in hydrocarbons, and for benzophenone with primary amines,[2,5,29] but two orders of magnitude less than for benzophenones with tertiary amines.[5,33] Values for k_{ir} for 2-naphthaldehyde with triethylamine in benzene and for 2-acetonaphthone in both nonpolar and polar solvents are low, $1\text{–}6 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, lower even than for the direct abstraction of hydrogen by benzophenones from alcohols. Since abstraction from alcohols is less easy than abstraction from amines, the inertness of the naphthyl carbonyl compounds to alcohols is readily understood. The naphthyl carbonyl compounds also show low values of k_d (see Table VI, ref 34), less than $10^4\ \text{sec}^{-1}$, more than an order of magnitude less than k_d for benzophenone.[34] Although these results are derived from the estimated low values of k_q for piperylene in these systems, it seems true that the π,π^* triplets of the naphthyl carbonyl compounds show relatively high stability and lifetimes, and low electrophilic reactivity.

The photoreduction of the naphthyl carbonyl compounds by triethylamine was not quenched appreciably by DABCO and by aniline despite their low ionization potentials. This result was unexpected since these compounds quench efficiently photoreduction of fluorenone by triethylamine.[26] That fluorenone is both photoreduced and quenched by DABCO, while the naphthyl carbonyl is neither photoreduced nor quenched appreciably, may support the proposal that both processes proceed *via* a common pathway. This may be a CT complex, eq 1, or a less readily described transition in which charge transfer and partial hydrogen transfer are involved. Subtle effects of structure on reactivity may not be apparent in reactions of highly reactive n,π^* triplets, while π,π^* triplets may better reveal such differences. They are generally less electrophilic[14] and react best with strongly electron-donating tertiary amines, less well with secondary and primary amines, and little if at all with alcohols. High triplet energies, as of *p*-aminobenzophenone, and features in the carbonyl compounds which stabilize radical anion structure, such as the potential cyclopentadienide character of fluorenone, favor interactions with electron donors which may lead to both photoreduction and quenching. Dipolar solvents favor such interactions and may increase reactivity if they do not decrease intersystem crossing.

Acknowledgment. This work was supported by National Science Foundation Grant No. GP 9247, 23516.

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The Beckmann–Chapman Rearrangement in the Solid State of Oxime Picryl Ethers[†,1]

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Abstract: The picryl ethers (**1a–c**) of benzophenone oxime and its syn and anti para bromo derivatives have been found to undergo a thermal Beckmann–Chapman rearrangement to give the *N*-picrylbenzanilides (**3a–c**, respectively); the product in each case is that formed by migration of the aromatic ring trans to the picryloxy group of the starting molecule. The reactions of **1b**,**c** follow approximately first-order kinetics and are slower than estimated rates in solution by factors of 5–15. A vapor-phase rearrangement in small pockets of vapor in equilibrium with the solid cannot account for the reaction. Differential thermal analysis (dta) studies of the picryl ethers and their mixtures with the rearrangement products show that reaction occurs well below the eutectic temperature in each case. ΔH for these reactions is of the order of −80 kcal/mol. The observation of the rearrangement of heated single crystals shows initial formation of solid solutions of product (15–30%) in the starting material matrix and subsequent separation of microcrystallites 10^3 Å in diameter and randomly oriented with respect to the original axes. Larger crystals undergo cracking during the initial stages of rearrangement due to strains introduced by buildup of product in the matrix of starting material; the cracking appears to have a catalytic effect on the rearrangement. The implications of the crystal structures with respect to these rearrangements are discussed.

In spite of a steady increase of interest in organic reactions in the solid state[4] relatively little is known about the mechanistic details of thermally induced intramolecular rearrangements of molecular crystals.

The thermal Beckmann–Chapman rearrangement[5] of benzophenone oxime picryl ether (**1a**) to *N*-picrylbenz-

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† Figure 3 of this paper appears on p 879.

(1) Taken from the Ph.D. Thesis of J. D. McCullough, Jr., submitted to the University of Illinois, Urbana, Ill., 1970.

(2) National Institutes of Health Predoctoral Trainee, 1968–1970. We are also indebted to the National Science Foundation and the National Institutes of Health for grants partially supporting this work.

(3) Alfred P. Sloan Research Fellow, 1968–1970.

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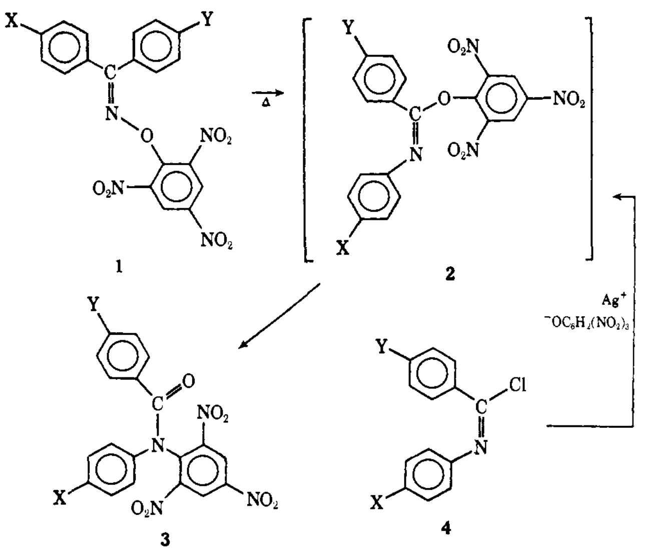
anilide (**3a**) had been discovered by Chapman and Howis[6] to proceed readily and essentially quantitatively in either polar or nonpolar solvents at moderate temperatures. Since, furthermore, the solid picryl ether **1a** had been observed[6] to be "transformed almost explosively at its melting point" this appeared to be an interesting candidate for study as an intramolecular rearrangement in the solid state. In addition to being highly exothermic[6] the reaction had been reported to be first order in solution and markedly accelerated by polar solvents.[7]



a, X = Y = H
b, X = H; Y = Br
c, X = Br; Y = H

Studies of picryl ethers derived from **1a** by introduction of a single substituent into the para position of one of the phenyl rings had shown the rearrangement to proceed stereospecifically with migration of that aryl ring trans to the picryloxy group and that the rate was increased by a para methyl substituent and decreased by para chloro or nitro groups.[8]

Reinvestigation of the solid state behavior of oxime ether **1a** showed that it does indeed undergo rearrangement without apparent melting when heated to 70° or even when allowed to stand at ambient temperatures of 25–30° for several months. This paper reports a study of the thermal rearrangement of crystalline picryl ether **1a** and the preparation and study of the previously unreported syn and anti bromo derivatives. The choice of the bromo substituent was made to facilitate the determination of crystal structures by X-ray crystallography. The structures of **1b,c** are reported in the accompanying paper.[9]

Although the picryl ethers **1b,c** had not been described, the parent oximes *syn-* and *anti-p-*bromobenzophenone oximes had been prepared[10] and the configurational assignments had been based on the assumption of trans stereochemistry in the Beckmann rearrangement. The oximes were readily converted to the picryl ethers **1b,c** in nearly quantitative yield. Each picryl ether rearranged stereospecifically and essentially quantitatively in refluxing benzene to the *N*-picryl derivative of the same benzanilide which had been obtained[8] from the Beckmann rearrangement of the corresponding oxime; thus, **1b** was converted to anilide **3b** and **1c** to **3c**. Each isomer gave the same product when the reaction was carried out in the solid state as was obtained in solution. It had been found by Chapman and Howis[6] that the treatment of the imino chloride **4a** (X = Y = H) with sodium picrate in aqueous ether at ambient temperature for only 1.5 hr gave, on evaporation of the ether, the picramide **3a** with none of the presumed intermediate imino ether **2a**. Subsequent workers [5b,11] had been successful in trapping the intermediate **2a** but such picryl imidates had not been isolated because of their great tendency to rearrange to *N*-picrylanilides. In the course of the present work, an attempt was made to isolate the intermediate imidates **2b,c** from imino chloride **4b,c**. It was hoped that their rate of formation could be accelerated by the use of silver picrate instead of the sodium salt and the employment of the relatively polar solvent diethylcarbitol. However, even at reaction times as short as 14 min and temperatures between −78 and 0° the only products isolated were the anilides **3b,c**.

Experimental Section

Melting points were determined with a calibrated Kofler hot stage. Infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer unless otherwise indicated. Nmr spectra were obtained with Varian A-60A or HA-100 instruments; some of the spectra were obtained by Mr. R. Thrift and his associates. Uv spectra were measured with a Bausch and Lomb Model 505 or Cary Models 14 and 15 instruments. Microanalyses were provided by Mr. J. Nemeth and his associates. Throughout "petroleum ether" refers to the fraction bp 30–60°.

Benzophenone Oxime Picryl Ether (1a).[6,12] Reaction of picryl chloride with benzophenone oxime gave the ether **1a** which was purified by addition of a two- to threefold amount of ethanol or petroleum ether (bp 30–60°) to a solution in acetone. At room temperature long needles were obtained which, when the suspension was cooled to 3°, were transformed to pale yellow prisms. Analytically pure crystals were obtained after two recrystallizations. Crystals for solid-state reaction studies were also prepared by recrystallization under an atmosphere of dry N_2 from acetone which had been purified by passage through a column of Linde 4A molecular sieves, followed by distillation twice through molecular sieves and a final distillation (Vigreux column) without molecular sieves. The petroleum ether employed for this crystallization was distilled twice from lithium aluminum hydride and a final time without LAH. On the hot stage **1a** melted abruptly between 103 and 105°, crystallized on continued heating, and remelted at 195–197° in agreement with the literature[6] mp for **3a**: ir max (KBr disk)

J. Chem. Soc., 1191 (1961); (j) D. T. Curtin and S. R. Byrn, *J. Amer. Soc.*, **91**, 1865 (1969); (k) W. D. Burrows, *J. Org. Chem.*, **33**, 3507 (1968); (l) A. J. Gordor, *Tetrahedron*, **23**, 863 (1967); (m) M. Tsuda and K. Kuratani, *Bull. Chem. Soc. Jap.*, **37**, 1284 (1964); (n) M. Pope, N. Geacintov, and S. Michelson, *Mol. Cryst.*, **1**, 125 (1966); (o) M. Ehrenberg, *Acta Crystallogr.*, **20**, 177, 182 (1966); (p) A. D. Site, *J. Org. Chem.*, **31**, 3413 (1966); (q) M. D. Cohen, I. Ron, G. M. J. Schmidt, and J. M. Thomas, *Nature (London)*, **224** 167, (1969); (r) see P. Sarti-Fantoni and R. Teroni, *Mol. Cryst. Liquid Cryst.*, **12**, 27 (1970), and references therein; (s) H. J. Milledge, *Acta Crystallogr., Sect. A*, **25**, S233 (1969); (t) J. Z. Gougoutas and J. C. Clardy, *ibid., Sect. B*, **26**, 1999 (1970); J. C. Clardy, Ph.D. Thesis, 1969, Harvard University; (u) V. C. Bastron and H. G. Drickamer, *J. Solid State Chem.*, **3**, 550 (1971).

(5) See (a) L. G. Donaruma and W. Z. Heldt, *Org. React.*, **11**, 1 (1960); (b) P. A. S. Smith, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 8; (c) J. W. Schulenberg and S. Archer, *Org. React.*, **14**, 1 (1965).

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(12) We are indebted to Dr. Charles Leir for the original sample of this compound.

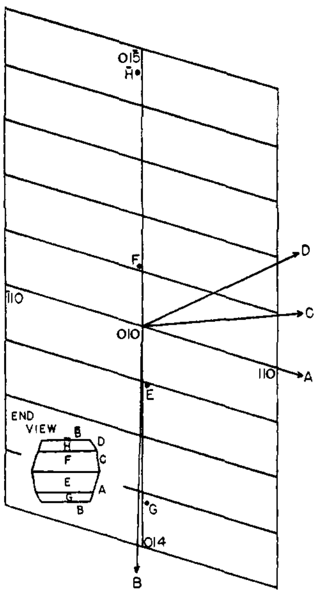

Figure 1. Gnomonic projection of **1b** together with a schematic drawing of a crystal looking down [0 1 0] which is generally its long direction.

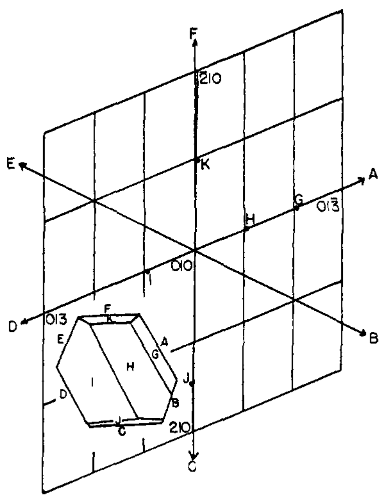

Figure 2. Gnomonic projection of **1c** together with a schematic drawing of a crystal looking down [0 1 0] which is generally its long direction.

3100, 3085 (d), 1612, 1551 cm^{-1}; uv max (CH_2Cl_2) 314 nm (ϵ 13,200); nmr (acetone-d_6) τ 1.1 (s, 2), 2.3–2.8 (m).

The crystals so prepared were nearly colorless monoclinic prisms. The picryl ether **1a** was found[9] to belong to space group *Cc* or *C*2/*c*. The prominent diamond-shaped faces of the crystals were {001} with the diagonals parallel to the *a* and *b* crystallographic axes.

***syn*-*p*-Bromobenzophenone oxime *O*-picryl ether (1b)** was prepared in yields of 80–88% by a method analogous to that used in the preparation of **1a**. The product was purified for analysis by washing successively in cold water, 95% ethanol, and petroleum ether followed by recrystallization from acetone–petroleum ether to give nearly colorless, well-formed prisms. More highly purified crystals for rearrangement studies were prepared as described for the unsubstituted picryl ether **1a**. When an attempt was made to determine the mp of **1b** (Kofler hot stage, heating rate 5°/min) the crystals developed a bright yellow color between 115 and 125° and, with little or no melting observable, became opaque and melted at 239–241°: **1b** had ir (KBr disk) 3100, 1612, 1550 cm^{-1} (sh); uv max (CH_2Cl_2) 315 nm (ϵ 13,100); nmr (acetone-d_6) τ 0.88 (s, 2), 2.3 (q, 4), 2.2 (s, punctuating the quartet).

The space group was $P2_1/c$ with the prismatic crystals generally elongated in the *b* direction and sitting on {001} or {100}. The crystal structure is described in the accompanying paper.[9] A gnomonogram is shown in Figure 1.

Anal. Calcd for $C_{19}H_{11}BrN_4O_7$: C, 46.8; H, 2.3; Br, 16.4; N, 11.5. Found: C, 46.8; H, 2.5; Br, 16.2; N, 11.3.

***anti*-*p*-Bromobenzophenone oxime *O*-picryl ether (1c)** was prepared by the method employed for the syn isomer and purified similarly (a 5-min reaction time gave 91% yield). A powdered sample heated at 10°/min on a Kofler hot stage became yellow with partial melting at 121° and had melted completely at 127–128°. On continued heating, recrystallization occurred at 135–155° and remelting at 202–203°. Other crystals, however, melted to give a glasslike isotropic phase which was not fluid until 140° and could be reformed on cooling the melt. **1c** had ir (KBr) 3100, 1605, 1595 cm^{-1} (sh); uv max (CH_2Cl_2) 316 nm (ϵ 14,300); nmr (acetone-d_6) τ 0.93 (s, 2), 2.6 (q, 4), 2.4 (s, punctuating the quartet). More highly purified crystals for rearrangement were prepared in an atmosphere of N_2 as described for the unsubstituted compound **1a**.

The space group was $P2_1/c$. In a first habit nearly colorless prisms were elongated in the *b* direction. A gnomonogram is shown in Figure 2. The crystal structure is described in the accompanying paper.[9] A second habit consisted of thin "hexagonal" plates shown by precession photographs to have the same unit cell dimensions and symmetry as the more common crystals. The "hexagonal" crystals had well-developed (100) faces.

Anal. Calcd for $C_{19}H_{11}BrN_4O_7$: C, 46.8; H, 2.3; Br, 16.4; N, 11.5: Found: C, 47.1; H, 2.4; Br, 16.4; N, 11.2.

***N*-Picrylbenzanilide (3a).**[6] Picryl ether **1a** (0.12 g) in 5 ml of dry benzene was heated under reflux for 6 hr. Evaporation of the solvent and recrystallization from acetone–petroleum ether gave in 74% yield **3a**: mp 197.5–199° (lit.[6] 198–199°); uv max 363 nm (ϵ 53,900); nmr (acetone-d_6) τ 0.91 (s, 2), 2.3–3.1 (m, 10). In general, when crystallized from acetone or from acetone–petroleum ether the product was obtained as yellow prisms melting normally (some sublimation prior to melting). In one instance crystallization from the mixed solvent gave clear yellow rods which became opaque when heated to 102° but melted normally at 199.5–200°. That they had crystallized with a substantial amount of incorporated petroleum ether was shown by heating a crystal immersed in a drop of water. At 30° bubbles appeared on the surface of the crystal and a separate liquid phase immiscible with water developed. This petroleum ether solvate of **3a** was not studied further.

Rearrangement of 1b. *N*-Picryl-*p*-bromobenzanilide (3b). When 2.5 g of picryl ether **1b** was heated in 50 ml of freshly distilled benzene for 6 hr under reflux the pale yellow solution became deep orange and some crystallization occurred; after several additional hours at room temperature crystallization appeared complete. Filtration gave 1.9 g (76%) of **3b**, mp 239–241° (sublimation apparent above 200°). Examination of the filtrate by tlc showed spots characteristic of starting material and product **3b**; the only other spot was a very weak one which failed to migrate with the eluent employed. Further purification by chromatography on alumina and three recrystallizations from acetone–petroleum ether gave **3b**: mp 241–243° dec; ir (KBr) 1670, 1609, 1600, 1588 (t), 782 cm^{-1}; nmr (acetone-d_6) τ 0.80 (s, 2), 2.2–2.9 (m, 9). The anilide **3b** could be recovered unchanged from boiling for 15 min with 10% aqueous acetone.

Anal. Calcd for $C_{19}H_{11}BrN_4O_7$: C, 46.8; H, 2.3; Br, 16.4; N, 11.5. Found: C, 47.1; H, 2.2; Br, 17.0; N, 11.6.

Rearrangement of 1c. *N*-(Picryl)benz-*p*-bromoanilide (3c). When **1c** was heated in dry benzene under reflux for 74 hr there was obtained the anilide **3c** in 86% yield as a benzene solvate in the form of large yellow plates which lost solvent and became opaque at 85–90° and melted at 202–204°. No further work was carried out with this solvate. Crystallization from acetone–petroleum ether gave solvent-free crystals of **3c**: mp 202–203.5° (sublimation below the melting point noted); ir (KBr) 1672, 1606, 1548, 758, 747 cm^{-1}; nmr (acetone-d_6) τ 0.90 (s, 2), 2.3–3.2 (m, 9) ($A_2'B_2'$ centered at τ 2.8). Unlike the isomer **3b** the anilide **3c** dissolved readily in acetone and other organic solvents. Treatment under reflux with aqueous acetone (10%) for 15 min gave no hydrolysis.

Anal. Calcd for $C_{19}H_{11}BrN_4O_7$: C, 46.8; H, 2.3; Br, 16.4; N, 11.5. Found: C, 46.8; H, 2.1; Br, 16.6; N, 11.7.

Analytical Methods Employed for Reaction Mixtures from the Rearrangements of Picryl Ethers 1a–c. (a) Tlc. Qualitative estimates of the extent of reaction could be made by dissolving partially reacted crystals in dry ethyl acetate and carrying out a separation with tlc on silica with a fluorescent indicator (Eastman type K301R) eluting with 85% petroleum ether–15% ethyl acetate. The only spots which migrated were those of the starting material and the product anilide whose R_f values were compared with those of the authentic starting material and product.

(b) Method of Dewar and Urch.[13] Uv spectra of solutions in CH_2Cl_2 of crystals after reaction were compared with spectra of the purified starting material and product.[13] A computer program written by Milligan[14] finds the slope and intercept of a plot of R/A_1 *vs.* A_2/A_1 for a plot of data for up to 16 wavelengths. (R is the absorbance of the unknown at a given wavelength; A_1 and A_2 are absorbances of known concentrations of the pure components at the same wavelength.) Control analyses of known mixtures of **1b** and its rearrangement product **3b** with [**1b**]/[**3b**] ranging from 75/25 to 10/90 gave correct analyses to within 1% absolute. In the region of composition of less than 25% of the product the error was ±5%.

(c) UVANL Method. Uv spectra of solutions of reaction products in CH_2Cl_2 were analyzed in comparison with spectra of known compounds using the least-squares program UVANL written by D. B. Pendergrass, Jr.[15] Comparison of results by this method with those of a gave agreement to within 1%.

(d) X-Ray Photography. Powder photographs of ground samples were taken with nickel-filtered Cu Kα radiation with a Debye-Scherrer Powder camera. Reactions were also followed by mounting a single crystal on a glass fiber in a Buerger precession camera fitted with a single-strip platinum furnace similar to one described previously.[16] The temperature was maintained to within ±2° with a controller equipped with a thermistor. Zirconium-filtered Mo Kα radiation was employed together with Polariod film.

Solid-State Rearrangement of Oxime Picryl Ether 1b. Single crystals of **1b** (0.5–1 mm in length) heated on a hot stage at 90° and observed (magnification × 100) with illumination through the crystal showed no indication of melting or softening and in less than 1 hr a yellowing occurred in the center part of the crystal due to accumulation of **3b** as a solid solution in **1b** (Figures 3a–b)† followed by development of a few cracks in the yellow region in the [0 1 0] direction. A V-shaped area at each end of the crystal often remained unchanged for several hours after reaction had begun to occur in the middle of the crystal. On continued heating the yellow color deepened but the yellow part of the crystal continued to transmit light—in fact some annealing of the cracks occurred—and the yellow areas showed the same extinction direction between crossed polaroids as did the original crystal. After a number of hours opaque regions developed and spread first through the yellow center part of the crystal and finally to the ends. The crystal at this stage still showed no signs of having melted or softened—the original faces were preserved—but it generally showed some increase in width (normal to [0 1 0]) as a bulge in the center of the crystal. Similar pattern development was noted when crystals were heated more uniformly in a rotating flask totally immersed in a constant temperature bath. Crystals prepared under N_2 in triply distilled solvent showed the same behavior as those less rigorously purified. Although the nature of the change was similar in many crystals, the time scale was characteristically irregular—different individuals typically underwent the change at different rates. In Table I are presented some results which indicate that the changes observed visually are indeed due to chemical rearrangement.

Table I. Analysis of Individual Crystals of **1b** Heated at 78° on a Hot Stage

Time heated, hr	Appearance	% **1b**	% **3b**
5.2	Initial yellow pattern	98–89[a]	2–11[a]
9.2	Initial yellow pattern	98–90[a]	2–10[a]
20–24	Some opaque regions had developed	91–85[a]	9–15[a]
31	Semiopaque	82[a]	18[a]
69	Opaque	64[a]	36[a]
236	Opaque	42[a]	58[a]
69[b]	Opaque	Trace[c]	100[c]

[a] Uv analysis (method b in the preceding section). [b] Heated at 90°. [c] Tlc showed only a slight indication of starting material even after heavy application. An X-ray powder photograph of a ground sample was identical with that of the product **3b**.

Attempts to detect the suspected intermediate picryl imidate **2b** were made by heating a powdered sample of **1b** to 118° on a hot stage. The bright yellow powder was subjected to tlc as described in the previous section and also an infrared spectrum (Nujol mull) was obtained. In neither case was there evidence of any products other than **3b**; neither the imidate **2b** nor its anticipated hydrolysis products[11] were detected. Similarly, samples of **1b** heated for 1.5 and 4 hr were hydrolyzed in aqueous acetone at 25°, conditions which might be expected to convert the imidate **2b** to bromobenzanilide and picric acid.[11] An infrared spectrum of the crude product (Nujol) showed neither the 3300-cm^{-1} NH nor the 1650-cm^{-1} CO absorption to be expected if such a hydrolysis occurred.

When substantial numbers of crystals were heated on a microscope slide very small single crystals of sublimate formed within a time as short as 3 hr at 90°. These appeared (magnification × 200) as thin parallelograms with a measured acute profile angle of 57°. When the temperature was raised these crystals of sublimate in turn sublimed at 140–150°. Authentic **3b** was found on heating to form similar sublimate crystals (profile angle 58°).

When a crystal of **1b** was aligned along [0 1 0] and heated in the precession camera at 110°, photographs at 1-hr intervals for 8 hr showed general and even fading of all reflections. After 3.5 hr only diffuse powder rings were discernible. At this time the external shape was still the same as it had been initially but the crystal had become opaque. When mounted (without grinding) in a powder camera and aligned along [0 1 0] it gave a photograph identical with that obtained from a powder sample of authentic **3b**. Thin-layer chromatography confirmed the presence of **3b** alone. An ir spectrum of heated crystals of **1b** showed no trace of absorption at 782 cm^{-1} where **3c** absorbs.

Solid-State Rearrangement of 1c. At 90° crystals of **1c** were transformed to an orange glassy material which showed no X-ray diffraction pattern and appeared isotropic when viewed through crossed polarizing filters. The temperature was, therefore, lowered to 60–70° for further studies. At these temperatures the crystals developed the yellow color characteristic of product in times of from 2 days to several weeks; there was great variation in the behavior of individual crystals. Analysis by tlc showed only spots attributable to the rearrangement product **3c** and unreacted starting materials. The ir spectrum of completely rearranged crystals showed no trace of absorption at 747 and 758 cm^{-1} where **3b** absorbs. As with the anilide **3b** the product **3c** was found to undergo appreciable sublimation when heated for several days as low as 70°. The behavior of many crystals of **1c** was similar at 70° to that of **1b** described above. In the case of **1c** there was a more marked development of a solid solution of product in starting material as shown by development of deep yellow regions which nevertheless remained clear and continued to extinguish in the original direction when examined between crossed polarizing filters. Such crystals with regions of solid solution often remained unchanged for some days when cooled to room temperature until at length separation of the product was indicated by development of an opaque region which then spread slowly (1 month) through the yellow part of the crystal. Crystals in which extensive solid solution formation had occurred but which still showed the original direction of extinction in polarized light showed no evidence of polycrystallinity when examined by X-ray methods. Rotation, Weissenberg, and precession photographs showed only intensities due to unreacted **1c**. (Weissenberg photographs of the *h*0*l* net showed a horizontal splitting of reflections with a tailing effect indicative of a slight separation of the lattice in the *a*–*c* plane.) Crystals containing such extensive regions of solid solution of **3c** in crystalline **1c** were shown by uv analysis (UVANL method above) to contain 5–32% of **3c**.

It was of interest that in the case of "hexagonal" crystals of **1c** the development of the yellow regions containing **3c** often occurred in a doughnut-shaped pattern and the center of the crystal remained essentially colorless long after yellowing had begun (Figure 3c,d,e).† This was behavior not observed with **1a** or with **1b**.

Solid-State Rearrangement of Benzophenone Oxime *O*-Picryl Ether 1a. The visual appearance of crystals of **1a** on heating had features described for the bromo derivatives **1b** and **1c**. Thick prismatic crystals often showed cracking after the beginning of development of the yellow color which occurred in a period of a

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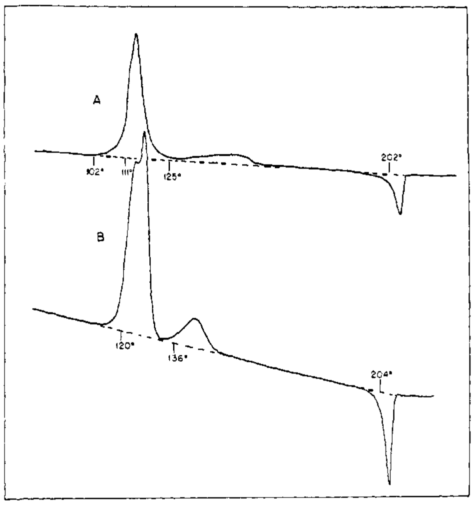

Figure 4. (A) Dta curve of sample of **1c**; heating rate 5°/min. (B) As A but sample of **1c** previously ground in a mortar and pestle.

Table II. Differential Thermal Analyses of Oxime Picrates **1** and Mixtures with Their Rearrangement Products **3**

	Composition, %, and extrapolated onset temperatures, °C						
	Mixtures of **1a** and **3a**						
% **1a**	100	63	24	0			
$T^{40°/\mathrm{min}}$	106[a]	117	104, 113				
$T^{5°/\mathrm{min}}$	101			200[b]			
	Mixtures of **1b** and **3b**						
% **1b**	100	93	73	51	25		0
$T^{40°/\mathrm{min}}$	137[c]	144	145[c]	140[d]	142		
$T^{5/°\mathrm{min}}$	124						240[b]
	Mixtures of **1c** and **3c**						
% **1c**	100	83	45	35	31	29	0
$T^{40°/\mathrm{min}}$	128	126	120	114	111	117[d]	
$T^{5°/\mathrm{min}}$	119						204[b]

[a] Average of four measurements (±1). [b] Melting endotherm. [c] Average of three measurements. [d] Average of two measurements.

number of months at room temperature. After the yellow color deepened, nucleation and separation of a new phase began and opaque areas spread through the crystal (Figure 3f,g,h). The same behavior was observed at 70° (when cracking occurred in 4–6 hr) or at ambient temperature when cracking required a year or longer. A crystal was heated at 70° until it yellowed and cracking had begun; no separation of a second phase could be detected microscopically at this point. The crystal was then allowed to stand at ambient temperature whereupon nucleation of the second phase occurred and opaque regions spread through the crystal over a period of about 40 days. Thin crystals, on the other hand, typically showed no evidence of cracking after standing either at 70° or for a year at room temperature. Careful inspection showed, however, that there had developed small crystallites which gave some light scattering and that the crystal had ceased to show extinction when rotated between crossed polarizing filters. Thin-layer chromatography again showed that as these changes in appearance occurred the rearrangement product **3a** was formed. A crystal heated at 70° in which polycrystalline disorder had spread through about half of the crystal was cut with a razor blade and the two parts of the crystal were analyzed by ir spectroscopy. The clear light-colored part had an ir spectrum (KBr disk) which showed only starting material; the polycrystalline region showed ir absorption (KBr disk) at 1677 cm^{-1} characteristic of the product **3a** in addition to absorption of **1a**.

A crystal of **1a** was aligned along [0 1 0] and heated at 55° in a precession camera. Successive photographs of the 0*kl* net showed a decrease of intensities of the reflections accompanied by the development of diffuse powder rings. When reflections due to **1a** were no longer evident the specimen was mounted in a powder camera. A photograph was identical with a powder photograph of ground purified **3a**. Tlc showed the presence only of **3a**.

As was observed during the rearrangements of **1b,c** microscopic rodlike crystals of sublimate formed after long reaction times or at higher temperatures. Their formation was very much accelerated by suspension of the starting material in mineral oil; under these conditions at 72° extensive rodlike crystals of what was probably the rearrangement product **3a** grew nearly at right angles to the parent crystal after 18 hr.

Differential Thermal Analyses of the Oxime Picryl Ethers 1a–c. Dta studies were carried out with a DuPont Thermograph. Tubes were 5 mm in diameter with ground glass in the reference tube.[17] **1a–c** heated at 5°/min each showed a strong exotherm (with complicated fine structures to be discussed later) followed by an endotherm, the latter at the melting point of the rearrangement product. Even at heating rates of 40°/min there was no sign of an initial endotherm preceding the first exotherm as had been observed in another set of rearrangements.[17] In order to obtain an estimate of the eutectic temperatures of binary mixtures of the oxime picrates with their respective products known mixtures were submitted to dta analysis. The extrapolated onset temperatures are reported in Table II. Although the interpretation of these results has difficulties resulting from uncertainty concerning the degree of mixing and the degree of thermal equilibrium, previous results[17] provide some assurance that conservative lower limits for the eutectic temperatures are for **1a–3a** 95°, **1b–3b** 126°, and for **1c–3c** 100°. Whether or not reaction giving rise to the first exotherm is initiated by microscopic melting there can have been no melting at temperatures below the first onset temperature.

The dta curve of the *anti*-oxime picryl ether (**1c**) measured at a heating rate of 5°/min showed two well-separated exotherms followed by the final endotherm due to melting of **3c** (Figure 4). When the sample was removed just after the first exotherm the material was observed under a microscope to have changed to a clear orange glass (optically isotropic between crossed polarizers). On further heating on the hot stage noticeable flow occurred at 130–145° and rapid crystallization took place at 140–150°. It seems clear that the first exotherm observed corresponded to rearrangement of **1c** to **3c** in a glassy state. The second exotherm resulted from crystallization of glassy **3c**. This view was confirmed by the observation that the area of the second exotherm was equal to the area of the subsequent endotherm. Similar observations were made with crystals of **1c** heated on a hot stage at approximately 5°/min. A spectrum of the final product was identical with that of **3c**. Analogous results were obtained with a ground sample of **1c** (Figure 4).

Thermograms obtained with a heating rate of 10°/min of 5-mg samples of **1c** were calibrated with dta's of 5-mg samples of *p*-toluic and *p*-nitrobenzoic acid.[17] This method gave a value of about 13 kcal/mol for the enthalpy of fusion of **3c** and −80 kcal/mol for the heat of reaction **1c** (solid) → **3c** (solid). These can only be considered rough estimates, however.

Dta's of **1a** and **1b** showed similar features but had partial separation of the first exotherm into two or three peaks. The exact curve shapes in these cases depended on whether or not the sample had been ground.

Kinetics of the Rearrangement of 1b,c in the Solid State. An unground sample of the oxime picryl ether **1b** or **1c** obtained by crystallization was placed in a long-necked round-bottomed flask and rotated mechanically in an oil bath at 60 ± 1°. Samples were periodically withdrawn and stored at −15°. Analyses were performed with uv spectra obtained in methylene chloride by the UVANL method. The reaction of **1c** was followed to 67% completion; the data which gave a respectable first-order plot are shown in Table III. A calculation of k_1 by a method of weighted least squares[18] gave a value of $k_1 = 1.61 \times 10^{-7}$. A similar study of the reaction of **1b** to only 37% completion (47,590 min) gave a $k_1 = (1.1 \pm 0.4) \times 10^{-7}\ \mathrm{sec}^{-1}$ at 60°

Discussion

The rearrangements of oxime picryl ethers **1a–c** when carried out at 70° or less are clearly occurring well below the eutectic temperature for mixtures of picryl ether and the product anilide and may thus be

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(17) For a study employing similar techniques see D. Y. Curtin, S. R. Byrn, and D. B. Pendergrass, Jr., *J. Org. Chem.*, **34**, 3345 (1969).

(18) See D. Y. Curtin and L. L. Miller, *J. Amer. Chem. Soc.*, **89**, 637 (1967).

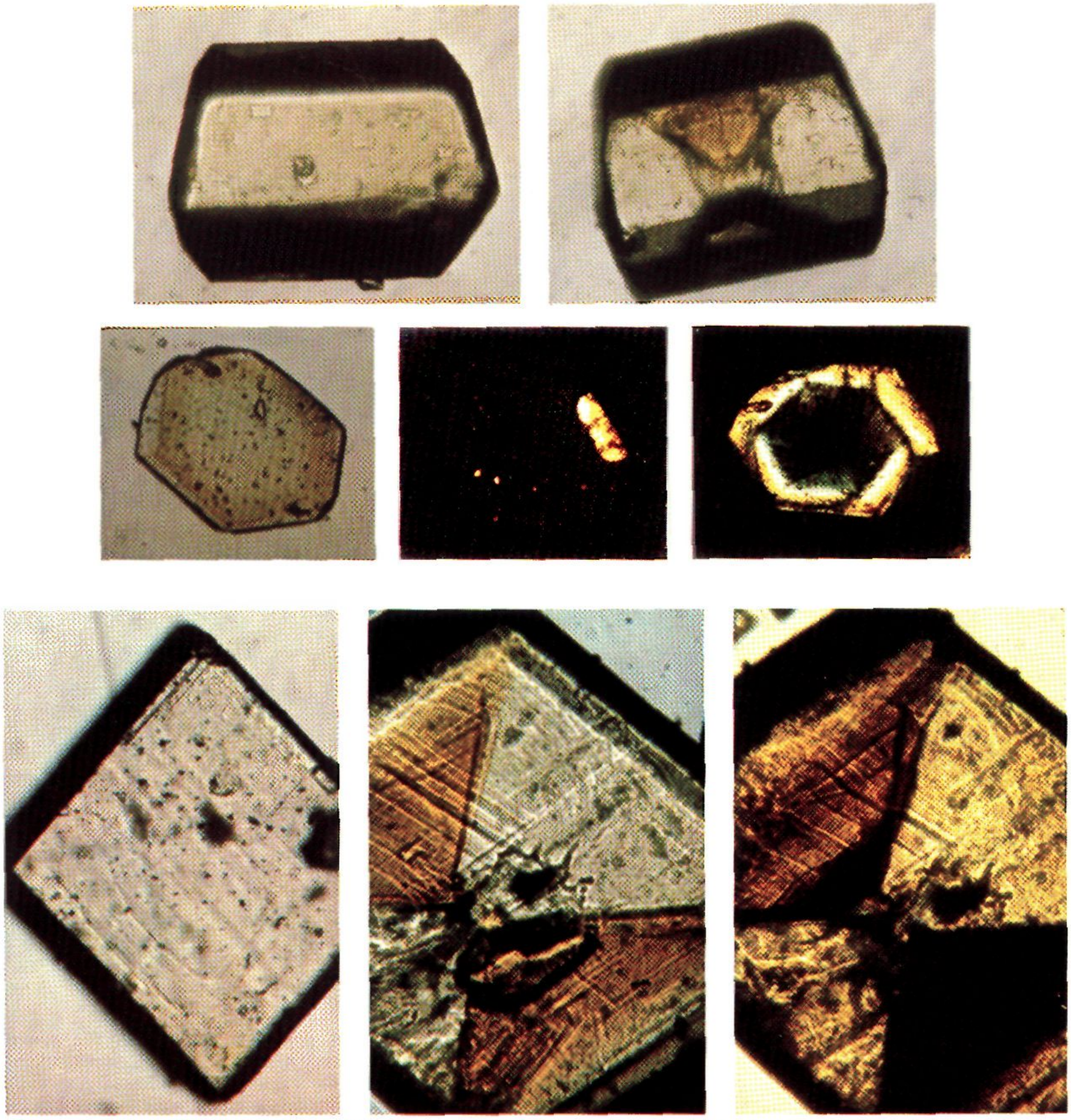

Figure 3 of McCullough, Curtin, and Paul. Crystals of the oxime picryl ethers **1a–c** undergoing thermal rearrangement. (a) A crystal of the syn isomer **1b** sitting on face A (110) of Figure 1. (b) A crystal similar to that in (a) after heating at 90° for 4 hr. (c) A "hexagonal" crystal of **1c** after 7 days at 60° followed by standing for 21 days at 25°. (d) The same crystal aligned in the extinction position of the starting crystal between crossed polaroids. Crystallization from the solid solution of **3c** in **1c** is indicated by the bright area at the upper right edge of the crystal. (e) The crystal shown in (d) after standing an additional 61 days at ambient temperature. (f) A crystal of **1a** seated on (001). (g) A crystal of **1a** after heating for 3 hr at 70°. (h) The crystal of **1a** shown in (g) after 5 hr at 70°.

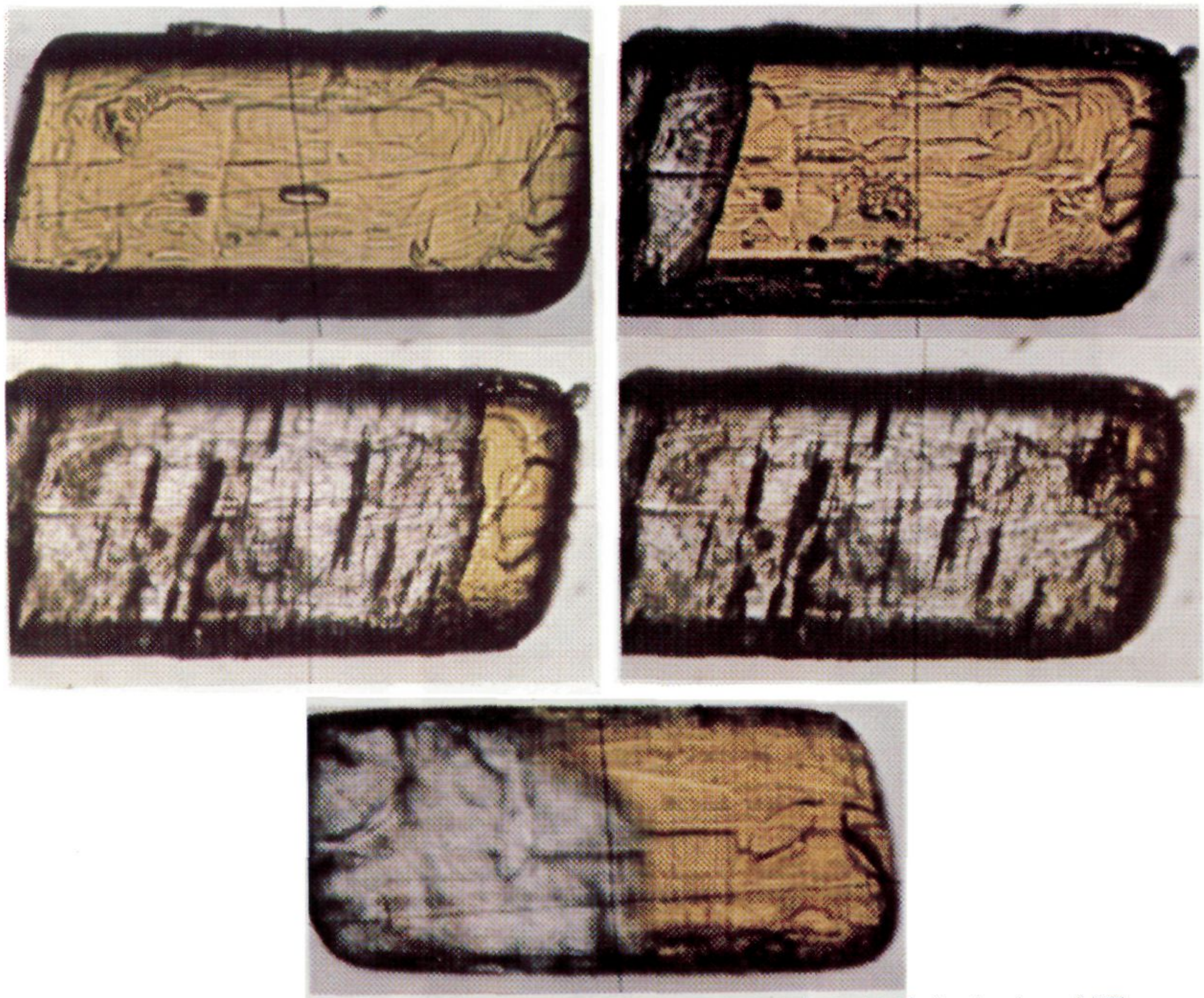

Figure 2 of Byrn, Curtin, and Paul. Rearrangement of a crystal of **Y-1** to **W-1**. (a) Crystal of habit I before heating. (b) The same crystal after 20 min at 115°. (c) The same crystal after 22.5 min at 115°. (d) The same crystal completely rearranged after 25 min at 115°. (e) A crystal of **Y-1** whose rearrangement was initiated at 140°. The blurred front is indicative of the increased rate of frontal movement (the entire rearrangement was complete in about 1 sec).

Table III. Kinetics of the Reaction of **1c** in the Solid State at 60°[a]

Time, min	% reaction	10^7k_1, sec^{-1}
1,450	5.3	6.26
5,770	8.0	2.41
10,110	13.5	2.39
18,722	19.9	1.97
27,397	32.1	2.36
60,480	50.8	1.95
82,070	55.0	1.62
91,095	58.6	1.61
106,285	66.8	1.73

[a] k_1 and standard deviation by method of weighted least squares, 1.61 ± 0.07.

Table IV. Comparison of the Rates of Rearrangement of Oxime Picryl Ethers **1b,c** in the Solid State with Solution Rates of the Chloro Analogs at 60°

Stereo-isomer	Sub-stituent	σ constant	10^7k_1	k(soln)/k(solid)
syn-**1b**	Para Br	+0.232	1.1[a]	14
	Para Cl	+0.227	15[b]	
anti-**1c**	Para Br		1.6[a]	5
	Para Cl		7.9[b]	

[a] Solid state, this paper. [b] Data for CCl_4 solution at infinite dilution (ref 8) extrapolated by the method of least squares to 60°.

classified as solid-state reactions. Although the reaction probably proceeds in two stages no evidence could be found for the accumulation of the presumed intermediate imidate esters **2a–c** in the solid state. The high ΔH of reaction of about −80 kcal/mol for the conversion **1c** → **3c** as determined by dta measurements is in satisfactory agreement with the value of −87 kcal/mol estimated from summing bond dissociation energies[19] of the starting material and product. It will be noted that the same trans stereospecific reactions of the monobromo compounds **1b,c** take place in the solid state as were observed in solution.

The possibility might have been considered that the preference found in solution for the migration of the aromatic ring trans to the leaving picrate group would be altered by the stereochemistry imposed by the crystal structure. The angle between the plane of the migrating trans phenyl ring and the best plane formed by the CC=NO group was 19° for the anti isomer **1c** and 23 and 18° for the two molecular conformations of **1b**.[9] Although in the transition state for the aryl ring migration this angle should ideally be 90° the solid state apparently does not provide sufficient constraint to alter the concerted trans process found in solution. The rates of reaction of the syn and anti picryl ethers are of particular interest. In view of the great spread in behavior of individual large crystals it is surprising to find any simple kinetic equation applicable in the solid state. As was described in the experimental section the rearrangement of **1b,c** followed approximately first-order kinetics; it may be noted that it is usual for a solid-state reaction to have an induction period.[20] There are no rates of rearrangement in the solution of **1b,c** for comparison but reaction rates of the corresponding chloro compounds in carbon tetrachloride solution in the temperature range 85–115° had been reported by Chapman and Fidler.[8] Although good first-order dependence was found during each run the rate depended on the initial concentration. The rate constants were therefore extrapolated to infinite dilution. In view of the very small difference in the Hammett substituent constants of the para chloro and para bromo substituents it is of interest to compare the rates of the bromo compounds **1b,c** in the solid state with the chloro compounds in solution, the latter rates being extrapolated to 60° (Table IV). It is seen that in each case the reaction rate of the syn isomer is slightly faster than that of the anti and that the solution rates are faster than those in the solid state by a factor of only 5–14. It has been observed[4d,21] on the basis of data then available that rates of isomerization reactions are greater in solution than in the solid state by two–four powers of ten. That the present reaction should be exceptional was suggested by the observation of Chapman and Fidler[8] that its rate is highly dependent on the polarity of the medium and in a nonpolar solvent increases markedly as the concentration of starting material is increased from 0.01 to 0.03 M. Since the solids are approximately 3.4 M no meaningful extrapolation of the solution data to permit a closer comparison is possible. One conclusion which can be drawn is that the reaction cannot be occurring by a gas-phase rearrangement of a small amount of vapor in equilibrium with the crystalline solid. Such a process would be much too slow since the rate constant for reaction in the vapor should be comparable to that found in nonpolar solvents at infinite dilution and only a very small fraction of oxime ether could be present as vapor at any time.

Study of the behavior of single crystals combining visual observation with chemical analysis and X-ray examination shows that the initial stage of the reaction of each of the oxime picryl ethers **1a–c** in the solid involves the formation of a solid solution of the product anilide **3a–c** in the parent crystal. At this stage up to 15% of the product may have formed and, in the case of **3c** where solid solution formation is most favored, as much as 30% of the product was present. The formation of further product is accompanied by the separation of the product anilide as microcrystallites randomly oriented and 10^3 Å or more in diameter. In the case of **1c** at higher temperatures, the product **3c** sometimes separated as a hard glass.

The striking formation of cracking patterns and preferred reaction in the cracked region which was observed with large crystals but not with thin ones are of particular interest. It seems likely that reaction occurs at first in a uniform way but that in larger crystals cracking occurs in those regions of the crystal where there develop greater mechanical strains resulting from accumulation of rearrangement product. The relief of strain by cracking appears to provide a catalytic effect on the rearrangement since the cracked center part of the crystal typically becomes quite yellow at a time when the ends have undergone almost no visible change. It is reasonable that in thin crystals where less mechanical strain is produced by a given fraction of reaction the cracking does not develop.

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(19) J. A. Kerr, *Chem. Rev.*, **66** 465 (1966).

(20) See, for example, P. W. M. Jacobs and F. C. Tomkins, "Chemistry of the Solid State," W. E. Garner, Ed., Academic Press, New York, N. Y., 1955, Chapter 7.

(21) R. T. Puckett, C. E. Pfluger, and D. Y. Curtin, *J. Amer. Chem. Soc.*, **88**, 4637 (1966).

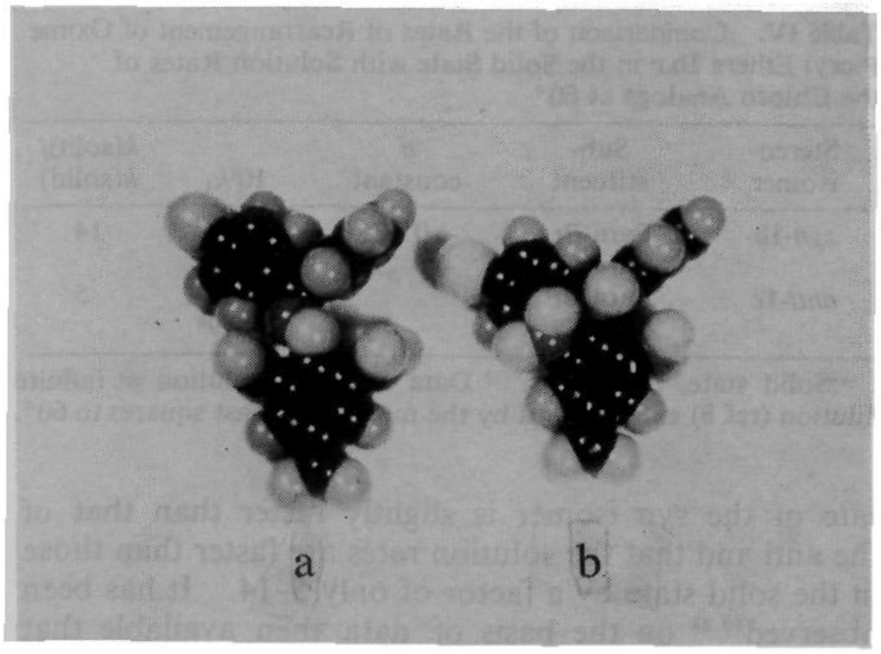

Figure 5. (a) **1c** in approximately the conformation it assumes in its crystalline state;[9] (b) the reaction product **3c** twisted so it assumes as much as possible the shape of the **1c** molecule.

Table V. Comparison of Crystal Data of the Oxime Picryl Ethers with Those of Anilides Produced by Rearrangement[a]

Compd	Space group	V/ molecule, Å^3	Packing fraction[b]
1a	$C2/c$ or Cc	478 ± 4	0.95
3a	$P2_1/c$	455 ± 3	
1b	$P2_1/c$	498 ± 3	0.96
3b	$P2_1/c$	476 ± 3	
1c	$P2_1/c$	492 ± 3	
3c	$Pnma$ or $Pn2_1a$ ($Pna2_1$)	489 ± 4	0.99

[a] Reference 9. [b] Defined[22c] as $1 - \Delta/\tau$ where Δ is the difference in molecular volumes and τ is the volume of the larger molecule.

Studies[22] of solid solution formation by molecular crystals have suggested that if there is to be extensive incorporation of molecules of one substance into a crystal of another there must be similarity in molecular size and shape but no particular relationship of functional groups is required. In Table V are compared molecular volumes of the oxime picryl ethers **1a–c** and their respective rearrangement products, **3a–c**, calculated from the X-ray data presented in the accompanying paper.[9] It is seen that conversion of **1a** to **3a** or **1b** to **3b** gives rise to a contraction of only about 5% and that the change when **1c** goes to **3c** is so small as to be less than the experimental error of the measurements. Although superficial inspection of the structures of oxime picryl ethers **1a–c** and their isomerization products suggests that they must have very different molecular shapes, there is ample freedom of rotation to allow the anilides **3a–c** to assume forms similar to their related oxime picryl ethers. In Figure 5 are shown Fisher–Hirschfelder models of **1c** in approximately the conformation it occupies in the crystalline state as determined by X-ray analysis[9] and the anilide **3c** twisted into a similar shape. This may account for the tendency in these rearrangements of the product to remain in the matrix of starting material. It is of interest that **1c** and **3c**, which show the greatest tendency toward solid solution formation, have the highest packing fraction.[22c] In any case, even in these rearrangements, where molecular shapes and interplanar spacings of starting material and product suggest minimal disruption of the crystal, the products separate as microcrystallites with no net orientation with respect to the parent crystal.

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(22) (a) A. I. Kitaigorodskii, "Organic Chemical Crystallography," English Translation, Consultants Bureau, Inc., New York, N. Y., 1961, p 231 ff; (b) A. I. Kitaigorodskii and R. M. Myasnikova, *Krystallografiya*, **5**, 247 (1960), and references cited therein; (c) P. M. Robinson, H. J. Rossell, H. G. Scott, and C. Legge, *Mol. Cryst. Liquid Cryst.*, **11**, 105 (1970).