Experimental Section

The chromatograph employed in the investigation was an F and M Model 300 with thermal conductivity detector. All chromatograms were obtained under isothermal column conditions. The column used was $^3/_{16}$ in. × 20 ft copper tubing filled with 100–200 mesh activated alumina coated with 20 wt % diethyl D-tartrate. Helium was the carrier gas and flow rate was maintained at 25 cc/min. The column was operated at 90°. These conditions essentially duplicate those of Karagounis.

Some resolutions have been reported subsequent to the original work of Karagounis,[4,5] but these involved the use of metal complexes. Most other resolutions by gas chromatography reported in the literature deal with the separation of diastereoisomers.

---

(4) G. Karagounis and E. Lemperly, *Z. Anal. Chem.*, **189**, 131 (1962).

(5) R. E. Sievers, R. W. Moshier, and M. L. Morris, *Inorg. Chem.*, **1**, 966 (1962).

Dimethyl Sulfoxide as a Solvent for the Lossen Rearrangement

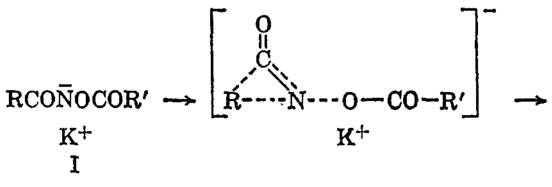
D. C. BERNDT AND W. J. ADAMS

Department of Chemistry, Western Michigan University, Kalamazoo, Michigan

Received September 20, 1965

Numerous examples of rate acceleration by use of dimethyl sulfoxide in place of protic solvents in bimolecular second-order reactions of anions with neutral substrates are well known.[1] We now wish to report moderate rate acceleration by use of dimethyl sulfoxide solvent in place of 0.1 *N* ammonia for three out of four cases for the Lossen rearrangement (eq 1b), a *unimolecular first-order* reaction of an anion (I).

$$RCO\overset{H}{N}OCOR' + KOH \longrightarrow RCO\bar{N}OCOR' + K^+ + H_2O \quad (1a)$$



I

$$\underset{K^+}{RCO\bar{N}OCOR'} \longrightarrow \left[R\cdots N\cdots O{-}CO{-}R' \right]^- \longrightarrow RN{=}C{=}O + R'CO_2^-K^+ \quad (1b)$$

The accepted mechanism[2-4] for this reaction is as shown above; migration of R occurs simultaneously or nearly simultaneously with the heterolytic cleavage of the hydroxamate anion (the transition state is represented by the species enclosed in brackets). Rate results obtained with dimethyl sulfoxide (DMSO) as a solvent are listed in Table I and are compared with the results of previous workers[2,3] who used 0.1 *N* ammonia as solvent.

The normal course of the Lossen rearrangement (eq 1b) in dimethyl sulfoxide was shown to obtain by trapping the isocyanate *via* reaction with *n*-butylamine (see Experimental Section).

Incomplete dissociation of the salts used in the rate measurements would influence the observed rates. Electrical conductance measurements were therefore made on potassium benzoyl *p*-methylbenzhydroxamate solutions at 25° to allow comparison with literature conductance data[5] for dimethyl sulfoxide solutions. The two lowest concentrations in Table II correspond to the concentration ranges previously used in determining the conductivity of numerous salts in dimethyl sulfoxide[5]—these salts were shown to be completely dissociated in the concentration ranges studied.[5] The equivalent conductances reported in Table II for the two lowest concentrations of potassium benzoyl *p*-methylbenzhydroxamate vary with concentration in the same manner as the equivalent conductances of the salts previously shown to be completely dissociated in this concentration range; therefore, it is highly likely that potassium benzoyl *p*-methylbenzhydroxamate is largely dissociated at these low concentrations. Further, since the equivalent conductances of this potassium salt do not change markedly upon going to higher concentrations, it is likely that it is largely dissociated at these concentrations (those used in the kinetic studies). The salts in Table I with R = phenyl or *m*-methylphenyl should be dissociated to extents comparable to that for R = *p*-methylphenyl. For R = *o*-methylphenyl, however, steric hindrance to solvation of the anion may be sufficient to reduce the extent of dissociation compared to the other salts; consequently, no conclusion as to the extent of dissociation of this *ortho* derivative can be drawn from the present data. Conductance measurements are rendered difficult in this system for two reasons: one, the Lossen rearrangement commences when the salt is dissolved and, two, the rate of solution of the salt is slow—very slow in the case of the *o*-methyl derivative—with the result that a significant portion of the salt will have reacted (eq 1b) before all of the salt has been dissolved (the conductance measurements will thus be affected but not the kinetics, since the rates are first order).

The general explanation[1a] offered for the acceleration of bimolecular reactions between anions and neutral substrates upon change from protic to dipolar aprotic solvents is applicable to the salts (except R = *o*-methylphenyl) in Table I if the transition state for the Lossen reaction has greater charge dispersal (which is likely) than the initial state. As has been recently discussed,[1c] however, rate acceleration by use of dimethyl sulfoxide in place of hydroxylic solvents is complicated and probably the result of several factors. The markedly different relative rate in Table I for R = *o*-methylphenyl *may* be due to incomplete dissociation of the salt in dimethyl sulfoxide; the proximity of the positive potassium ion to the negative charge delocalized over the amide-like portion of anion I would be expected to retard the formation of the carboxylate ion from I.

---

(1) See, for example: (a) A. J. Parker, *Quart. Rev.* (London) **16**, 163 (1962); (b) D. D. Roberts, *J. Org. Chem.*, **29**, 2039 (1964); (c) C. A. Kingsbury, *ibid.*, **29**, 3262 (1964); (d) E. Tommila and M. Murto, *Acta Chem. Scand.*, **17**, 1947 (1963).

(2) R. D. Bright and C. R. Hauser, *J. Am. Chem. Soc.*, **61**, 618 (1939).

(3) W. B. Renfrow, Jr., and C. R. Hauser, *ibid.*, **59**, 2308 (1937).

(4) P. A. S. Smith, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 528–541.

(5) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.* **60**. 1433 (1956).

Table I

Rate Data for K[$RCONOCOC_6H_5$] and Physical Constants for $RCONHOCOC_6H_5$

R	10^3k,[a] min^{-1}	Relative rates[b,c]	Mp, °C	
			Obsd[d]	Lit.[e]
Phenyl	7.06	5.12	163.5–164.5	161–162, 163–164
p-Methylphenyl	11.8	3.29	159–160	161–162, 163–164
m-Methylphenyl	9.47	4.38	121–123	123–125
o-Methylphenyl	7.05	0.198	106–107	108–109

[a] First-order rate constant at 30 ± 0.02° in DMSO; average of four or five runs, average deviation from mean less than 3.4% (except R = *o*-methylphenyl, two runs, 4.5%). [b] At 30°; rate in DMSO/rate in 0.1 *N* NH_3. [c] Rates in ammonia solution are from ref 2 and 3. [d] Corrected. [e] References 2 and 3.

Table II

Equivalent Conductance of K[p-$CH_3C_6H_4CONOCOC_6H_5$] in DMSO

Concn, *M*	Equiv conductance,[a] cm^2 equiv^{-1} ohm^{-1}
0.0250	15.1
0.0125	16.6
0.00833	17.9
0.00500	21.2
0.000536	24.8

[a] At 25.0 ± 0.1°.

Experimental Section

The benzoyl acylhydroxamates were prepared by adaptation of previous methods[2,3,6] as were the potassium salts[7,8] used in the rate measurements. Melting points are listed in Table I. The colorimetric method previously developed[8] for following the rate of disappearance of the alkali hydroxamates was adapted for the present system. Kinetic runs were made to approximately 75% complete reaction, first-order kinetics being observed in all cases. Initial concentrations of salts were 0.0248 to 0.0258 *M* (one run for R = phenyl, 0.0168 *M*). Rate constants were calculated as before,[8] except that the slopes of the graphs were evaluated by the least-squares method. The dimethyl sulfoxide was dried over barium oxide and distilled at reduced pressures.

The conductance measurements were made with a Serfass conductivity bridge using a dip cell with platinum black coated electrodes calibrated against 0.100 *N* potassium chloride. A potassium benzoyl *p*-methylbenzhydroxamate solution in dimethyl sulfoxide (0.0250 *M*) was prepared. Conductance measurements were then made as rapidly as possible on this solution and on diluted solutions. A second set of conductance measurements were made beginning with a 0.00500 *M* solution.

N-*n*-Butyl-N′-phenylurea.—Potassium benzoyl benzhydroxamate (0.73 g, 0.0026 mole) and *n*-butylamine (3.00 g, 0.0411 mole) were added to dimethyl sulfoxide (30 ml), and the resulting solution was maintained at 30° for sufficient time to ensure complete rearrangement of the hydroxamate. The solution was evaporated to dryness *via* an air current and the resulting residue was extracted with hot benzene. N-*n*-Butyl-N′-phenyl urea was crystallized from the benzene: mp 125–128°, lit.[9] mp 129–130°, 83% crude yield. The melting point and infrared spectrum of the urea were the same as those of a sample prepared independently from phenyl isocyanate and *n*-butylamine.

Acknowledgment.—We wish to express our thanks to the National Science Foundation for financial support of this work and to Dr. R. H. Anderson for use of his least-squares computer program.

---

(6) E. Mohr, *J. Prakt. Chem.*, **71**, 133 (1905).

(7) L. W. Jones, *Am. Chem. J.*, **20**, 1 (1898); L. W. Jones and A. W. Scott, *J. Am. Chem. Soc.*, **44**, 407 (1922); L. W. Jones and L. Neuffer, *ibid.*, **39**, 659 (1917).

(8) D. C. Berndt and H. Shechter, *J. Org. Chem.*, **29**, 916 (1964).

(9) T. L. Davis and N. D. Constan, *J. Am. Chem. Soc.*, **58**, 1802 (1936).

An Efficient Synthesis of *cis*-Jasmone

G. Büchi and H. Wüest

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

Received October 18, 1965

The flower oils of several varieties of Jasminum contain the ketone *cis*-jasmone (**6**). Although *cis*-jasmone constitutes less than 5% of these essential oils, it is indispensable in the reproduction of jasmine fragrance from substances of synthetic origin. An early synthesis[1] yielded mainly *trans*-jasmone with less desirable olfactory properties. Total syntheses of authentic *cis*-jasmone (**6**) have been described,[2–4] but the routes employed are somewhat lengthy and the substance remained relatively inaccessible. We have now developed a synthesis which allows the production of *cis*-jasmone (**6**) on a large scale and in good over-all yield.

Metalation of 2-methylfuran (**1**) with butyllithium in tetrahydrofuran solution yielded 2-lithio-5-methylfuran (**2**)[5] which on condensation with *cis*-1-bromohex-3-ene (**3**), prepared from *cis*-hex-3-en-1-ol[6] gave *cis*-5-methyl-2-hex-2′-enylfuran (**4**) whose nmr spectrum ($CDCl_3$) had resonances at τ 3.95 (2 H, singlet), 4.42 (2 H, multiplet), 7.68 (3 H, singlet), and 9.04 (3 H, triplet, J = 7 cps). Purification of this intermediate was not necessary and hydrolysis of the crude product in aqueous acetic acid containing some sulfuric acid furnished the known diketone[4] **5** with nmr absorptions (in $CDCl_3$) at τ 4.46 (2 H, multiplet), 7.21 (4 H, singlet), 7.74 (3 H, singlet), and 9.01 (3 H, triplet, J = 7 cps). Finally, base-catalyzed cyclization of the diketone **5**, using Hunsdiecker's conditions, gave *cis*-jasmone (**6**), $\nu_{max}^{CHCl_3}$ 1685 and 1645 cm^{-1}; λ_{max}^{EtOH} 234 mμ (ϵ 13,930), further characterized by a 2,4-dinitrophenylhydrazone, mp 115–117°.[7] An infrared spectrum of synthetic *cis*-jasmone (**6**) was identical with that of an authentic sample.[3] Careful gas chromatographic analysis of the final product showed that the *cis/trans* ratio in synthetic jasmone is not lower than that in the 1-bromohex-3-ene (**3**) used demonstrating that *cis–trans* isomerization does not accompany the final stages of the

---

(1) W. Treff and H. Werner, *Ber.*, **68**, 640 (1935).

(2) H. Hunsdiecker, *ibid.*, **75**, 460 (1942).

(3) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 869 (1952).

(4) G. Stork and R. Borch, *J. Am. Chem. Soc.*, **86**, 936 (1964).

(5) Method of V. Ramanathan and R. Levine, *J. Org. Chem.*, **27**, 1216 (1962).

(6) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 873 (1950); F. Sondheimer, *ibid.*, 877 (1950).

(7) Y. R. Naves and A. V. Grampoloff, *Helv. Chim. Acta*, **25**, 1500 (1942).