TABLE II
MELTING RANGES OF IMIDOYL CHLORIDES AND IMIDES

	1		3	
Comp	Mp, °C found	Mp, °C reported	Mp, °C found	Mp, °C reported
a	54–57	52[a]	146–146.5	142–144[e]
b	42–45	39–41[b]	162.5–164.5	163–164[f]
c	62.5–64.5	68[c]	158–159	159–160[g]
d	52–54.5		162–163.5	159[f]
e	69.5–71.5	66–67[d]	130–132	
f	114.5–117	118–120[b]	209–210.5	203[h]

[a] F. Just, *Ber.*, **19**, 980 (1886). [b] Reference 11. [c] H. Ley, *Ber.*, **31**, 241 (1898). [d] G. H. Coleman and R. E. Ryle, *J. Amer. Chem. Soc.*, **68**, 2007 (1946). [e] Reference 1. [f] M. P. Freunler, *Bull. Soc. Chim. Fr.*, **31**, 623 (1904). [g] S. Birtwell, *J. Chem. Soc.*, 2561 (1949). [h] O. Mumm, *Ber.*, **43**, 890 (1910).

Preparation and Determination of Half-Lives of the Substituted Benzoyl *N*-Phenylbenzimidates (Isoimides).—The isoimides were prepared in the following way. A chloroform solution of triethylammonium benzoate (10 ml, 1 *M*, 0°) was rapidly pipetted into a chloroform solution of the appropriate imidoyl chloride (5 ml, 2 *M*, 0°). The resulting solution was well mixed and kept in an ice bath while the reaction to form isoimide proceeded. With the faster reacting imidoyl chlorides, temperature rises of up to 8° were noted within a minute or two. The developing band in the infrared spectrum (*ca.* 1737 cm^{-1} in $CHCl_3$) was observed during this period to ascertain when the isoimide had completely formed [maximum attainment of this band relative to the adjacent band (*ca.* 1680 cm^{-1}) of the C=N]. In all cases except that with *N*-*p*-nitrophenylbenzimidoyl chloride, the isoimide **2** formed completely before any rearrangement could be detected.

The half-lives of the isoimides were determined as follows. The isoimide solution as prepared above was allowed to stand at room temperature for several hours until rearrangement to imide was complete. A 5-ml aliquot was then accurately diluted to 25 ml with chloroform (solution 0.133 *M* in imide).

Now a fresh solution of isoimide was prepared as described above. A 5-ml aliquot of this isoimide solution was diluted accurately to 25 ml with chloroform thermostated at 19.6° (solution about 0.133 *M* in isoimide), and the diluted mixture was thermostated at 19.6° (solution A).

A 10-ml aliquot of the imide solution (thermostated at 19.6°) was mixed ($t = t_0$) with a 10-ml aliquot of the isoimide (solution A), and this mixture was thermostated at 19.6° (solution B). This solution then simulated solution A after rearrangement of half of the isoimide.

The infrared spectrum between 1800 and 1650 cm^{-1} was determined for these two mixtures (A and B) every 1 to 3 min (depending on length of half-life) until the isoimide (*O*-acyl carbonyl) band became only a shoulder on the imide carbonyl band. In practice, the spectra were taken only with solution B at first until the isoimide band became a shoulder; then only solution A spectra were taken for the balance of the run.

The values for the half-lives were determined by measuring the time difference between identical solution A and solution B spectra using as a basis of comparison the distance between the isoimide maximum and the minimum between it and the adjoining carbonyl peak (*ca.* 1680 cm^{-1}), linearly interpolating as required. The results are tabulated in Table I.

Preparation and Rearrangement of Benzoyl *N*-(*p*-Chlorophenyl)benzimidate (2c) in the Presence of Excess Benzoate.—The general procedure described above was followed except that solution A was prepared in such a way that it was 0.1 *M* in isoimide and 0.314 *M* in triethylammonium benzoate. The results are tabulated in Table I.

Dibenzoylaniline.—The chloroform solutions remaining from the experimental measurement of the rate of rearrangement of benzoyl *N*-phenylbenzimidate were combined and evaporated. The residue was extracted with benzene (125 ml). After filtration, the benzene solution was concentrated to about 40 ml. After being cooled to room temperature, the product was isolated by filtration, yield 6.8 g (45%), mp 162.5–164.5° (lit.[14] mp 163–164°).

(14) M. P. Freundler, *Bull. Soc. Chim. Fr.*, **31**, 630 (1904).

Acylation Tests Using Benzoyl *N*-Phenylbenzimidate.—Two acylation experiments were run with varying amounts of aniline. The solution of the acylating agent was prepared in each case as follows. A solution of *N*-phenylbenzimidoyl chloride (5 ml of 2 *M* chloroform solution) at 0° was mixed with a solution of triethylammonium benzoate (10 ml of 1 *M* chloroform solution) at 0°. Within a few minutes the reaction to form isoimide was complete (ir) after a temperature rise of 8°. The mixture was cooled to 0° before adding to the aniline.

Run 1.—A 10-ml aliquot of the isoimide (*ca.* 6.67 mmol) was pipetted as soon as it had been formed into a tube containing aniline (0.621 g, 6.67 mmol) at 0°. This mixture, together with the remaining 5-ml solution of isoimide, was kept at 0° for the balance of the experiment. After 4 hr, the ir enol ester band was still the same intensity in each sample although a major portion of the isoimide had rearranged. After a total of 17 hr at 0°, the ir enol ester band had disappeared from each sample. The reaction mixture (isoimide–aniline) was treated with enough chloroform to dissolve the product which had precipitated during the last hours of standing. The resulting solution was extracted with water, 6 *N* HCl, water, saturated aqueous $NaHCO_3$, and finally water. The chloroform layer was dried (Na_2SO_4). The solution ir was identical with that of dibenzoylaniline. The chloroform was evaporated, and the residue was crystallized from benzene to yield pure dibenzoylaniline, yield 1.24 g (62%), mp 159–161.5°, ir ($CHCl_3$) identical with that of authentic dibenzoylaniline.

Run 2.—The procedure was the same as that of run 1 except as noted below. The aniline used was ten times that of run 1. Examination of the ir spectra of the two solutions periodically disclosed that the ir enol ester carbonyl band diminished at about the same rate in each solution and had completely disappeared after 8.5 hr at 0°. At this point the reaction containing aniline was removed from the ice bath and stored at room temperature overnight. Work-up was as in run 1. The chloroform solution was evaporated to dryness to yield benzanilide, yield 2.22 g (85%), mp 162–163.5°, ir ($CHCl_3$) identical with that of authentic benzanilide.

Preparation of Imides.—The chloroform solutions from the rate runs for each isoimide were combined after rearrangements were complete. The resulting solution was extracted with water twice, dried with anhydrous sodium sulfate, and taken to dryness. The resulting residue was crystallized from benzene. The melting ranges of the various imides are given in Table II.

Registry No.—**1d**, 34916-13-7; **2a**, 34916-14-8; **2b**, 34916-15-9; **2c**, 34934-83-3; **2d**, 34916-16-0; **2e**, 34916-17-1; **2f**, 34916-18-2; **3e**, 34916-19-3; **7**, 93-98-1.

Orbital Symmetry Control in the Cycloadditions of Ketenes to Norbornadiene

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Recent reports of orbital symmetry control in the cycloadditions of ketenes to cyclopentadiene[2] prompt us to communicate our results with cycloadditions of ketenes to norbornadiene. The cycloadducts of dichloroketene with norbornene and norbornadiene have

(1) IAESTE Student, Summer, 1971.

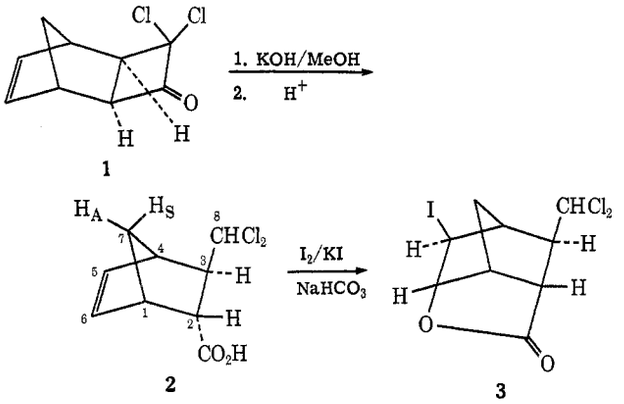
(2) (a) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, **92**, 4618 (1970); W. T. Brady and E. F. Hoff, Jr., *J. Org. Chem.*, **35**, 3733 (1970); (b) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970); (c) P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970).

TABLE I
ADDITION OF RXC=C=O TO NORBORNADIENE (A) AND NORBORNENE (B)

Compd	R	X	Yield in cyclohexane, %	*syn*-Halo epimer, %[a]	Yield in MeCN, %	*syn*-Halo epimer, %[a]
6[b,c]	A Me	Cl	16.2	0	7.5	60
7[b,d]	A Et	Cl	14.3	0	7.8	56
8[b,e]	A *i*-Pr	Cl	5.7	0	1.0	0
9[b,f]	A Me	Br	16.7	0	5.2	100
10	A *t*-Bu	Br	0		0	
11[b,g]	B Me	Cl	12.4	0	5.4	50

[a] Analyzed by nmr spectroscopy; see text. [b] Satisfactory combustion analytical data (±0.35%) were provided for these compounds. Ed. [c] Bp 53–59° (0.06 mm). [d] Bp 63–64° (0.1 mm). [e] Bp 80–87° (0.3 mm). [f] Bp 88–90° (0.5 mm). [g] Bp 72–74° (0.1 mm).

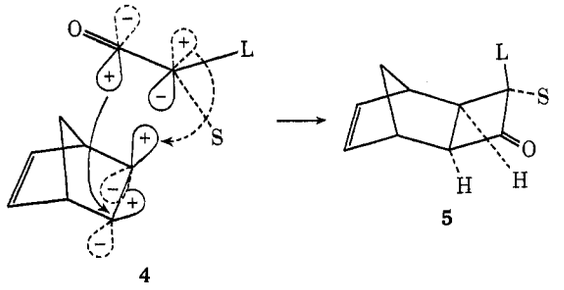
the exo configuration by nmr inference,[3] which is confirmed by the following degradative scheme.



Thus, treatment of **1** with methanolic KOH yields the product of Conia-type opening,[4] *endo*-2-carboxy-*exo*-3-dichloromethylbicyclo[2.2.1]hept-5-ene,[2] which has epimerized at C-2, apparently owing to the unfavorable steric interaction of two bulky cis substituents. Conversion of **2** to the iodolactone **3** fixes the endo configuration of the carboxy group and consequently the exo configuration of the dichloromethyl. The nmr spectra of **2** and **3** correlate unambiguously with those of the corresponding monochloro analogs.[5]

That this is a stereospecific exo cycloaddition not involving endo cycloaddition and isomerization[6] is concluded from the observation[7] that the retro Diels–Alder reactions in these norbornadiene cycloadducts do not occur below 450°. Furthermore, the dichloroketene cycloadduct with norbornene (also exo) is not capable of this type of retro Diels–Alder isomerization.

Hence, it is reasonable to consider that the reacting ketene approaches norbornadiene from the exo side. If one assumes an orthogonal approach for a concerted $_{\pi}2_{s} + {}_{\pi}2_{a}$ cycloaddition[8] taking into account the steric requirements, it is most probable that the oxo moiety of the ketene should approach first as pictured in **4**. This would lead on closing to the least expected isomer, **5**, with the largest group, L, in the syn configuration.[9]



The experimental results (Table I) are consistent with this interpretation. Based on the downfield shift of the O-bridge protons with halogen anti, the alkyl substituent is exclusively syn in this series (Me to *i*-Pr) with cyclohexane as solvent. However, using acetonitrile as solvent increases the effective size of the halogen and of the whole ketene by greater solvation, resulting in the appearance of syn halo cycloadduct and diminished yields. In comparison to the results of cycloadditions of haloketenes to cyclopentadiene, norbornadiene has a considerably higher steric requirement, which is reflected in the greater stereoselectivity and much reduced yields. Examination of Dreiding models of **4** indicates that this system approaches the limit of steric interaction that will allow the reaction to proceed. Approach and cycloaddition of ketenes from the endo side of norbornadiene are prohibited by interaction of the nonreacting π electrons with the oxo nonbonding and π electrons and of norbornene by the severe steric interaction of the ketene substituent with the dimethylene bridge in the rotating and closing step.

Experimental Section

***endo*-2-Carboxy-*exo*-3-dichloromethylbicyclo[2.2.1]hept-5-ene (2).**—A mixture of 4.06 g (0.02 mol) of 3,3-dichloro-4-oxotricyclo[4.2.1.$0^{2,5}$]non-7-ene (**1**),[3] 3.6 g (0.06 mol) of KOH, and 100 ml of methanol was heated at reflux for 1 hr, concentrated to dryness, and extracted with ether. The solid residue was taken up in water and acidified with concentrated HCl, depositing 2.10 g (47.6%) of colorless crystalline product, mp 130–134°. Recrystallization from water–methanol raised the melting point to 137–138°.

The 90-MHz nmr had the following absorptions ($CDCl_3$, decoupled): δ 3.30 ($J_{1,2}$ = 3.5 Hz), 2.85 ($J_{2,1}$ = 3.5, $J_{2,3}$ = 4.5 Hz), 2.60 ($J_{3,2}$ = 4.5, $J_{3,4}$ = 1.0, $J_{3,8}$ = 9.0 Hz), 3.07 ($J_{4,3}$ = 1.0, $J_{4,5}$ = 3 Hz, $J_{4,7}$ small), 6.38 ($J_{5,4}$ = 3, $J_{5,6}$ = 5.5 Hz, $J_{5,1}$ small), 6.14 ($J_{6,5}$ = 5.5, $J_{6,7}$ = 2.5 Hz), 1.59 ($J_{7A,7S}$ = 10.5 Hz, $J_{7,other}$ small), 5.61 ($J_{8,3}$ = 9.0 Hz).

Anal. Calcd for $C_9H_{10}Cl_2O_2$: C, 48.9; H, 4.6; Cl, 32.1. Found: C, 48.7; H, 4.7; Cl, 32.1.

The iodolactone **3** was prepared in 64.6% yield, mp 99–100° (ether–ligroin).

Anal. Calcd for $C_9H_9Cl_2IO_2$: C, 31.2; H, 2.6; Cl, 20.4; I, 36.6. Found: C, 31.5 H, 2.8; Cl, 20.1; I, 36.6.

Addition of Haloketenes to Norbornenes (General Procedure).—To a stirred solution of 50.5 g (0.5 mol) of triethylamine, 125

(3) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971).

(4) J. M. Conia and J. L. Ripoll, *Bull. Soc. Chim. Fr.*, 763 (1963).

(5) H. Christol, A. Donche, and F. Plénat, *ibid.*, 1315 (1966); H. Christol, J. Coste, and F. Plénat, *ibid.*, 3934, 3939 (1969).

(6) S. Selzer in "Advances in Alicyclic Chemistry," Vol. 2, Academic Press, New York, N. Y., 1968, p 1.

(7) A study of this reaction will be reported elsewhere.

(8) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(9) M. J. S. Dewar, *Angew. Chem.*, **83**, 859 (1971), utilizing the basis sets of orbitals for the ketene and the alkene, predicts a "skew" approach for maximum orbital interaction in the transition state but the same product stereochemistry as for "orthogonal" approach. The data presented here and in ref 2 do not allow a distinction to be made between the "skew" and "orthogonal" mechanisms.

ml of norbornadiene, and 1 l. of cyclohexane (or acetonitrile) at reflux under nitrogen was added gradually (2 hr) a solution of 0.5 mol of the requisite haloacyl halide in 50 ml of cyclohexane (or acetonitrile). The mixture was refluxed for an additional 1 hr, allowed to stand overnight at room temperature, filtered through Celite, concentrated under vacuum, and distilled. The distillate was freed from halogenated impurities generally present by placing in ten volumes of hexane and treating gradually with one volume of 1,5-diazabicyclo[4.3.0]non-5-ene. After standing for 1 hr, the upper layer was decanted, washed four times with water, dried over anhydrous sodium sulfate, and distilled. The isopropyl derivative was more sensitive and required washing with 10% aqueous NaOH and subsequent chromatography on Florisil. Properties of these products are presented in Table I.

Registry No.—**2**, 34922-27-5; **3**, 34922-28-6; *syn*-**6**, 34922-29-7; *anti*-**6**, 34934-85-5; *syn*-**7**, 34934-86-6; *anti*-**7**, 34934-87-7; *syn*-**8**, 34922-30-0; *anti*-**8**, 34922-31-1; *syn*-**9**, 34934-88-8; *anti*-**9**, 34934-89-9; *syn*-**11**, 34922-32-2; *anti*-**11**, 34922-33-3.

Tautomerism of a Secondary Azo Compound Accompanying Thermal Decomposition[1]

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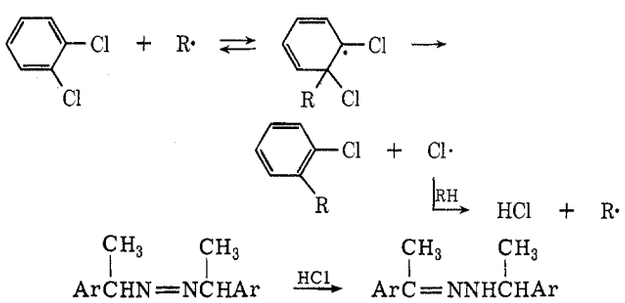
Received December 22, 1971

While studying[2] the thermal decomposition of some symmetrical secondary aralkyl azo compounds in solution, we found that in chlorinated solvents and with halogen-substituted azo compound, in addition to radical decomposition products, variable amounts of the starting material were diverted to a material that ultimately yielded the ketone of the initial moieties of the azo compound. α-Phenylazoethane (**1a**), when decomposed in a wide series of solvents (Table I), gave close to 100% yield of radical products (by glpc analysis). In *o*-dichlorobenzene, however, only 80% of the starting azo compound was accounted for when analysis was performed upon opening the sealed ampoule. After the ampoule had stood open for approximately 1 day a peak corresponding to acetophenone appeared. This peak grew with time and after 2 weeks finally accounted for all the α-phenethyl moieties in the starting material. A similar result was found for azo compound **1b** (*p*-chlorophenylazoethane) in benzene.

Addition of pyridine to an *o*-dichlorobenzene solution of **1a** prevented the side reactions; upon thermolysis only normal azo decomposition products were noted. Similarly, **1b** yielded almost theoretical radical products, and no ketone, upon addition of pyridine to the decomposition solution. Addition of dry 0.01 *M* HCl to fresh benzene solutions of **1a** and **1b** resulted in rapid rearrangement of the azo compounds to hydrazones as seen by nmr (*vide infra*). Under the conditions of these studies the hydrazones were stable in the sealed ampoules. Upon opening to air, a rapid oxidation occurred which produced one molecule of ketone for each azo compound originally added. After the ampoules had stood for about 1 week a second molecule of ketone was found, at this point accounting for all the starting material. These data are summarized in Table I. It is interesting to note that the radical–radical reaction rate constant ratio (k_d/k_c) remains constant for both compounds independent of the side reaction leading to ketone.

When **1a** was decomposed at 118° in benzene in a degassed and vacuum-sealed nmr tube for 24 hr (*ca.* 8 half-lives), the nmr peaks for the diphenylbutanes (*meso* and *dl*) as well as those for ethylbenzene and for styrene were evident. Glpc analysis showed only these products in close to quantitative yield. A similar experiment using dichlorobenzene as solvent showed, in addition to the peaks noted for the benzene solution, a doublet at τ 8.56, an equal-sized singlet at τ 8.25, and a small quartet at τ 5.5, readily assignable to the corresponding hydrazone. When this nmr tube was opened to air and allowed to stand overnight, the three peaks attributed to hydrazone disappeared and were replaced by a singlet at τ 8.5 (identical with acetophenone). The *p*-chloroazo compound, **1b**, showed analogous behavior in benzene. In degassed ampoules at room temperature all the secondary aralkyl azo compounds that we have examined in a wide range of solvents including the chlorinated benzenes are indefinitely stable to decomposition and rearrangement.

It is clear that we are observing an acid-catalyzed (by the pyridine experiment) rearrangement of the azo compound to hydrazone accompanying the radical decomposition, and subsequent formation of ketone from hydrazone in two steps, one fast and one slow. We conclude that the acid-catalyzed rearrangement accompanies the radical decomposition, a likely path being



The reversible addition of a radical to the aromatic nucleus probably occurs in benzene as well, but when chlorine is attached to the ring, the reverse reaction must compete with the loss of a stable chlorine atom. A very small amount of this process would produce sufficient acid to catalyze the rearrangement.

Immediately after opening, analysis in all cases showed no trace of acetophenone. The decomposed solution of **1a** in dichlorobenzene was examined by glpc after opening and exposure to anaerobic water in one experiment, and to dry oxygen in another. The oxygenated sample showed 1 mol of acetophenone per mole of hydrazone within 15 min, but the aqueous sample showed only small traces of acetophenone. It thus seems that the first mole of acetophenone arises from the reaction of hydrazone with oxygen. Several in-

(1) Taken in part from the Ph.D. dissertation of R. C. C., University of California, Riverside, 1971. Support by the Air Force Rocket Propulsion Laboratory (R. C. C.) and the Intramural Fund of the University of California is gratefully acknowledged.

(2) M. J. Gibian and R. C. Corley, *J. Amer. Chem. Soc.*, **94**, 4178 (1972).