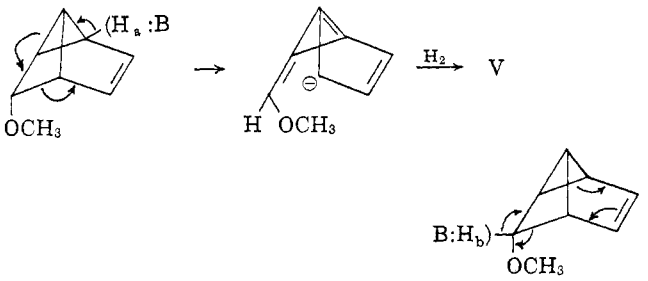
(m), 810 (m), and 795 (m) cm^{-1}, and CH_3O absorption at 1118 cm^{-1}. The existence of a cyclopropyl ring was also supported by the first overtone of the cyclopropyl CH stretching vibration observed at 6020 cm^{-1}.[9] The nmr peaks (in CCl_4) of a C_2 proton at τ 6.29 (quartet, J_{C_1-H,C_2-H} = 3.8, J_{C_2-H,C_3-H} = 8.0 cps (apparent J value)), of a C_3 proton at τ 7.35 (multiple doublet), and of three cyclopropyl and four C_4,C_5 protons at τ 8.0–8.7 (complex multiplets) were entirely consistent with the structure of 2-methoxytricyclo[4.1.0.$0^{3,7}$]-heptane. The coupling constants of the C_2 proton indicated the methoxyl substituent to be exclusively in the *endo* orientation as observed in some related reactions.[10,11] Consequently, the structure of the labile intermediate, the main product obtained in the methanolysis, was established as *endo*-2-methoxytricyclo-[4.1.0.$0^{3,7}$]hept-4-ene (III).

The formation of ring-opened V would be rationalized by base-catalyzed isomerization of III into 1-(2-methoxyvinyl)cyclopentadiene, which involves abstraction of the acidic cyclopropyl proton H_a and generation of a stable cyclopentadienide ion, followed by saturation of three double bonds.[12,13] The use of H_b, instead of the bridgehead H_a, may be another possibility. The



formation of VI was also observed in the methanolysis of *anti*-7-norbornenyl *p*-toluenesulfonate with alkali, but in only 1% yield.

While the results obtained here have interesting implications as to the structure of the cation from I and similar derivatives,[2,3] we prefer not to examine these implications at this time.

(9) Refer to H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, **30**, 2259 (1965).

(10) P. R. Story, *J. Am. Chem. Soc.*, **83**, 3347 (1961).

(11) H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965). The cyano substituent in 2-cyanotricyclo[4.1.0.$0^{3,7}$]heptane obtained in the reaction of *anti*-7-chloronorbornene with sodium cyanide was recently proved to be exclusively in the *endo* position by the coupling constants of the C_2 proton at τ 6.81 (in CCl_4, quartet), J_{C_1-H,C_2-H} = 3.7, J_{C_2-H,C_3-H} = 8.3 cps, and by hydrogenolysis to *endo*-2-cyanonorbornane.

(12) Highly strained small-ring hydrocarbons are said to have unusually high acidity. Refer to G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 2022 (1963).

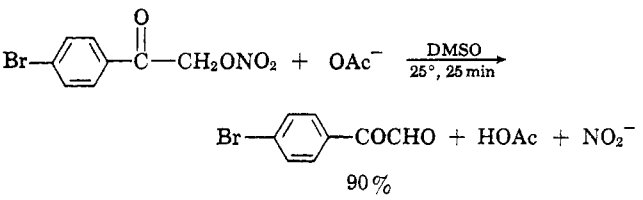
(13) We acknowledge the suggestion of this mechanism to a referee.

Hiroshi Tanida, Teruji Tsuji, Tadashi Irie
Shionogi Research Laboratory, Shionogi & Co., Ltd.
Fukushima-ku, Osaka, Japan
Received August 24, 1965

A New and Convenient Synthesis of Glyoxals, Glyoxalate Esters, and α-Diketones

Sir:

We wish to describe a convenient synthesis of glyoxals, glyoxalate esters, and α-diketones, the utility of which may be appreciated when it is recognized that Tables I and II record the yields of analytically pure products. The reaction upon which the synthesis depends is the conversion of nitrate esters to carbonyl compounds under the influence of sodium acetate, *e.g.*



In practice, one may start with the corresponding halide, convert it to the nitrate ester, and, without isolating, transform this into the carbonyl compound; the yields (Table I) are almost identical with those obtained on starting with pure nitrates (Table II).[1]

Table I.[a] Conversion of >CHBr to >C=O

Halide	Product	Yield, %
p-$BrC_6H_4COCH_2Br$	*p*-$BrC_6H_4COCHO \cdot H_2O$	85
p-$ClC_6H_4COCH_2Br$	*p*-$ClC_6H_4COCHO \cdot H_2O$	82
p-$O_2NC_6H_4COCH_2Br$	*p*-$O_2NC_6H_4COCHO$[c]	83
p-$C_6H_5C_6H_4COCH_2Br$	*p*-$C_6H_5C_6H_4COCHO \cdot H_2O$	86
$C_6H_5COCHBrC_6H_5$	$C_6H_5COCOC_6H_5$	95
$CH_3(CH_2)_3CHCH_2OCCH_2Br$[b]	$CH_3(CH_2)_3CHCH_2OCCHO$	82
C_2H_5 O	C_2H_5 O	

[a] All reactions in DMSO at 20–25° for 25 min using 10 mole % sodium acetate trihydrate except as otherwise noted. [b] One equivalent of sodium acetate trihydrate. [c] Isolated as the dimedon derivative.

Table II.[a] Conversion of >CHONO$_2$ to >C=O

Nitrate	Product	Yield, %
p-$BrC_6H_4COCH_2ONO_2$	*p*-$BrC_6H_4COCHO \cdot H_2O$	90
p-$ClC_6H_4COCH_2ONO_2$	*p*-$ClC_6H_4COCHO \cdot H_2O$	85
p-$O_2NC_6H_4COCH_2ONO_2$	*p*-$O_2NC_6H_4COCHO$[c]	86
p-$C_6H_5C_6H_4COCH_2ONO_2$	*p*-$C_6H_5C_6H_4COCHO \cdot H_2O$	94
$C_6H_5COC(C_6H_5)HONO_2$	$C_6H_5COCOC_6H_5$	98
$C_6H_5COC(CH_3)HONO_2$[b]	$C_6H_5COCOCH_3$	94

[a] All reactions in DMSO at 20–25° for 25 min using 10 mole % sodium acetate trihydrate, except as otherwise noted. [b] One equivalent of anhydrous sodium acetate for 55 min. [c] Isolated as the dimedon derivative.

It is an important feature of this synthesis that anhydrous conditions are not necessary. Sodium acetate trihydrate works as well as anhydrous sodium acetate, and, since nitrite ion is liberated in the reaction,[2] it would be anticipated that a catalytic amount of acetate would suffice; this, indeed, proves to be the case. Most of the reactions were carried out with a

(1) Nitrate esters may, of course, also be prepared by esterification of alcohols: R. Boschan, R. T. Merrow, and R. W. Van Dolah, *Chem. Rev.*, **55**, 485 (1955); E. G. Ausell and J. Honeyman, *J. Chem. Soc.*, 2779 (1952); J. Honeyman and J. W. W. Morgan, *ibid.*, 3660 (1955); A. F. McKay, R. H. Meen, and G. F. Wright, *J. Am. Chem. Soc.*, **70**, 430 (1948).

(2) We shall subsequently present evidence that the oxidizing agent is not DMSO and that we deal here with a base-catalyzed elimination of nitrate esters.

catalytic amount (10 mole %) of sodium acetate trihydrate, despite which they proceed to completion in less than 25 min at 25°.

As a typical example: *p*-bromophenacyl bromide (5.55 g) is dissolved in 20 ml of acetonitrile and to this a solution of 4.25 g of silver nitrate in 20 ml of acetonitrile is added. After stirring for 24 hr at room temperature the mixture is filtered, the silver bromide is washed with ethyl ether, and the combined filtrate and washings are evaporated at 30 mm (30°). The residue is taken up in ether, washed with water, and dried, and the solvent is removed. The crude nitrate ester (5.17 g) is dissolved in 100 ml of DMSO and to the stirred solution a suspension of sodium acetate trihydrate (0.27 g) in 40 ml of DMSO is added. After 25 min at 20–25° the reaction mixture is poured into 400 ml of ice water, saturated with sodium chloride, and ether extracted. The ether solution is washed with water and saturated aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. Evaporation at 30 mm (30°) yields 4.19 g (92% yield) of *p*-bromophenyl glyoxal monohydrate, mp 124–126°. Recrystallization from aqueous acetone gives 3.87 g (85% yield), mp 125–126.5°. The nmr spectrum of the recrystallized product (in DMSO) has a triplet centered at δ 5.79 (area = 1.00, J = 6.0 cps) and a doublet centered at δ 6.87 (area = 2.05, J = 6.0 cps). This accords with the structure $ArCOCH(OH)_2$.[3] *Anal.* Calcd for $C_8H_5BrO_2 \cdot H_2O$: C, 41.58; H, 3.06; Br, 34.59. Found: C, 41.65; H, 3.31; Br, 34.79.

Although the base-catalyzed elimination of nitrite ion from nitrate esters has been recognized for many years, the reaction has never achieved the status of a synthetically useful means of producing carbonyl compounds.[4] We find that even under our conditions this reaction leaves something to be desired as a method of synthesizing aromatic and aliphatic aldehydes, for, while *p*-nitrobenzyl nitrate gives an 80% yield of *p*-nitrobenzaldehyde on treatment with sodium acetate, *p*-bromobenzyl nitrate is converted into *p*-bromobenzyl acetate (59% yield), along with only a minor amount of *p*-bromobenzaldehyde (11% yield); *i.e.*, with *p*-bromobenzyl nitrate displacement of nitrate ion is the major process. In contrast, the reaction of *p*-bromobenzyl nitrate with sodium phenoxide gives an 81% yield of the aldehyde; however, sodium phenoxide transforms *n*-octyl nitrate into *n*-octyl phenyl ether (72% yield). Finally, sodium fluoride converts *n*-octyl nitrate to *n*-octaldehyde (46% yield), but a temperature of 100° for 23 hr is necessary. Clearly the preparation of aldehydes from nitrate esters lacks the elegance which characterizes the glyoxal, glyoxalic ester, and α-diketone syntheses.

(3) D. E. McGreer, R. Stewart, and M. M. Mocek, *Can. J. Chem.*, **41**, 1024 (1963); H. D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1895 (1963); O. L. Chapman and B. R. King, *J. Am. Chem. Soc.*, **86**, 1256 (1964).

(4) J. U. Nef, *Ann.* **309**, 175 (1899); G. R. Lucas and L. P. Hammett, *J. Am. Chem. Soc.*, **64**, 1937 (1942); J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952); N. Kornblum and H. E. De La Mare, *J. Am. Chem. Soc.*, **73**, 880 (1951); M. P. Cava, D. R. Napier, and R. J. Pohl, *ibid.*, **85**, 2076 (1963); R. Breslow, D. Kivelevich, M. J. Mitchell, W. Fabian, and K. Wendel, *ibid.*, **87**, 5132 (1965).

(5) National Institutes of Health Predoctoral Fellow, 1962–1965.

Nathan Kornblum, Harry W. Frazier[5]
Department of Chemistry, Purdue University
Lafayette, Indiana 47907
Received January 12, 1966

Transfer of Asymmetry from Nitrogen to Carbon in the Stevens Rearrangement

Sir:

The classic work of Pope and Peachey[1] in the resolution of the allylbenzylmethylphenylammonium cation (I) into optical antipodes demonstrated that organic molecules could owe their optical activity to centers of asymmetry other than carbon. Since that time, a host of optically active compounds of silicon, germanium, nitrogen, phosphorus, arsenic, antimony, and sulfur have been prepared.

This investigation was undertaken to see whether asymmetry due to a tetravalent atom other than carbon could be transferred to carbon. The transfer of asymmetry, *i.e.*, the creation of one asymmetric center simultaneous with the destruction of another,[2] has been a valuable method of study of transition-state geometry.[3] For this purpose, we have investigated the Stevens rearrangement of optically active I.

Reaction of (+)-I iodide, $[\alpha]D$ +39.6°, with potassium *t*-butoxide in dimethyl sulfoxide gave, in addition to N-methylaniline (35%) and 1-(N-methylanilino)-4-phenylbutene-1 (III, isolated as the corresponding aldehyde), 15% of 3-(N-methylanilino)-4-phenylbutene-1 (II), $[\alpha]D$ −18.4°. The structure of II was assigned from its mass spectrum[4] (parent peak 237.1506; $C_{17}H_{19}N$ requires 237.1517), in which the base peak at 146.0971 is due to the ion $C_{10}H_{12}N^+$ (calcd, 146.0969) resulting from α cleavage of the benzyl group, and from the nmr spectrum, which showed absorption at τ 7.25 (3 H, singlet), 7.10 (2 H, doublet), 5.5 (1 H, broad), 4–5 (3 H, multiplet), and 3 (10 H, broad). Confirmation came from synthesis of the dihydro derivative (Chart I).

This reaction is believed to be the first demonstration of transfer of asymmetry from nitrogen to carbon.[5] Until the maximum rotation of II is known, it is difficult to assess the degree of stereospecificity, but based on rotations reported for similar amines, conservation of optical purity during the rearrangement to II appears to be high.

It is possible, however, by determining the absolute configurations of I and II, to deduce the transition-state geometry in this reaction. Diimide reduction of (+)-I iodide gave (*R*)-(+)-benzylmethylphenylpropylammonium iodide (IV) of established configuration.[6] The (*S*) configuration of (−)-II was proved by relating it to (*R*)-(−)-1-phenyl-2-butanol,[7] using the reactions shown in Chart I. The absolute configurations found

(1) W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, 1127 (1899).

(2) The term "self-immolative" has been suggested to describe this special kind of asymmetric synthesis; see K. Mislow, "Introduction to Stereochemistry," W. Benjamin, Inc., New York, N. Y., 1965, p 131.

(3) See, *inter alia*, (a) R. K. Hill and R. M. Carlson, *J. Am. Chem. Soc.*, **87**, 2772 (1965); (b) R. K. Hill and A. G. Edwards, *Tetrahedron Letters*, 3239 (1964); (c) R. K. Hill and M. Rabinovitz, *J. Am. Chem. Soc.*, **86**, 965 (1964); (d) H. L. Goering and W. I. Kimoto, *ibid.*, **87**, 1748 (1965); (e) E. P. Burrows, F. J. Welch, and H. S. Mosher, *ibid.*, **82**, 880 (1960), and previous papers; (f) W. von E. Doering and R. W Young, *ibid.*, **72**, 631 (1950).

(4) We are greatly indebted to Dr. Henry Fales, National Heart Institute, for his aid in obtaining and interpreting this spectrum.

(5) For an example of transfer of *biphenyl* dissymmetry to asymmetric carbon in the Stevens rearrangement, see G. Wittig and H. Zimmermann, *Chem. Ber.*, **86**, 629 (1953); also K. Mislow and H. Joshua, *J. Am. Chem Soc.*, **87**, 666 (1965).

(6) L. Horner, H. Winkler, and E. Meyer, *Tetrahedron Letters*, 789 (1965).

(7) P. A. Levene and A. Walti, *J. Biol. Chem.*, **90**, 81 (1931).