Communications

See Editorial, *J. Org. Chem.*, **37**, No. 19, 4A (1972).

Friedel–Crafts Reactions of Amino Compounds. New Method for the Preparation of 1-Amino-4-hydroxyanthraquinone[1]

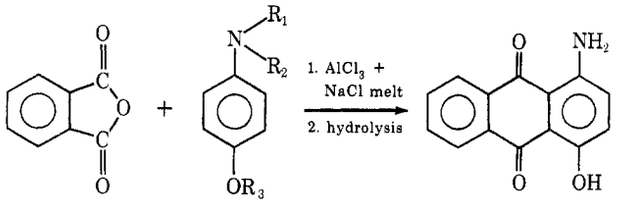
Summary: Friedel–Crafts reaction of substituted amines has resulted in a new method for the preparation of 1-amino-4-hydroxyanthraquinone.

Sir: The Friedel–Crafts acylation and cyclization reactions have been used for the direct synthesis of anthraquinones and related compounds.[2-5] However, no aminoanthraquinones have yet been prepared by this method where amino derivatives are directly involved as reaction species.

We wish to report the direct synthesis of 1-amino-4-hydroxyanthraquinone (III), commercially known as Celliton Fast Pink B and used as dye for all classes of fibers.[6] The dye has been prepared earlier from anthraquinone derivatives.[7-9]

The reaction of 4-aminophenol and its derivatives was studied in detail where aminophenols IIa–e were condensed with phthalic anhydride I in presence of $AlCl_3$–NaCl melt (Scheme I).

SCHEME I



I II III

IIa, $R_1 = R_2 = R_3 = H$
b, $R_2 = R_3 = H$; $R_1 = COCH_3$
c, $R_2 = R_3 = H$; $R_1 = COC_6H_5$
d, $R_1 = R_2 = R_3 = COC_6H_5$
e, $R_1 = R_2 = R_3 = COCH_3$

The reactions were carried out at various temperature ranges, between 170 and 210°, and time durations, 15 to 45 min, yielding compound III, 3% from 4-aminophenol (IIa), 10% from *N*-acetyl-4-aminophenol (IIb), 15% from *N*-benzoyl-4-aminophenol (IIc), 20% from tribenzoyl-4-aminophenol (IId), and 45% from triacetyl-4-aminophenol (IIe).

1-Amino-4-hydroxyanthraquinone (III) from IIe.—An intimate slurry of IIe (4 g) and I (4 g) was gradually added with stirring to a clear melt of anhydrous $AlCl_3$ (40 g) and NaCl (10 g) at 170–180°. The mixture was further stirred at 200–210° for 45 min, cooled, and digested with 2 *N* hydrochloric acid. The reaction product was thoroughly washed with water and dried and its benzene extract was chromatographed over silica gel. The pink band obtained, after eluting the column with benzene–acetone mixture (90:10), and on crystallization from benzene gave pink plates III, 2.5 g, mp 215°. The purity of the compound was checked by tlc (R_f 0.32; silica gel–benzene), analytical data (Calcd for $C_{14}H_9O_3N$: C, 70.29; H, 3.76; N, 5.85. Found: C, 70.42; H, 3.69; N, 5.78.) and spectral results [ir ν_{max} 3500, 3400, 1640, 1600, 1540, 1470, 1250, 1190, 840, 800, 740 cm^{-1}; mass spectrum ($M \cdot^+$) *m/e* 239, 212, 211, 183, 182, 107, 100, 76].

It was observed that fully protected amino groups yield better results as is evident from reactions with IId and IIe. It is interesting to note that IIe gave the best yield (45%) of the anthraquinone III. The lesser yield of III with IId may possibly be due to steric factor, the benzoyl group shielding the reactive center.

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Preparation of 7-*cis*-Ionyl and -Ionylidene Derivatives and Other Sterically Hindered Olefins by One-Way Sensitized Geometric Isomerization[1]

Summary: Quantitative preparations of many sterically hindered olefins have been achieved by selective triplet sensitization.

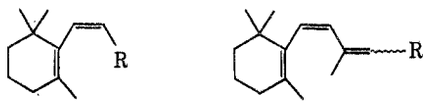
Sir: The severe steric hindrance (methyl–methyl or methyl–hydrogen interaction) present in the 7- and 11-cis isomers of vitamin A and carotenoids once cast doubt on their possible existence,[3] but, since then, 11-cis vitamin A (the less hindered of the two) and other compounds with similar steric interactions have been routinely prepared by selective hydrogenation of the corre-

(1) Presented in part at the Chemists Convention Bombay, India, 1971.
(2) C. Buehler and D. E. Pearson, "Survey of Organic Synthesis," Wiley, New York, N. Y., 1970, p 737.
(3) N. S. Dokunikhim, Z. Moisoeva, and U. A. Maytrikova, *Zh. Org. Khim.*, **2** (3), 516 (1966).
(4) V. M. Chari, S. Neelkantan, and T. R. Seshadri, *Indian J. Chem.*, **4**, 330 (1966).
(5) N. S. Bhide and A. V. Rama Rao, *Indian J. Chem.*, **7**, 997 (1969).
(6) K. Venkatraman, "The Chemistry of Synthetic Dyes," Academic Press, New York, N. Y.: Vol. II, 1952, p 805; Vol. III, 1970, p 391.
(7) I. G. Farbenindustrie, A. G., German patent 558,459 (1930); *Chem. Abstr.*, **27**, 309 (1933).
(8) Y. Bansho and K. Kondo, *J. Chem. Soc. Jap.*, **57**, 751 (1954).
(9) V. I. Gadzenko, V. A. Lavrishchev, N. I. Shuliko, and V. Z. Maslosh, U. S. S. R. patent 243,118 (1969); *Chem. Abstr.*, **71**, 82640 (1969).

(1) Photochemistry of Polyenes. III. The material on which this communication is partially based was presented in a plenary lecture at the 23rd IUPAC Congress, Boston, Mass, July 1971. The proceedings of this congress have been published.[2]
(2) R. S. H. Liu, *Pure Appl. Chem., Suppl. (23rd Congr.)*, **1**, 335 (1971).
(3) L. Pauling, *Fortschr. Chem. Org. Naturstoffe*, **3**, 203 (1939).

sponding dehydro compounds.[4] A similar method, however, failed to give 7-cis vitamin A,[5] in fact up to now there is no general method for preparation of this class of sterically hindered olefins.[6] Naturally the properties of such compounds are virtually unknown. In this communication we wish to report a simple photochemical method that shows promise as a general route to these compounds.

The method of choice is photosensitized isomerization under conditions where selectivity of energy transfer to the trans isomer is such that the eventual stationary state consists entirely of the hindered cis isomer. Selective energy transfer to the geometric isomer of lower triplet energy resulting in enrichment of the higher energy one is a well-known phenomenon in mechanistic studies of sensitized isomerization of olefins,[7] but, previously, in no case was the synthetically desirable condition of complete conversion to the high energy isomer reached.[7b] Now, we have found that in the series of β-ionyl derivatives (I), because of the high energy required for excitation of the skewed cis isomer,[8] conditions for selective energy transfer to the trans isomer can be easily found. For example, irradiation of a dilute solution of *trans*-β-ionol in the presence of 2-acetonaphthone, under the usual conditions for sensitized isomerization, results in rapid and quantitative formation of the cis isomer. The product is readily identified by its pmr spectrum ($J_{7,8}$ = 11.2 Hz with the remaining features similar to that of *trans*-ionol).[2] Similarly, other *trans*-β-ionyl derivatives are quantitatively converted to the corresponding cis isomers and, with fluorenone, β-ionone to an equilibrium mixture of *cis*-ionone and the related α-pyran[9] (Table I).



I II

That the observed one-way sensitized isomerizations are indeed due to selective energy transfer to the trans isomers can be inferred from a study of the dependence of photostationary state compositions on sensitizer triplet excitation energy, a method commonly employed in such mechanistic studies.[7] Results with β-ionol are shown in Figure 1. Clearly, the plot indicates that any sensitizer with energy below ~65 kcal/mol produces one-isomer stationary states. With higher energy sensitizers, larger amounts of the trans isomer are present, presumably because increased rates of energy transfer to the cis isomer reduce the selectivity of transfer to the trans. The plot also suggests that the triplet energy of *cis*-ionol is ~75 kcal/mol, expectedly higher

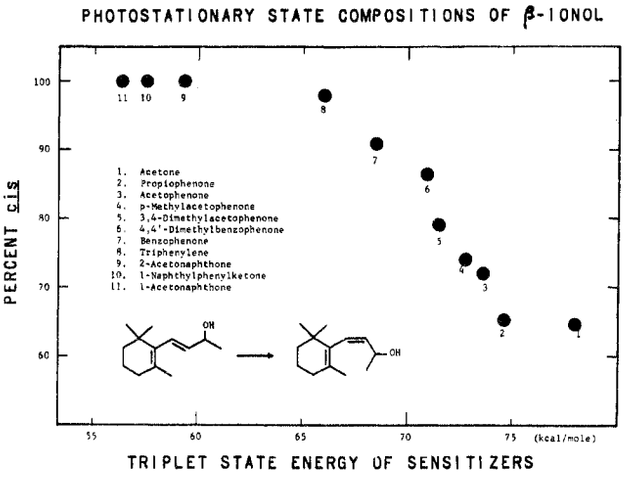


Figure 1.

TABLE I
PRODUCTS FROM ONE-WAY SENSITIZED GEOMETRIC ISOMERIZATION[a]

Product	R	Critical sensitizer (E_T, kcal/mol)[b]
I	CH_3	2-Acetonaphthone (59.3)
	C_2H_5	
	CH_2OH	
	$CH(CH_3)OH$	
	CN	
	$COCH_3$	9-Fluorenone (51)
	CO_2H	
	C_6H_5	Benzanthrone (47)
II[c]	CO_2CH_3	Benzanthrone (47)
	$CO_2C_2H_5$	
	CO_2H	
	CN	
2,4,6-Trimethylstyrene	β-Methyl	Benzophenone (68.5)
	β-Ethyl	
2,4,6-Trimethylstilbene		2-Acetonaphthone (59.3)

[a] Starting from the corresponding trans isomer or, in II, mixtures of 7-trans isomers. [b] Reference 7a. [c] Mixtures of 7-cis isomers, *e.g.*, for R = $CO_2C_2H_5$, 7-*c*-9-*t* (56%), 7-*c*-9-*c* (44%).

than the values for common conjugated dienes (55–60 kcal/mol).[10]

The usefulness of this method for preparing hindered olefins has been further demonstrated by preparing mixtures of 7-*cis*-ionylidene derivatives (II), *cis*-2,4,6-trimethylstyryl derivatives, and *cis*-2,4,6-trimethylstilbene[11] (Table I). Clearly in some cases sensitizers of lower E_T have to be used to achieve quantitative conversion to the cis isomer.[12]

cis-ionyl and -ionylidene derivatives show remarkable thermal stability. For example, *cis*-β-ionol is stable below 150° and dehydrates at higher temperatures, while ethyl ionylideneacetate is stable below 100° and cyclizes at higher temperatures. Being thermally stable and now readily available, these compounds are clearly potential intermediates to the presently unknown iso-

(4) For a up-to-date treatise on carotenoids see "Carotenoids," O. Isler, Ed., Birkhäuser Verlag, Basel and Stuttgart, 1971.

(5) G. Wald, P. K. Brown, R. Hubbard, and W. Oroshnik, *Proc. Nat. Acad. Sci.*, **41**, 438 (1955); **42**, 578 (1956).

(6) Photochemically 7-*cis*-ionylidene compounds have been observed as intermediates or components of a complex product mixture; see M. Mousseron, *Advan. Photochem.*, **4**, 195 (1966). In only one case was selective hydrogenation reported to give an ionyl derivative; see J. Redel, J. Boch, and S. Tchen, *C. R. Acad. Sci. Paris*, **259**, 2466 (1964).

(7) (a) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964); (b) J. Saltiel, *et al.*, *Org. Photochem.*, in press.

(8) From values of long range coupling constants the ring–chain dihedral angle in *cis*-β-ionol has been estimated to be 40–52°: V. Ramamurthy, T. T. Bopp, and R. S. H. Liu, *Tetrahedron Lett.*, 3915 (1972).

(9) The equilibrium was reported by E. N. Marvell, G. Caple, T. A. Gosnik, and G. Zimmer, *J. Amer. Chem. Soc.*, **88**, 619 (1966).

(10) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *ibid.*, **87**, 3406 (1965).

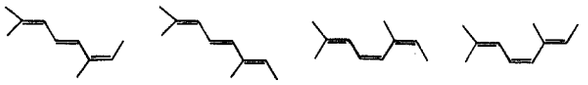
(11) Isomerization of hindered stilbenes by high energy sensitizers was reported by D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, **90**, 3907 (1968).

(12) As pointed out by a referee with low energy sensitizers these systems behave differently as in stilbenes where nonvertical excitation was postulated to account for the results. Mechanistic implications of our results are being examined in detail and will be reported in detail.

mers of 7-cis vitamin A and carotenoids. Such possibilities are being examined in our laboratory.

For less hindered compounds the method of selective sensitization for quantitative conversion to the cis isomer apparently does not apply. For example, in the case of alloocimene,[13] a model for the C_9–C_{13} fragment of carotenoids containing the less hindered C_{11}–C_{12} double bond, sensitization by a variety of sensitizers fails to give mixtures containing entirely the central cis isomers even though some enrichment is noted (Table II).[14]

TABLE II
PHOTOSTATIONARY STATE MIXTURES OF ALLOOCIMENE



Sensitizer (E_T)	Alloocimene i	ii	iv	v
Benzophenone (68.5)	25	39	19	15
Benzanthrone (47)	25	34	25	15
Dimethylbenzanthracene (44)	19	38	26	18

Acknowledgment.—The work was partially supported by grants from the Sloan Foundation, The Public Health Service (RO1 EY-AM 00918-01), and the U. H. Biomedical Research Program.

(13) R. S. H. Liu and Y. Butt, *J. Amer. Chem. Soc.*, **93**, 1532 (1971).

(14) In this case there is a dependence of stationary composition on triene and sensitizer concentrations; therefore values extrapolated to zero sensitizer and triene concentration are reported.

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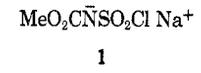
The Fragmentation of Substituted 1,4,3,5-Oxathiadiazine Dioxides to *N*-Sulfonylamines

Summary: Certain nitriles react with the sodium salt of carbomethoxysulfamoyl chloride to afford 6-substituted 2-methoxy-1,4,3,5-oxathiadiazine dioxides, **2**, whose thermal cycloreversion gives methyl-*N*-sulfonylurethane, **4**, which participates in subsequent cycloadditions with alkenes.

Sir: In connection with synthetic studies[1,2] on the generation of *N*-sulfonylamines *via* dehydrohalogenation of sulfamoyl chlorides we investigated the chemistry of adducts derived from nitriles and this heterocumulene. The salt (**1**) derived[2] from reaction of carbomethoxysulfamoyl chloride with sodium hydride at −78° reacts with acetonitrile at 0–30° to afford (75%) an adduct,[3] mp 102–102.5° dec, which displayed nmr[4] singlets at δ 4.08 and 2.37 and intense ir ($CHCl_3$) absorption at 1705 and 1615 cm^{-1}, and underwent facile hydrolysis (H_2O/THF, 30°) to *N*-acetyl-*N'*-carbomethoxysulfamide, mp 149–150° dec. Although such spectral[5,6] and chemical evidence is consistent with either structure **2a** or **3** for this adduct, the former was shown to be correct based on the following results. The reaction of *N*-chlorosulfonyl-*N'*-methyl-*N'*-phenylurea[7] with an excess of phenylmethylcyanamide in THF at 30° gave (80%) of the symmetrically disubstituted oxathiadiazine **2b**, mp 175–176°, which exhibited the same C=N ir double absorption at 1685 and 1605 cm^{-1} but had symmetry consistent with the observed unsplit 6 H methyl group signal at δ 3.26 in the nmr. As final support for this argument, **1** reacts



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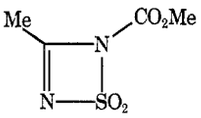

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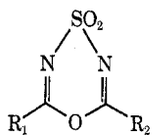
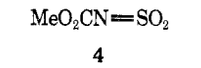


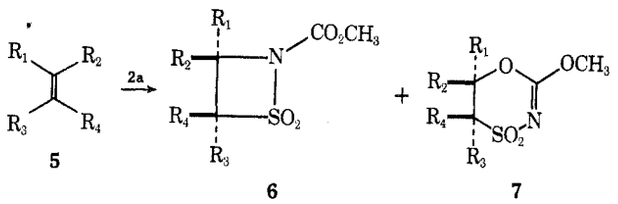
2a, R_1 = Me; R_2 = OMe
b, R_1 = R_2 = $C_6H_5(CH_3)N$
c, R_1 = *p*-$MeOC_6H_5$; R_2 = OMe
d, R_1 = Me_2N; R_2 = OMe



4

with dimethylcyanamide to give **2d**, mp 162–163°, whose ir (in $CHCl_3$, 1700 and 1620 cm^{-1}) and nmr [δ 4.08 (s, 3 H), 3.13 (s, 6 H)] are similar to those of **2a**.

These substituted 1,4,3,5-oxathiadiazine dioxides apparently undergo a thermal [2 + 4] cycloreversion at moderate temperatures in a variety of solvents to provide, along with the corresponding nitrile, *N*-sulfonylurethane **4** as evidenced by the isolation of cycloadducts by reaction with appropriate alkenes. Reaction of **2a** with **5a**, **5b**, and **5c** in THF or acetonitrile at



5 **6** **7**

Compd	R_1	R_2	R_3	R_4
a	Ph	Ph	H	H
b	Ph	H	H	H
c	Me	Me	Me	H
d	Ph	H	Ph	H

30–60° gave the 2-carbomethoxy-1,2-thiazetidines[2] **6a**, **6b**, and **6c** and the 2,3-dihydro-6-methoxy-1,4,5-oxathiazines[2] **7b** and **7c** whose distribution was both

(1) E. M. Burgess and G. M. Atkins, Jr., *J. Amer. Chem. Soc.*, **94**, 6135 (1972).

(2) E. M. Burgess and W. M. Williams, *ibid.*, **94**, 4386 (1972).

(3) Satisfactory elemental analyses and exact mass spectra were obtained on the new compounds reported herein.

(4) All nmr spectra were recorded in $CDCl_3$ at 60 MHz.

(5) The possibility that the oxathiadiazine **2a** has a coupled C=N vibration leading to resonance splitting to give the 1705 cm^{-1} ir signal could not be discounted at this point.

(6) The nitrogen core binding energy signal observed in the ESCA spectrum was so broad that no definitive structural assignment could be made. We thank Dr. David Hercules at the University of Georgia for this measurement.

(7) This precursor is available from the reaction of chlorosulfonylisocyanate and *N*-methylaniline: R. Graf, *Angew. Chem. Int. Ed. Engl.*, **7**, 172(1968).