6.1	315	373
12	1-Isopropyl-3-methyl-pyrazol-5-yl (isolan)		281	5.1	311	383

[a] $\Delta\omega$ in Hz. t_s = highest temperature at which the maximum splitting of the above mentioned signal is observed; t_c = temperature of coalescence of a doublet; t_m = temperature at which no further narrowing of the coalesced line is observed; $\Delta\omega$ = peak separation at t_s. The splitting $\Delta\omega$ reflects the chemical-shift difference for the *cis*- and *trans*-methyl protons only if the t_s is higher than 233°K, the lowest temperature attainable with the equipment at hand. The line widths at t_s are made up by the natural line widths as well as by temperature-dependent contributions from coupling with N ($^2J_{HN}$) and field inhomogeneities owing to temperature gradients in the sample and the spectrometer. [b] B = broad single peak. [c] Doubling of CH_2 quartet. [d] No splitting observed at normal probe temperature (304°K).

No attempt should be made to correlate the electron-donating or -withdrawing power[7] of X groups in R_2NCOOX with t_s, t_c, t_m, or $\Delta\omega$. The only parameter suitable for such a correlation is the energy of activation (E_a). This could be obtained from Arrhenius plots. Our data could be used in principle for such a calculation of E_a. However, the results would be of little significance. Large corrections in the calculation of E_a are required when the contributions from (a) self-association in the case of neat liquids and (b) association with the solvent in the case of carbamate–solvent systems are considered. Simple inductive effects within the molecule alone are not sufficient to explain the observation that aliphatic and substituted aromatic N,N-dialkylcarbamates both exhibit hindered rotation.

(1) A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Physik. Chem.*, **67**, 280 (1963).
(2) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).
(3) E. Lustig and W. B. Moniz, *Anal. Chem.*, **38**, 331R (1966).
(4) A. G. Whittaker and S. Siegel, *J. Chem. Phys.*, **42**, 3320 (1965).
(5) A. G. Whittaker and S. Siegel, *ibid.*, **43**, 1575 (1965).
(6) The doublet for $XOC(=O)N(H)CH_3$ ($J_{HH} \sim 4.5$ Hz) is independent of temperature and magnetic field and thus can be distinguished from the doublet for $XOC(=O)N(CH_3)_2$.
(7) T. M. Valega, *J. Org. Chem.*, **31**, 1150 (1966).