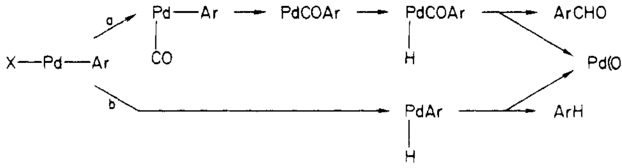
Scheme I



a heterogeneous catalyst is used, nonselective reactions occur, even under low pressures of hydrogen. The adsorption of hydrogen gas into the metal surface and the formation of a reaction zone in which the hydrogen concentration is high enough to compete the aryl halide addition explain the heterogeneous catalyst activity, even under low hydrogen pressure.

In spite of the obvious advantages of the homogeneous catalyzed transfer hydrogenolysis reaction, there are only a few scattered reports of it.[7] A similar reaction applying sodium formate as a hydrogen donor in DMF solution was reported,[8] where debromination of aryl bromides occurred. This reagent was also studied in this work, in MeCN/Me_2SO (1:1) solution and was found to be applicable also to vinyl bromides, α-bromo ketones, and aryl iodides. Results are given in Table II.

Conversion of α-bromostyrene under these conditions was nearly 100%; however, only 35% of styrene was detected (entry 2) by GLC, probably as the result of excessive polymerization of styrene under the experimental conditions. A similar result was observed in the reaction of 4-bromostyrene (entry 3) which gave a quantitative conversion of the starting material but only 40% yield of styrene.

The existence of this homogeneous catalyzed transfer hydrogenolysis of organic halides enables one to gain additional information on the mechanism of the H-transfer formylation of aryl halides performed under similar conditions.[4] While in the formylation reaction a fast carbonyl insertion is followed by a slow H-transfer and reductive elimination (Scheme I, path a), in the transfer hydrogenolysis reaction a direct reductive elimination of the hydrido Pd (II) arene seems to be the final step in the catalytic cycle (Scheme I, path b). The close relation between these two reactions can also be observed when the reaction is carried out under low carbon monoxide pressures. Under such conditions, the product of transfer hydrogenolysis is accompanied by the product of H-transfer formylation, as a result of the competition between the pathways.

Experimental Section

General Procedure of Transfer Hydrogenolysis of Organohalides. In a typical example, a mixture of 8 mL of CH_3CN/Me_2SO (1:1), 50 mg (0.03 mmol) of $Pd(PPh_3)_4$, 400 mg (1.4 mmol) of tribenzylamine, 157 mg (1.0 mmol) of bromobenzene, and 0.4 mL of PMHS were placed under nitrogen atmosphere in a sealed reaction vessel, stirred magnetically, and heated on an oil bath at 110 ± 1 °C. After 18 h the reaction mixture was cooled to room temperature and diluted with acetonitrile to 10 mL, and benzene (59 mg, 0.75 mmol; 75% yield) was determined by GLC in the crude filtered solution.

Isolation of nonvolatile products was achieved by the addition of 1:1 mixture of 1 N HCl and ether, followed by filtration of the precipitated catalyst, tribenzylamine salt, and polymer. The aqueous layer was then extracted with ether. After removal of the ether, the residue contained mostly the desired product, which was finally purified by distillation or chromatography.

Acknowledgment. We are grateful to Prof. J. Blum for his advise and helpful discussions.

Registry No. PMHS, 9004-73-3; PhI, 591-50-4; PhBr, 108-86-1; 4-BrC_6H_4Cl, 106-39-8; PhCH=CHBr, 103-64-0; $H_3CCH(Br)CO_2H$, 598-72-1; $PhCOCH_2Br$, 70-11-1; 4-BrC_6H_4Ac, 99-90-1; 4-$NO_2C_6H_4Br$, 586-78-7; 4-$BrC_6H_4C_6H_4Br$-4′, 92-86-4; 4-BrC_6H_4CHO, 1122-91-4; 4-$BrC_6H_4CO_2H$, 586-76-5; $PhCH(Br)CO_2H$, 4870-65-9; PhH, 71-43-2; PhCl, 108-90-7; $PhCH{=}CH_2$, 100-42-5; $CH_3CH_2CO_2H$, 79-09-4; PhAc, 98-86-2; $PhNO_2$, 98-95-3; PhPh, 92-52-4; PhCHO, 100-52-7; $PhCO_2H$, 65-85-0; $PhCH_2CO_2H$, 103-82-2; 4-$BrC_6H_4CH{=}CH_2$, 2039-82-9; 4-$IC_6H_4NO_2$, 636-98-6; sodium formate, 141-53-7.

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[7] (a) Yasui, S.; Nakamura, K.; Ohno, A. *Chem. Lett.* **1984**, 377. (b) Bar, R.; Sasson, Y.; Blum, J. *J. Mol. Catal.* **1982**, *16*, 175. (c) Four, P.; Guibe, F. *J. Org. Chem.* **1981**, *46*, 4439.

[8] Helquist, P. *Tetrahedron Lett.* **1978**, 1913.

Some Observations on *N*-Chlorosuccinimide Halogenations. A New Bromination Technique

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Although there has been recent controversy concerning the nature of the chain-carrying radicals in *N*-bromosuccinimide (NBS) brominations,[1-3] it now seems clear that most of the data are consistent with competing succinimidyl radical (S·) and Br· chains, with no conclusive evidence for participation of two electronic states of S·.[1h,2c-e]

In unreactive media, CH_2Cl_2, $CHCl_3$, and hydrocarbons containing only primary and secondary C–H bonds, quite clean S· chains can be observed in the presence of olefins which lack allylic C–H bonds and act as halogen atom traps, but in more reactive media Br· chains become increasingly difficult to suppress.[4]

Much less information is available on the chain carriers in *N*-chlorosuccinimide reactions, although, a priori the high rate of Cl· reactions compared to Br· might lead one to expect that they would be much more difficult to suppress.[5] We here report some of our observations on this reagent.

Reaction Rates. Some comparisons of rates of photoinduced decompositon of NCS in methylene chloride and chloroform under varying conditions are listed in Table I. Although they represent single points, they are representative of a larger number of runs, and the differences

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[1] (a) Day, J. C.; Kasaros, M. G.; Kocher, W. D.; Scott, G. E.; Skell, P. S. *J. Am. Chem. Soc.* **1978**, *100*, 1950. (b) Skell, P. S.; Day, J. C. *Acc. Chem. Res.* **1978**, *11*, 381. (c) Tlumak, R. L.; Day, J. C.; Slanga, J. P.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7257. (d) Tlumak, R. L.; Skell, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 7267. (e) Skell, P. S.; Tlumak, R. L.; Seshadri, S. *J. Am. Chem. Soc.* **1983**, *105*, 5125. (f) Skell, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 1838. (g) Skell, P. S.; Seshadri, S. *J. Org. Chem.* **1984**, *49*, 1650. (h) Skell, P. S.; Lüning, U.; McBain, D. S.; Tanko, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 121.

[2] (a) Walling, C.; El Taliawi, G. M.; Zhao, C. *J. Am. Chem. Soc.* **1983**, *105*, 5119. (b) Tanner, D. D.; Tomoki, C.-S. R.; Takiguchi, H.; Guillaume, A.; Reed, D. W.; Setiloane, B. P.; Tan, S. L.; Meintzer, C. P. *J. Org. Chem.* **1983**, *18*, 2743. (c) Tanner, D. D.; Meintzer, C. P.; Tan, S. L. *J. Org. Chem.* **1985**, *50*, 1534. (d) Tanner, D. D.; Reed, D. W.; Tan, S. L.; Meintzer, C. P.; Walling, C.; Sopchik, A. *J. Am. Chem. Soc.* **1985**, *107*, 6576. (e) Tanner, D. D.; Meintzer, C. P. *J. Am. Chem. Soc.* **1985**, *107*, 6584.

[3] Chow, Y. L.; Naguib, Y. M. A. *J. Am. Chem. Soc.* **1984**, *106*, 7557.

[4] In addition, some reactions of the NBS–Br_2–CH_2Cl_2–neopentane system suggest the presence of a third chain-carrying radical of intermediate selectivity.[1h,2d]

[5] It is of interest that the initial suggestion of a halogen atom chain in these systems was made for the NCS–toluene reaction, in part because of its acceleration traces of HCl: Goldfinger, P.; Gosselain, P. A.; Martin, R. H. *Nature* (*London*) **1951**, *158*, 30.

0022-3263/86/1951-0736$01.50/0

Table I. Rates of NCS Photohalogenations of CH_2Cl_2 and $CHCl_3$[a]

substrate	light	[NCS]	additive [M]	time, h	% react
CH_2Cl_2	UV	0.44		1.0	60
CH_2Cl_2	UV	0.46	DCE [0.18]	17	18
CH_2Cl_2	vis	0.48		22	9
CH_2Cl_2	vis	0.36	HCl [0.071	0.2	68
CH_2Cl_2	vis	0.47	Br_2 [0.09]	0.25	19
$CHCl_3$	UV	0.30		1.0	55
$CHCl_3$	UV	0.27	DCE [0.12]	14	24
CH_2Cl_2	UV	0.22[b]		0.5	43
CH_2Cl_2	UV	0.24[b]	DCE [0.34]	1.5	50
CH_2Cl_2	UV	0.22[b]	Br_2 [0.37]	0.5	60

[a] At 15 °C under standard light intensities, see Experimental Section. [b] NBS experiments.

are so large as to clearly significant. Addition of 1,1-dichloroethylene (DCE) as a Cl· trap strongly retards reaction, while addition of HCl, which generates Cl_2 by the fast reaction accelerates it. The data are certainly consistent

$$HCl + NCS \rightarrow Cl_2 + \text{succinimide (SH)} \tag{1}$$

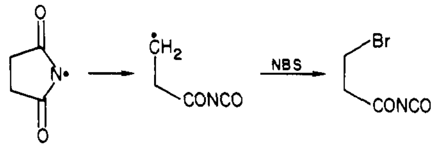
with a fast Cl· chain taking over in the absence of DCE, and reactions with no additive are, in fact, somewhat autocatalytic, as might be expected since here additional Cl· (and consequently HCl and Cl_2) is continually being generated by NCS photolysis. Addition of Br_2 also leads to fast reaction and is discussed further below.

For comparison, some NBS data are also included, and as noted previously,[2a] effects here are much smaller, implying similar propagation rates for S· and the chain carrier in the presence of Br_2.

The only surprising result is that NCS–DCE systems react much more slowly than NBS–DCE systems. This may be due to a smaller photolysis rate for NCS or the slowness of radical attack on NCS, making (2) a rate controlling step.[6]

$$R\cdot + NCS \rightarrow RCl + S\cdot \tag{2}$$

β-Chloropropionyl Isocyanate. The major product (>90%) of NBS photolysis in CH_2Cl_2 in the presence of Br· traps is β-bromopropionyl isocyanate (BPI) formed via the ring-opening reaction, but Skell has reported that no β-chloropropionyl isocyanate is formed from NCS under comparable conditions.[1c] Although initial runs in our laboratory also failed to detect isocyanate, we have repeated some of these experiments, using the more sensitive analytical technique (high-field NMR analysis after hydrolysis of isocyanate to amide) developed by Tanner.[2c,d] We find that photolysis of NCS in either CH_2Cl_2 or CD_2Cl_2 gives reaction mixtures with 400-MHz NMR spectra (after hydrolysis) showing clearly resolved triplets at δ 2.67 and 3.80, identical with those of authentic β-chloropropionamide. However yields are much lower than with NBS, 7% and 9% in CH_2Cl_2 and CD_2Cl_2, respectively, and could well have escaped previous analyses.



(3)

Skell[1c] has proposed that isocyanate formation from NCS is suppressed by the reversibility of ring opening, reaction 3 coupled with the slowness of reaction 2. The reduced yields we see are also consistent with either this explanation or the failure to completely eliminate fast Cl· chains, even in the presence of DCE.

The NCS–Br_2 System. As shown in Table I, addition of Br_2 to NCS in CH_2Cl_2 leads to very rapid photolysis. Further examination of such reactions shows that Br_2 is consumed, and, as long as any is present, the product is almost entirely $CHCl_2Br$. Most interesting is the selectivity of the NCS–Br_2 mixture. Halogenation of a mixture of CH_2Cl_2 and neopentane gives a virtually quantitative yield of neopentyl bromide, while *n*-butane give *n*-butyl and *sec*-butyl bromides in a ratio of 1:1.89. These selectivities are typical of Cl· (or S·) radicals, and the situation is reminiscent of halogenations using mixtures of Cl_2 and Br_2, which yield alkyl bromides but with a Cl· selectivity.[7] A chain involving ClBr has been proposed, and it is possible that ClBr is present in the NCS–Br_2 system via the overall process.

$$Cl\cdot + RH \rightarrow R\cdot + HCl \tag{4}$$

$$R\cdot + ClBr \rightarrow RBr + Cl\cdot \tag{5}$$

$$NCS + Br_2 \rightleftarrows NBS + ClBr \tag{6}$$

Regardless of mechanism, the reaction should provide a convenient, low-temperature technique for bromination of hydrocarbons containing only primary C–H bonds. However, extension to cyclopropane bromination was unsuccessful, giving chiefly 1,3-dibromopropane, the usual product of reaction of cyclopropane with Br_2.

Experimental Section

Materials and techniques were essentially those described previously.[2a] NCS was recrystallized commercial material.

Rate experiments were carried out in NMR tubes after flushing with N_2 or argon. The tubes were placed in a thermostated bath and irradiated by a 450-W Hanovia immersion lamp at a distance of 10 cm (UV) or a 660-W incandescent lamp at a distance of 20 cm (visible light). Samples were analyzed for succinimide and unreacted NCS by 60-MHz NMR. In the experiment in which HCl was added, the yield was based on the NCS not consumed in the original NCS–HCl reaction.

Detection of β-Chloropropionyl Isocyanate. A reaction mixture consisting of NCS (0.17 mmol), DCE (0.12 mmol), and CH_2Cl_2 (32.5 mmol) in a NMR tube was flushed with N_2 and irradiated for 4 h by a medium-pressure mercury arc in a bath at room temperature. Water (3 μL) and 0.15 mL of CD_2Cl_2 (as an NMR lock) were added and the 400-MHz NMR spectra taken on with a Varian LX-400 instrument. Reaction was almost complete and two triplets at δ 2.67 and 3.80 (identical with those of authentic β-chloropropionamide) were clearly identifiable and well resolved. Based on comparison with the succinimide peak at δ 2.72, the yield was 7% of the NCS reacted. A similar experiment in CD_2Cl_2 indicated a 9% yield, with an experimental uncertainty in each of about 1%.

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(6) Kinetics of NBS reactions are often zero order in NBS, indicating termination via two S· radicals, so that (2) does not appear in the overall rate equation.[2a] However, Davies et al. (Davies, A. G.; Roberts, B. P.; Smith, N. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2221) have reported that NBS reacts with *n*-propyl radicals 7.3 times as rapidly as NCS, which could change the rate-determining step.

(7) Speier, J. L. *J. Am. Chem. Soc.* **1951**, *75*, 826. For discussion, see: Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; p 379.

NCS–Br_2 Reaction. CH_2Cl_2. In a typical experiment a mixture of 0.24 mmol of NCS, 0.045 mmol of Br_2, and 7.78 mmol of CH_2Cl_2 was irradiated with visible light at 15 °C. After 15 min the solution was still colored. By NMR analysis 19% of the NCS had reacted and $CHCl_2Br$ could be detected. On further irradiation the solution became colorless, and when all the NCS was consumed, analysis indicated 0.16 mmol of $CHCl_3$ and 0.081 mmol of $CHCl_2Br$ (90% based on Br_2). In a similar experiment with equal quantities of Br_2 and NCS, $CHCl_2Br$ was the sole halogenated product detected.

Neopentane. Similar photolysis of 0.30 mmol of NCS, 0.49 mmoles of Br_2, 1.88 mmol of neopentane, and 12.3 mmol of CH_2Cl_2 showed complete consumption of NCS in 10 min, with neopentyl bromide the only product detected by NMR (essentially quantitive based on NCS). Several other experiments, using up to 10 mmol of NCS and equivalent amounts of Br_2 gave similar results.

***n*-Butane.** Similar photolysis of 0.32 mmol of NCS, 0.27 mmol of Br_2, and 1.47 mmol of *n*-butane in 7.59 mmol of CH_2Cl_2 was complete in 15 min. NMR analysis showed both *sec*- and *n*-butyl bromides, and GLC analysis showed peaks agreeing with authentic samples: areas (*sec*-butyl:*n*-butyl) 1.89:1.

Cyclopropane. A similar reaction with cyclopropane gave a very rapid reaction. GC analysis showed chiefly 1,3-dibromopropane with no evidence of cyclopropyl bromide.

Acknowledgment. Partial support of this work by a grant from the National Science Foundation is gratefully acknowledged.

Registry No. NCS, 128-09-6; DCE, 75-35-4; Br_2, 7726-95-6; CH_2Cl_2, 75-09-2; $CHCl_2Br$, 75-27-4; $CHCl_3$, 67-66-3; HCl, 7647-01-0; β-chloropropionyl isocyanate, 54898-89-4; β-chloropropionamide, 5875-24-1; neopentane, 463-82-1; neopentylbromide, 630-17-1; *n*-butane, 106-97-8; *sec*-butyl bromide, 78-76-2; *n*-butyl bromide, 109-65-9; 1,3-dibromopropane, 109-64-8; cyclopropane, 75-19-4.

A Strained Cyclopropanobicyclo[3.2.1]octanone

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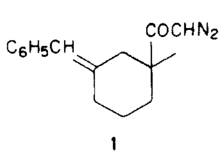
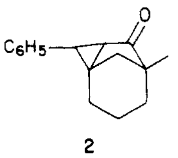
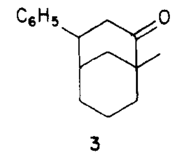
A short 1976 communication[1] described the preparation of tricyclic ketone **2** via the decomposition of diazo ketone **1** under the influence of light, heat, and cupric oxide and the conversion of the product into bicyclic ketone **3** on reduction with lithium in ammonia. These observations are so unexpected, bordering on disbelief,[2] as to invite repetition of the experiments. The first reaction involved the formation of an extraordinarily strained ring system in a diazo ketone decomposition in the face of alternate, low-energy decomposition routes.[3] The second reaction, considered unusual even by the authors (as illustrated by the communication's title, "Unusual Ring Opening of Conjugated Phenylcyclopropyl Ketone; A New Route to Bicyclo[3:3:1]nonane Intermediate", and by their early comments[1]), constituted a violation of the well-known lithium–ammonia reduction mode of cyclopropyl ketones, i.e., cleavage of the cyclopropane bond most closely paralleling the neighboring keto π orbital.[4] The present paper represents an experimental reevaluation of the earlier work.



1

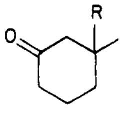


2

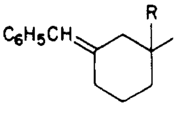


3

The preparation of the diazoketone had been initiated by a Wittig reaction with benzyltriphenylphosphorane on a keto acid (**4b**)[5] of unspecified origin.[1] To facilitate the reaction scheme, the Wittig reaction now was carried out on keto nitrile **4a**,[5] prepared by the hydrocyanation of 3-methyl-2-cyclohexenone.[6] Alkaline hydrolysis of the resultant olefinic cyanide isomers (**5a**) led to a difficultly separable, ca. 1:1 stereoisomer mixture of acids **5b**. In order to make the first comparison with the literature data, the acids were transformed into the esters **5c** with diazomethane. The olefinic ester mixture had been reported to exhibit the following spectral data:[1] UV (EtOH) λ_{max} 250 nm (ϵ 20 040);[7] IR ($CHCl_3$) 1725, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 1.1, 1.2 (3 H, 2 s from C-3 methyl protons), 3.42, 3.62 (3 H, 2 s from CO_2Me protons), 6.2 (1 H, s) 7.13 (5 H, s). It now revealed the ensuing data: UV (EtOH) $\lambda_{shoulder}$ 227–250 nm; IR ($CHCl_3$) 1711 (s, C=O), 1590 (w, C=C) cm^{-1}; ^1H NMR δ (CCl_4) 1.03, 1.18 (s, 3 total, Me of each isomer), 3.44, 3.53 (s, 3 total, OMe of each isomer), 5.29, 5.38 (s, 1 total, olefinic H of each isomer), 7.00 (br.s, 5, Ar H). The two sets of data were divergent, albeit not dramatically.



4a, R = CN
b, R = CO_2H



5a, R = CN
b, R = CO_2H
c, R = CO_2Me

Treatment of the acids **5b** with oxalyl chloride and the resultant acid chlorides with diazomethane yielded diazo ketones **1** [IR ($CHCl_3$) 2113 (s, CHN_2), 1622 (s, C=O), 1600 (w, C=C) cm^{-1} (lit.[1] IR ($CHCl_3$) 2110, 1600 cm^{-1})]. Decomposition of the latter under the literature conditions led in 41% yield to a five-membered-ring $C_{16}H_{18}O$ ketone [IR ($CHCl_3$) 1700 (s, C=O), 1610 (w, C=C) cm^{-1} (lit.[1] IR ($CHCl_3$) 1705, 1600 cm^{-1}); MS, *m/e* (relative intensity) 226 (M^+, 9), 225 (41), 135 (34), 107 (53), 91 (73), 43 (base) (lit.[1] MS, *m/e* 226], whose ^1H NMR spectrum [δ (CCl_4) 0.90 (s, 3, Me), 2.69, 2.84, 2.92, 3.07 (four-line AB, 2, *J* = 14 Hz, *c*-Pr H), 6.9–7.2 (m, 5, Ar H)] was compatible with structure **2** but in disagreement with the published ^1H NMR spectral results [δ (CCl_4) 0.78 (1 H, s, cyclopropane H), 0.93 (3 H, s), 3.33 (1 H, m, benzyl H), 7.16 (5 H, s)][1]. The ^{13}C NMR spectrum (carbon shifts being listed on

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[1] Sarkar, A.; Chatterjee, S.; Dutta, P. C. *Tetrahedron Lett.* **1976**, 4633.

[2] The credibility of the work was lowered on discovery of the untrustworthiness of a later publication (Chatterjee, S. *Tetrahedron Lett.* **1979**, 3249) of one of the coauthors as an independent investigator (see: Cornforth, Sir John *Ibid.* **1980**, 709. Cornforth, Sir John; Pengelly, T. *Ibid.* **1982**, 2213) and the dubiety of some of the results of another paper (Chatterjee, S. *J. Chem. Soc., Chem. Commun.* **1979**, 620) by the same contributor (see: Paquette, L. A.; Han, Y.-K. *J. Org. Chem.* **1979**, *44*, 4014; *J. Am. Chem. Soc.* **1981**, *103*, 1835).

[3] Wenkert, E.; Davis, L. L.; Mylari, B. L.; Solomon, M. F.; da Silva, R. R.; Shulman, S.; Warnet, R. J.; Ceccherelli, P.; Curini, M.; Pellicciari, R. *J. Org. Chem.* **1982**, *47*, 3242.

[4] Dauben, W. G.; Deviny, E. J. *J. Org. Chem.* **1966**, *31*, 3794.

[5] Whitmore, W. F.; Roberts, C. W. *J. Org. Chem.* **1948**, *13*, 31.

[6] Cf.: Wenkert, E.; Strike, D. P. *J. Am. Chem. Soc.* **1964**, *86*, 2044.

[7] Benzylidenecyclohexane has been reported to exhibit a UV absorption maximum in ethanol solution at 247 nm (log ϵ 4.04) (Christol, H.; Laurent, A.; Mousseron, M. *Bull. Soc. Chim. Fr.* **1961**, 2313).

0022-3263/86/1951-0738$01.50/0