Benzil Dianion from Alkali Metals. The procedure was the same as above except 100 mmoles + 10% excess of metal was used. $Bz_2{}^{2-}$ is red-orange.

Benzil Anion Radical from Naphthalene and Stilbene Anion Radicals. A solution of the desired anion radical in 150 ml. of solvent was prepared from 50 mmoles of the substrate and 50 mmoles + 10% excess of alkali metal; 10.5 g. (50 mmoles) of Bz_2 was then added either at once through a powder funnel or in 100 ml. of solvent through a dropping funnel. The electron transfer is immediate, as shown by the color change to the purple of $Bz_2{}^-$.

Benzil Dianion from Naphthalene and Stilbene Anion Radicals and Tetraphenylethylene Dianion. Anion radical (100 mmoles) or 50 mmoles of dianion was prepared as above and 10.5 g. (50 mmoles) of benzil added through a powder funnel.

Reaction with Benzoyl Chloride. The solutions of $Bz_2{}^-$ or $Bz_2{}^{2-}$, prepared as above, were cooled to below room temperature in an ice bath, and 100 mmoles + 25% excess of benzoyl chloride was added through a dropping funnel. The purple or red color disappeared during the addition, but stirring was usually continued overnight to assure complete destruction of the excess alkali metal. The addition of 100 ml. of solvent at this stage facilitated stirring. The reaction mixture was then added cautiously to 300–500 ml. of water, the organics were extracted into chloroform, the chloroform was re-extracted to remove nonvolatile polar organic solvents when necessary and, after drying over sodium sulfate, the solvent was evaporated, leaving a viscous oil. Addition of *ca.* 50 ml. of hexane followed by 5–10 ml. of ethanol and heating crystallized the esters. The suspension was then cooled in ice and filtered. The esters thus obtained were nearly pure, as determined by infrared analysis. The pure *cis*

isomer has absorptions at 5.78, 7.92, 8.08 (sh), and 9.20 μ; the *trans* at 5.78, 8.08, and 8.99 μ. The 9.20-μ *cis* and 8.99-μ *trans* absorptions, presumably corresponding to the respective C–OBz stretches, were used in the analysis. This consisted of comparing the product ester with prepared mixtures of the two pure isomers; it was reproducible to less than 5%. The *trans* isomer has m.p. 186°, λ_{max}^{EtOH} 261 mμ (ϵ 11,400); the *cis*, m.p. 159°, λ_{max}^{EtOH} 266 mμ (ϵ 6100).[1,11]

Isomerizations Using Solvent Additives. The anion radical or dianion was prepared as described above, the appropriate amount of solvent additive was added, and the solution either was allowed to stand or refluxed for the desired time interval. The solution was then cooled in an ice bath and then quenched with benzoyl chloride and the reaction product was worked up as described above.

Preparation, Isomerization, and Conformational Analysis of the Enolate ($Bz_3{}^-$). $Bz_2{}^{2-}$ (50 mmoles) was prepared in THF, the solution cooled, and 25 mmoles of benzoyl chloride was added, whereupon the previously red solution became a light yellow. DMF was then added to 10% (by volume) and the solution was refluxed for 1 hr., cooled, and quenched. Work-up was the same as usual.

HMO Calculations. Overlap was neglected; $\alpha_0 = \alpha + 2\beta$ and $\beta_{CO} = \beta\sqrt{2}$ were assumed. π-Electronic rotational barriers were calculated by subtracting the π-electronic energy of planar $Bz_2{}^-$ from that of one Bz (benzoyl group) and one Bz^- and of planar $Bz_2{}^{2-}$ from that of two $Bz_2{}^-$.

Acknowledgments. The author is grateful to the National Science Foundation and the University of Texas Research Institute for generous support.

(11) L. F. Fieser, *J. Chem. Educ.*, 31, 291 (1954). These two references jointly establish the structures of the isomeric esters.

Ambident Reactivity of Thiocyanate Ion. Thiocyanate Ion Catalysis in the Isomerization of Organic Thiocyanates[1a]

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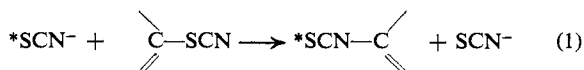
Alkali thiocyanates catalyze the isomerization of benzyl thiocyanate to the isothiocyanate. The catalysis is not a salt effect as it is specific for the thiocyanate ion and the isomerization rate is first order with respect to ionic thiocyanate. The catalytic effect is interpreted as a nucleophilic displacement of thiocyanate carried out by the N end of the thiocyanate ion: $SCN^- + RSCN \rightarrow SCNR + SCN^-$. By comparing the rate of isomerization by this mechanism with the rate of isotopic exchange: $^-NCS^* + RSCN \rightleftarrows NCS^*R + SCN^-$, which is a nucleophilic displacement of thiocyanate carried out by the S end of the SCN^- ion, the reactivity ratio, k_S/k_N, of the two "teeth," S and N, of the ambident nucleophile SCN^-, has been found to range between 10^2 and 10^3. Temperature dependence and solvent effect on the k_S/k_N ratio have been evaluated and discussed.

It has recently been shown[2] on the basis of kinetic evidence that the general mechanism through which organic thiocyanates isomerize to isothiocyanates is, except for substrates of allylic structure,[3] an ionization one.[5]

We wish to describe in this report a second, quite general, mechanism which may provide the main path for isomerization under certain conditions. These conditions are (a) the presence of substantial amounts of ionic thiocyanate, SCN⁻, and (b) an organic substrate which readily undergoes bimolecular substitution and does not undergo facile ionization. Under such circumstances, the organic thiocyanate may isomerize essentially by means of a direct nucleophilic displacement carried out by the nitrogen end of SCN⁻. Reaction 1 results in simultaneous isomerization of the

$$*SCN^- + \quad \overset{\diagdown}{\underset{\diagup}{C}}\!\!-\!SCN \longrightarrow *SCN\!-\!\overset{\diagup}{\underset{\diagdown}{C}} + SCN^- \quad (1)$$

action 1 results in simultaneous isomerization of the organic thiocyanate and exchange of the ionic for the "organic" SCN group.

The view that this isomerization mechanism exists is based upon the measurement of the rate of isomerization of benzyl thiocyanate as a function of the concentration of sodium thiocyanate, in methyl ethyl ketone to which enough sodium perchlorate was added to keep the total electrolyte concentration constant at 0.1 M. The conditions and the rate data are reported in Table I.

Table I. Rate Coefficients for Isomerization of Benzyl Thiocyanate at 110° in Methyl Ethyl Ketone[a]

[NaSCN], M	...	0.02	0.05	0.1
[NaClO₄], M	0.1	0.08	0.05	...
$10^6 k_1$, sec.$^{-1}$	<0.2[b]	1.4	3.6	6.7
$10^5 k_2$, (mole/l.)$^{-1}$ sec.$^{-1}$	...	7.0	7.2	6.7

[a] Analysis by infrared spectrophotometry. [b] Estimated by isotopic dilution analysis.

The first-order specific rate appears to increase linearly with increasing concentration of sodium thiocyanate, while the second-order specific rate remains practically constant over a 5-fold variation of NaSCN concentration. Moreover, the rate is immeasurably slow when 0.1 M NaClO₄, but no NaSCN, is present. Thus, under the conditions of these experiments, the contribution of the ionization mechanism to the total rate is negligible and isomerization arises entirely from a path which involves one molecule each of organic thiocyanate and ionic thiocyanate. It seems most reasonable to identify this path with the direct displacement (eq. 1).

It is interesting to compare the rate of isomerization by this route with the rate of bimolecular exchange of the

(2) (a) A. Iliceto, A. Fava, and U. Mazzuccato, *Tetrahedron Letters,* **11,** 27 (1960); (b) A. Iliceto, A. Fava, U. Mazzuccato, and P. Radici, *Gazz. chim. ital.,* **90,** 919 (1960); (c) A. Iliceto, A. Fava, U. Mazzuccato, and O. Rossetto, *J. Am. Chem. Soc.,* **83,** 2729 (1961); (d) P. A. S. Smith and D. W. Emerson, *ibid.,* **82,** 3076 (1960).

(3) For thiocyanates of this structure, the shift of the allylic double bond provides a much easier path to isomerization. Of course, if the allylic substrate is nonsymmetrically substituted, a rearrangement of the carbon skeleton also results.[2a,2d,4]

(4) O. Mumm and H. Richter, *Ber.,* **73,** 843 (1940).

(5) A recent review by A. Fava in "Organic Sulfur Compounds," Vol. II, N. Kharasch, Ed., Pergamon Press Ltd., London, summarizes and discusses the mechanisms of organic thiocyanate isomerization and reports much unpublished work by the author and his associates.

SCN group, as it may be obtained from measurements of isotopic exchange rates (with ³⁵SCN⁻). In fact, the former represents the rate of displacement by the N end of SCN⁻, and the latter, the sum of the rates of displacement by both the N and the S ends.

$$^-NCS^* + \quad \overset{\diagdown}{\underset{\diagup}{C}}\!\!-\!SCN \longrightarrow NCS^*\!\!-\!\overset{\diagup}{\underset{\diagdown}{C}} + SCN^- \quad (2)$$
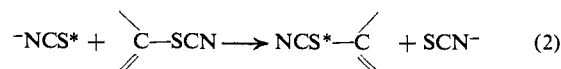
The rate of exchange between benzyl thiocyanate and potassium thiocyanate has already been measured.[6] However, to allow a more significant comparison, it has now been remeasured over a range of temperatures and in two solvents. Also the rate of isomerization has been measured over a range of temperatures and in the same two solvents. The pertinent data are reported in Tables II and III.

Table II. Second-Order Specific Rates of Isotopic Exchange between Benzyl Thiocyanate and K³⁵SCN[a]

	Solvent acetonitrile			
Temp., °C.	50.0	60.0	65.0	70.0
$10^4 \times k$, l. mole^{-1} sec.$^{-1}$	1.37	3.53	5.58	8.32
	Solvent methyl ethyl ketone			
Temp., °C.	50.0	60.0	65.0	70.0
$10^4 \times k$, l. mole^{-1} sec.$^{-1}$	3.79	9.47	14.7	23.0

[a] [C₆H₅CH₂SCN] = 0.1 M; [K³⁵SCN] = 0.1 M.

Table III. Second-Order Specific Rates of Isomerization of Benzyl Thiocyanate in the Presence of Ionic Thiocyanate

	Solvent acetonitrile			
Temp., °C.	70.0	80.0	105.0	115.0
$10^6 \times k$, l. mole^{-1} sec.$^{-1}$	1.26	2.93	34.7	82.0
	Solvent methyl ethyl ketone			
Temp., °C.	70.0	80.0	90.0	105
$10^6 \times k$, l. mole^{-1} sec.$^{-1}$	2.40	5.98	14.2	59.0

[a] [C₆H₅CH₂SCN] = 0.1 M; [KSCN] = 0.1 M.

From the data of Tables II and III the temperature coefficients for both displacements may be obtained. The Arrhenius energy of activation (E) and pre-exponential factor (A), as obtained from least-square analysis of the data, are collected under Table IV, together with the "thermodynamic" activation quantities.

Discussion

It is evident from the data of Tables II and III that the isotopic exchange is so much faster than isomerization that isomerization does not contribute appreciably to the exchange rate in the temperature range 50–70°. Consequently, the ratio of the rate of exchange to the rate of isomerization, k_{ex}/k_{is}, gives directly the reactivity ratio (relative nucleophilicity) k_S/k_N, of the two ends, S and N, of the ambident[7] nucleophile SCN⁻ toward the benzyl carbon of benzyl thiocyanate.

As the energies of activation of the two processes differ considerably, about 4 kcal./mole (Table IV), the relative nucleophilicity is strongly temperature

(6) A. Fava and A. Iliceto, *Ric. Sci.,* **25,** 54 (1955). The kinetic features indicate that the exchange occurs by way of a bimolecular nucleophilic displacement.

(7) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.,* **77,** 6269 (1955).

Table IV. Activation Parameters for Isomerization and Isotopic Exchange of Benzyl Thiocyanate in the Presence of KSCN

Reaction	Solvent	E	log A	ΔH*	ΔS*c
Exchange	MeCN[a]	20.82 ± 0.36	10.19 ± 0.20	20.1	−14.1
	MEK[b]	19.85 ± 0.11	10.00 ± 0.06	19.2	−14.9
Isomerization	MeCN[a]	25.10 ± 0.48	10.06 ± 0.24	24.4	−14.7
	MEK[b]	23.55 ± 0.49	9.36 ± 0.25	22.9	−17.9

[a] Acetonitrile. [b] Methyl ethyl ketone. [c] At 70°.

dependent. Since, however, both the activation energy is smaller and the pre-exponental factor larger for exchange than for isomerization, the k_S/k_N ratio, although decreasing with increasing temperature, will always be greater than unity. At the temperatures employed, k_S/k_N ranges between 10^2 and 10^3. For example, at 100° in methyl ethyl ketone and acetonitrile the values are 650 and 460, respectively; at 70° the values are 1000 and 725.

Although the ratio k_S/k_N is expected to be substrate dependent,[7] it is not likely to vary a great deal for other direct displacements at primary carbon atoms. If this is so, the fraction of isothiocyanate formed in direct nucleophilic substitution reactions by thiocyanate ion on primary substrates can be expected to be on the order of 0.1%. Actually in these substitutions the product (which is kinetically controlled) is commonly reported to consist exclusively of thiocyanate.

The large values of the k_S/k_N ratio for the primary substrate, benzyl, are in keeping with the generalizations expressed by Kornblum in his first fundamental paper on the reactivity of ambient nucleophiles. With changing substrate, the relative reactivity of the nitrogen end may be expected to increase with increasing carbonium ion character of the nucleophilic substitution.[7,8] This is indeed observed: in the extreme case of thiocyanate ion reacting with a carbonium ion intermediate, either formed in deamination or in solvolysis of suitable substrates, k_S/k_N ratios ranging from 2 to 9 have been observed by Taft.[9,10] This trend of changing relative reactivity with changing electrophilic character of the reaction center has been extensively discussed by Kornblum.[7] It may be easily rationalized on the basis of the recent discussions by Edwards and Pearson[12] and by Hudson[13] on the factors which determine the nucleophilic reactivity of reagents vs. different substrates. Thus, as the electrophilic character of the reaction center increases, the reactivity of the more basic nitrogen atom, which forms the stronger bond to carbon, increases with respect to that of the more polarizable sulfur atom.

A few comments about the effect of solvent may be warranted. As the data show, larger rates are observed in the ketone solvent (Tables II and III) and larger activation parameters in the nitrile solvent (Table IV), for both isomerization and exchange. This behavior is consistent with the idea that the re-

actions involved are direct displacements by an ion onto a neutral molecule, in which charge is dispersed at the transition state.

As to the effect on the ambident reactivity of SCN⁻, the medium change realized here, acetonitrile to methyl ethyl ketone, has proved inadequate to reveal sufficiently large changes either in the relative rate, k_S/k_N, or in its activation parameters to allow any sound rationalization. Both solvents in fact are of the "dipolar aprotic" type and may be expected to exhibit comparable solvating abilities.[14] Greater changes are to be expected between protic and nonprotic solvents, but unfortunately, the reactivity of the latter media toward thiocyanates and isothiocyanate inhibited their usage in our system. Recently Kornblum and his associates[15] have shown that the change from a protic to a nonprotic solvent may cause very large changes in the relative reactivity, carbon vs. oxygen, in the reaction of phenoxide or naphthoxide ions with a benzyl substrate.

One further comment may be warranted concerning the exploitation of reaction 1 to obtain isothiocyanates. The method may be of considerable value in those cases where the nature of the substrate is such as to allow neither the isomerization of the thiocyanate via ionization nor the conventional route of reacting the amine with carbon disulfide.

For example p-nitrobenzyl isothiocyanate which cannot be prepared by the conventional routes above was obtained in moderate yield by heating p-nitrobenzyl thiocyanate with KSCN in acetone.[16]

Experimental Section

Materials. Reagent grade methyl ethyl ketone was refluxed over KMnO₄, distilled, dried over Drierite, and redistilled, b.p. 79.3–79.4°.

Acetonitrile was first dried over Drierite, refluxed over phosphorus pentoxide, and distilled. From the redistillation over anhydrous potassium carbonate the fraction boiling at 81.5–81.6° was collected.

Benzyl thiocyanate was prepared according to standard procedures and recrystallized from absolute ethanol, m.p. 43–43.5° (lit.[17] m.p. 43–43.5°). The procedures to obtain labeled (³⁵S) ionic thiocyanate and to measure the rates of isotopic exchange has been previously described.[6] The isomerization rates have been measured by infrared spectrophotometry, as described previously.[2c] The estimation of the upper limit for the rate of isomerization of benzyl thiocyanate in the absence of ionic thiocyanate and in the presence of NaClO₄ (Table I) was made through isotopic dilu-

(8) N. Kornblum and A. L. Lurie. *J. Am. Chem. Soc.*, **81**, 2705 (1959), footnote 27.
(9) L. G. Cannell and R. W. Taft, Jr., 129th National Meeting of the American Chemical Society, Dallas, Texas, April 1956, Abstracts of Papers, Organic Division, p. 40N.
(10) A value of k_S/k_N = 5 has been reported very recently for SCN⁻ reacting with *p,p'*-dimethylbenzhydryl carbonium ion in acetonitrile.[11]
(11) A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Am. Chem. Soc.*, **87**, 1045 (1965).
(12) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).
(13) R. F. Hudson, *Chimia*, **16**, 173 (1962).
(14) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).
(15) (a) N. Kornblum, P. J. Berrigan, and W. J. le Noble, *J. Am. Chem. Soc.*, **85**, 1141 (1963); (b) N. Kornblum, R. Seltzer, and P. Haberfield, *ibid.*, **85**, 1148 (1963).
(16) U. Tonnellato, G. Levorato, and A. Fava, unpublished.
(17) H. L. Wheeler and H. F. Merriam, *Am. Chem. J.*, **23**, 294 (1901).

tion analysis according to the following procedure. Labeled benzyl thiocyanate was prepared (by exchange with Na^{35}SCN) having a specific activity of 0.5 mc./mmole, which in our counting system corresponded to about 150,000 counts/min./per thick-layer sample of BaSO$_4$ of 0.6 cm.^{2} area. Methyl ethyl ketone solutions (2 ml.) which were 0.1 M in labeled benzyl thiocyanate and 0.1 M in NaClO$_4$, were kept at 110° in a thermostat for 225 hr.; afterward, benzyl isothiocyanate carrier (0.2 mmole) was added and the solution extracted with cyclohexane–water. The cyclohexane layer after washing with water (three times) and drying with Drierite was treated with piperidine. The N-benzyl-N′-piperidinthiourea which precipitated out was oxidized to obtain BaSO$_4$, as described previously for a different thiourea.[2c] The activity found on the thiourea–sulfur corresponded to an isomerization fraction of about 0.2% and was practically undistinguishable from the zero-time fraction, which could be due either to incomplete separation or, more likely, to isothiocyanate initially present in the thiocyanate sample.

Relative Reactivities of Some Benzocyclenes in Aromatic Nitration and Electrophilic Side-Chain Reaction.[1-5] A Remarkable Effect of the Bicyclo[2.2.1]heptene System
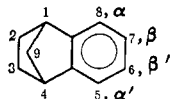
Hiroshi Tanida and Ryonosuke Muneyuki

Contribution from the Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, Japan. Received May 28, 1965

Relative reactivities and orientations in aromatic nitration of benzonorbornene (I), benzobicyclo[2.2.2]octene (II), indane (III), tetralin (V), 1,3-dimethylindane (VI), and 1,2,3,4-tetrahydro-1,4-dimethylnaphthalene (VII), by means of nitric acid in a mixed solvent of sulfuric acid and nitromethane at 0°, were determined. The relative partial reactivities at their β-positions were 3.63, 1.50, 1.32, 1.01, 1.00, and 0.72, respectively. The relative rates of hydrolyses of the corresponding 1-(α- or β-benzocyclenyl)ethyl chloride in 80% aqueous acetone at 25° were in the β-series, for I$_{β \cdot Cl}$, 6.10; for II$_{β \cdot Cl}$, 2.36; for III$_{β \cdot Cl}$, 1.63; for IV$_{β \cdot Cl}$, 1.36; for V$_{β \cdot Cl}$, 1.22; VI$_{β \cdot Cl}$, 1.00; and for VII$_{β \cdot Cl}$, 0.60. Relative rates in the α-series were for I$_{α \cdot Cl}$, 1.73; and for VI$_{α \cdot Cl}$, 1.00, respectively. The remarkable rate enhancement in the bicyclo[2.2.1]heptene system is discussed in terms of internal strain and 1,2-σ bond participation in the transition state. In addition, extraordinarily low nitration at the α-positions of the bridged compounds I and II was observed.

Introduction

The influence of the attached alicyclic ring on the chemistry of benzocyclenes has received considerable attention from three main points of view. The first is the almost out-dated hypothesis of bond fixation of Kekulé benzene structures suggested by Mills and Nixon[6,7] in order to explain the influence of an alicyclic ring condensed with the benzene nucleus on the direction of electrophilic substitution, as in 5-hydroxy-indane and 6-hydroxy-1,2,3,4-tetrahydronaphthalene. The second is the influence of strain energy in the ground state, arising from fusion of the alicyclic ring, as evidenced by heats of combustion and hydrogenation.[8]

It is known that the ultraviolet spectra of highly strained benzocyclenes, for example benzocyclobutene, are characteristic. The question of the Baker–Nathan effect (hyperconjugation)[10] of the alicyclic ring, in which the conformation of the ring may be quite significant, is the third main viewpoint. However, to the best of our knowledge, a precise and extensive experimental investigation of the relative reactivities of benzocyclenes using modern analytical tools has not been carried out.

The chemistry of bicyclo[2.2.1]heptane and bicyclo-[2.2.2]octane systems is under active investigation. In previous papers,[11,12] the benzonorbornene system has been demonstrated to be a good model compound for

(1) Paper X of a series on Bicyclic Systems. Paper IX: H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, **30**, 2259 (1965).

(2) Some of the results of this paper appeared in preliminary form: H. Tanida and R. Muneyuki, *Tetrahedron Letters*, No. **38**, 2787 (1964).

(3) Presented, in part, at the 15th Organic Reaction Mechanism Symposium of the Chemical Society of Japan in Nagoya, Oct. 1964.

(4) For the designation of the term, electrophilic side-chain reaction, refer to L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 3323 (1959).

(5) The numbering of bridged benzocyclenes used in this paper is as shown

(6) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).

(7) For reviews of the Mills–Nixon effect, see (a) W. Hückel, "Theoretische Grundlagen der Organischen Chemie," Vol. II, Akademische Verlagsgesellschaft Geest u. Portig K.-G., Leipzig, 1957, p. 691; (b) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 197.

(8) Experimental data concerning heats of combustion or hydrogenation of the benzocyclenes themselves seem to be lacking. The only direct data may be those of Kistiakowsky, *et al.*,[9] who showed the heat of hydrogenation of indane ($-\Delta H$) to be markedly smaller than of o-xylene or ethylbenzene. However, many available data on cycloalkenes[9] suggest the degree of strain of benzocyclenes.

(9) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *J. Am. Chem. Soc.*, **59**, 831 (1937).

(10) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

(11) (a) H. Tanida, T. Tsuji, and H. Ishitobi, *J. Am. Chem. Soc.*, **86**, 4904 (1964); (b) H. Tanida, *ibid.*, **85**, 1703 (1963).

(12) (a) P. D. Bartlett and W. P. Gidding, *ibid.*, **82**, 1240 (1960); (b) W. P. Gidding and J. Dirlam, *ibid.*, **85**, 3900 (1963).