

effects of Table VIII are computed do not warrant its discussion in terms of mechanism. The total d_5 isotope effect on the other hand is significant although we still feel that only qualitative conclusions can be drawn from it. The magnitude of such effect is in fact about the maximum one would expect for this kind of reaction from previous work on alkyl halides²²⁻²⁴ and esters.²⁵ It implies a large degree of involvement of the hydrogen in the activation act.

Thermodynamics of the Elimination. In view of the fact of the variation of the ratio (final pressure)/(initial pressure) with initial pressure and temperature, we suggest the establishment of an endothermic equilibrium. Based on eq I, the equilibrium constant K_p can be written as

$$K_1 = \frac{P_{\text{HCNS}}P_{\text{C}_2\text{H}_4}}{P_{\text{EtSCN}}}$$

$$K_2 = \frac{P_{\text{HCNS}}P_{\text{C}_2\text{H}_4}}{P_{\text{EtNCS}}}$$

$$K_p = \frac{P_{\text{HCNS}}P_{\text{C}_2\text{H}_4}}{P_{\text{EtSCN}} + P_{\text{EtNCS}}}$$

with, of course, $K_p = K_1K_2/(K_1 + K_2)$. A preliminary calculation showed that $K_1 \gg K_2$ and so $K_p = K_2$. Values of $K_p = (P_f - P_0)^2/(2P_0 - P_f)$ are shown in Table IX. Reliable values for the thermodynamic

(22) A. T. Blades, *Can. J. Chem.*, **36**, 1043 (1958).

(23) A. T. Blades, P. W. Gilderson, and M. G. H. Wallbridge, *ibid.*, **40**, 1533 (1962).

(24) K. Dees and D. W. Setser, *J. Chem. Phys.*, **49**, 1193 (1968).

(25) A. T. Blades and P. W. Gilderson, *Can. J. Chem.*, **38**, 1401 (1960).

Table IX. Equilibrium Constants for the Ethyl Thiocyanate Pyrolysis

T, °K	576.1	579.7	593.6	603.8	610.7
K_p	0.69	0.70	0.95	1.16	1.41

functions of the species involved in the equilibrium are not available in the literature.

Experimental Section

Ethyl Thiocyanate. A commercial sample from Eastman Organic Chemical, Rochester, N. Y., was purified by fractional distillation to give a compound 99.5% pure.

Ethyl-1,1- d_5 Thiocyanate. This was prepared from ethyl-1,1- d_5 bromide (98% isotopic purity) obtained from Merck Sharp and Dohme of Canada and potassium thiocyanate in dimethylformamide. After purification by standard procedures, the compound showed a chemical purity of 98.8%. Mass spectrometric analysis indicated that 97.7 molecules out of 100 are dideuterated.

Ethyl- d_5 thiocyanate was prepared from the corresponding perdeuterated bromide (99% of isotopic purity). The sources of materials and the method of preparation were the same used for the previous compound. The isotopic purity of the final product was at least 98%. All compounds were analyzed by gas chromatography in a Perkin-Elmer F-11 flame ionization instrument, by nmr in a Varian A-60 spectrometer, and by ir in a Perkin-Elmer Model 337 grating spectrophotometer. Mass spectra were taken on a G.E.C.-A.E.I. MS-9 instrument.

Quantitative determinations of thio- and isothiocyanates were accomplished by gas chromatography using the method of internal standards and those of thiocyanic acid by titration with standard alkali. Details of the techniques are given elsewhere.¹²

The kinetic study was carried out in a standard, high-vacuum, all-glass system using the static manometric method. Temperature was kept constant within 0.2° by means of a RT-3R/2 temperature controller (A.E.I.).

Thermal Decomposition of 2,2'-Diphenyl-2,2'-azohexafluoropropane

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Received December 8, 1970

Abstract: Azohexafluorocumene (2,2'-diphenyl-2,2'-azohexafluoropropane) has been prepared from the corresponding amine and iodine pentafluoride. The thermal decomposition reaction in toluene solvent yields the rate expression $k = 10^{17.8 \pm 0.8} \exp(-32,800 \pm 1300)/RT \text{ sec}^{-1}$. The reaction products in toluene are 2-phenyl-2-*p*-(1,1,1,3,3,3-hexafluoro-2-propyl)phenylhexafluoropropane—the product of para coupling of the hexafluorocumyl radicals—and the products obtained by the coupling of benzyl and hexafluorocumyl radicals. The cage effect in toluene has been determined at 55° with iodine as a scavenger.

Azo compounds have been very widely used in the study of the reactions of free radicals.¹ The relationship between the radical-stabilizing effects of groups attached to the free radical center and the ease of decomposition of azo compounds has been pointed out^{2,3} but

(1) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Amer. Chem. Soc.*, **92**, 867 (1970). This paper contains a large selection of references to the use of azo compounds as free radical sources.

(2) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 137, 143 (1966).

(3) S. A. Weiner and G. S. Hammond, *ibid.*, **91**, 926 (1969).

the nature of such groups has been confined to aryl, alkyl, cyano, and chloro.⁴

We report here on the synthesis and pyrolysis in benzene and toluene solution of azohexafluorocumene (2,2'-diphenyl-2,2'-azohexafluoropropane). The study was undertaken to investigate the effect of the trifluoromethyl group—a group which can be unequivocally

(4) S. Goldschmidt and B. Acksteiner, *Justus Liebigs Ann. Chem.*, **618**, 173 (1958).

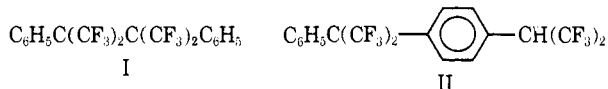
classified as one exerting a strong electron-withdrawing effect by an inductive mechanism—on the reactivity of the benzyl free radical.

Results

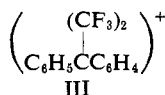
We have determined the nature and distribution of the reaction products of the thermal decomposition of azo-hexafluorocumene, and the effect of the scavenger, iodine, on these products. We have measured the kinetics of the reaction.

Reaction Products. The solvent used in most of these experiments was toluene. A few experiments were carried out in benzene. Analyses of the reaction products by vapor phase chromatography gave two main peaks for the reaction in toluene. These two peaks will be referred to, for reasons which will become evident below, as the dimer peak and the mixed coupling product peak. For the reactions in benzene, the dimer peak was also found but the mixed coupling peak was absent.

Since mass spectroscopic investigations of the dimer peak at several points within the peak gave identical results, it was concluded that the peak represented a single compound. The formula $C_{18}H_{10}F_{12}$ was assigned to this compound on the basis of the observed molecular ion peak, 454, as 74% of the base peak. The intensity ratio of the 455 mass peak, the highest mass observed, to the 454 peak was 0.20, in good agreement with the value of 0.18 predicted on the basis of isotope ratios.⁵ The two structures considered for this dimer are I and II.



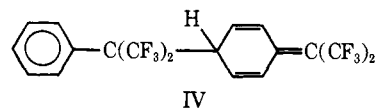
In analogy with the results for azocumene,² one might expect that structure I would be the correct one. The presence in the mass spectrum of a sizable peak (37% of the base peak) as a mass of 303, which could only reasonably be assigned to the structure III, was the first in-



dication that structure II was correct. Confirming evidence was obtained by examination of the ^{19}F nmr spectra⁶ of the thermal decomposition products obtained in benzene. The ^{19}F nmr spectrum showed a singlet of 6004 Hz and a doublet of 6163 and 6172 Hz, both measured upfield from $CFCl_3$. The area of the singlet and the combined areas of the doublet peaks were found to be equal, within the experimental error of the area measurements.

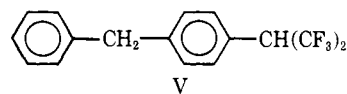
The proton nmr spectrum of the benzene solution showed a septet at τ 6.37. The coupling constant of the septet and the doublet was 9 Hz. The fluorine nmr spectrum was scanned from 10,000 Hz downfield of the observed peaks to 10,000 Hz upfield from them and no evidence of another peak was observed. Thus structure I is not found in any significant amount.

It seems most reasonable that the quinoid dimer, IV, is formed first but rapidly aromatizes. The nmr data



rule out IV as the structure of the dimer because the J_{HF} coupling constant is typical for a hexafluoroisopropyl group. Para attack in preference to ortho is assumed because of steric hindrance considerations.

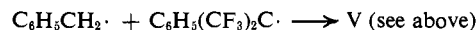
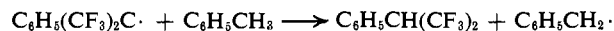
The second peak observed in the vapor phase chromatographic analysis of the reaction products when toluene was the solvent has a shape that indicated the presence of two compounds. Since mass spectral examination of this peak at various points showed no differences in the spectra it was concluded that two isomeric species of very similar structure were present. The molecular ion peak of mass 318 suggests a product from reaction of a benzyl radical and a hexafluorocumyl radical. The presence in the spectrum of a substantial peak at mass 167 which could only be reasonably assigned to $C_6H_5CH_2C_6H_4^+$ is evidence in favor of structure V below for one of the components. Other struc-



tures, *i.e.*, the ortho isomer of V or the head-to-head product are possible. The structure was not further investigated.

The ratio of peak area of the mixed coupling product to that of the dimer was measured in a few cases and found to be 0.25 ± 0.05 . For equal sensitivities, this represents the ratio of these species as products. Thus the fraction of radicals ending up as dimer is about 0.75 and that ending up as mixed coupling products is about 0.125. (The remainder, see below, ends up as hexafluorocumene.) An independent determination of these quantities was carried out by a different method and yielded results in reasonable agreement with this one. This is described at a later point.

One may then write, for the reactions of the radicals in toluene



The scheme shown above indicates hexafluorocumene as a product. Our results indicate that this compound was present and that its vapor phase chromatographic peak was hidden under the large solvent toluene peaks. Thus, the examination of the mass spectrum taken of the toluene peak yielded, in addition to the toluene mass spectrum, mass peaks corresponding to the molecular ion for hexafluorocumene, mass 228, and for other characteristic fragments, including those in which F, F plus HF, and CF_3 were lost.

Since the evidence on the disproportionation of perfluoroalkyl radicals is a bit contradictory,^{7,8} a thorough search was made for the disproportionation product heptafluorocumene. The retention time of an authentic sample of this compound⁹ was determined using a toluene solution and by comparison of the peak areas for

(5) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1963, p 36.

(6) We are indebted to Dr. Elizabeth Hansen, U. S. Pure Food and Drug Administration, for running the ^{19}F nmr spectra.

(7) S. V. R. Mastrangelo, *J. Amer. Chem. Soc.*, **84**, 1112 (1962).

(8) G. O. Pritchard and G. H. Miller, *J. Phys. Chem.*, **63**, 2074 (1959).

(9) We thank Dr. W. A. Sheppard for kindly supplying us a pure sample of this compound.

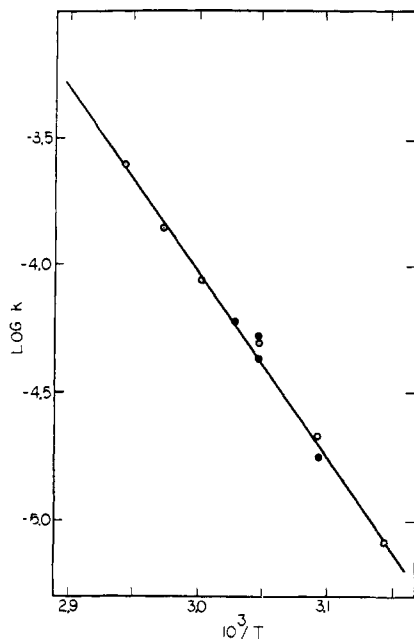


Figure 1. Arrhenius plot of azohexafluorocumene thermal decomposition rates. The open circles are manometric rates; the filled circles are rates determined spectroscopically.

samples of known concentration with the chromatograms of reaction product solutions, it was concluded that less than 0.4% of the radicals formed in the azo compound pyrolysis engaged in the disproportionation reaction. This is an upper limit on this figure.

Reaction Kinetics. Reaction rate measurements for the thermal decomposition reaction in toluene were made either by following the rate of nitrogen evolution or by measuring the rate of iodine consumption with solutions containing added iodine. Measurements were made from 45.0 to 67.0° and good first-order curves were obtained in all cases. The results are summarized in Table I and plotted in Figure 1.

Table I. Rate of Thermal Decomposition of Azohexafluorocumene in Toluene

Run	Temperature, °C	$k^a \times 10^5$, sec ⁻¹	Method of determination
1	45.0 (±0.25)	0.836	Pressure
2	50.0	2.16	Pressure
3	50.0	1.79	I ₂
4	55.0	4.92	Pressure
5	55.0	4.44	I ₂
6	55.0	5.08	I ₂
7	57.0	6.03	I ₂
8	60.0	8.81	Pressure
9	63.0	14.1	Pressure
10	67.0	24.6	Pressure

^a Visual examination of these graphs showed that the slopes had a possible error of <2%. Since differences between runs at the same temperature were significantly in excess of this, no detailed statistical analysis of the errors in the individual rate constants was made.

The Arrhenius plot yielded the general rate expression $k = 10^{17.8 \pm 0.8} \exp(-32,800 \pm 1300)/RT \text{ sec}^{-1}$.¹⁰

(10) The preexponential factor and activation energy values were determined by the method of least squares on an IBM 360/50 computer on a program supplied by Dr. Ann Hanratty. The errors were calculated using the method described in ref 11.

(11) J. Topping, "Errors of Observation and Their Treatment," Reinhold, New York, N. Y., 1960, pp 105-112.

The entropy of activation is calculated as $\Delta S = 20 \pm 1 \text{ eu}$.

Experiments on the Cage Effect. Experiments concerned with the extent to which radical recombination occurred within the solvent cage were performed using iodine to scavenge the radicals.¹² (Since the disproportionation does not occur the only radical-radical reaction is recombination.)

The fraction of radical reaction occurring within the cage, denoted as a , can be defined as follows.

$$a = 1 - \frac{\text{moles iodine consumed}}{\text{moles azo decomposed}}$$

Results were obtained in this way for toluene solvent and are given in Table II.

Table II. Cage Effect Measurements in Toluene for Azohexafluorocumene

Temperature (°C)	a
50	0.15
55	0.14
55	0.12
57	0.11
57	0.10

In addition to the above, the effect of iodine on the yield of dimer was determined directly on the gas chromatograph. Bibenzyl, which has a suitable retention time and sensitivity and is not formed in detectable amounts as a product, was used as an internal standard. Two samples, identical with respect to azo compound and bibenzyl concentration and differing in that only one contained iodine, were subjected to thermal decomposition. Area ratios of dimer to bibenzyl were determined in each case and from these the ratios of dimer yields were calculated. These are given in Table III.

Table III. The Effect of Iodine Scavenger on the Dimer Yield in Toluene at 55°

Entry	r^a
1	0.21
2	0.17
3	0.20
4	0.17
5	0.16
	0.18 ± 0.02 ^b

^a r = ratio of dimer yield in scavenged solution to that in unscavenged solution. ^b The indicated error is the root mean square deviation from the average value.

In order to consider the significance of r , it is convenient to make the following definitions: D_c = dimer formed in cage, D_e = dimer formed outside of cage, M = mixed coupling product. Then $r = D_c/(D_e + D_c)$ and $a = D_c/(D_e + D_c + M)$. It can be seen that $(r/a) - 1 = M/(D_e + D_c) = 0.37 \pm 0.13$.¹³

The value for the ratio of mixed coupling product to dimer that was found by direct comparison of the peak areas in the gas chromatograms was 0.25 ± 0.05 . The

(12) G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Amer. Chem. Soc.*, **77**, 3244 (1955); H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1911 (1964); R. C. Lamb and J. C. Pacifci, *ibid.*, **86**, 914 (1964).

(13) The indicated error is calculated from the error in r .

two values, obtained by completely independent measurements, are in reasonable agreement.

Discussion

Reaction Products and Cage Effect. In the consideration of the reaction products the question may be asked: why do the hexafluorocumyl radicals couple exclusively by para coupling while cumyl radicals show this sort of coupling to an extent of about 2%² of head-to-head coupling? It seems most reasonable that part of the answer, at least, lies in the steric resistance encountered when two hexafluorocumyl radicals approach in a head-to-head arrangement. Steric hindrance seems to be a decisive factor in the para coupling recently reported¹⁴ for certain diphenylmethyl radicals, and there is evidence that trifluoromethyl groups have a greater steric requirement than methyl groups.¹⁵

Along with the above observation must go the conclusion that para coupling does not, apparently, present severe steric demands. Thus the cage effect observed for the hexafluorocumyl radicals is about half that for cumyl radicals, not a particularly large difference. For 3-methyl-2-phenyl-2-butyl radicals, a cage effect of less than 0.01 has been reported¹⁶ and it must be concluded that para coupling as well as head-to-head coupling are impeded there. Apparently the hexafluorocumyl radical satisfies the case for pronounced resistance to head-to-head coupling along with little resistance to para coupling. The present results are likewise consistent with the conclusions of Green, *et al.*,¹ that rotation of radicals of this sort in the solvent cage is rapid compared to diffusion out of the cage.

Although it is also clear that aromatization of the postulated intermediate quinoid dimer, IV, must be rapid since that dimer was not observed, it is not clear how this can be related to the structures of the fluorinated species or to the coupling process. It may be noted that the quinoid dimer formed from cumyl radicals was consumed by reaction other than aromatization.²

The fact that the hexafluorocumyl radical can abstract a hydrogen from toluene at a velocity competitive with radical dimerization while the cumyl radical cannot, does not lend itself to unambiguous interpretation. Recombination rates for radicals of this type can vary by rather large factors³ and in the absence of a direct comparison for the recombination rate constants for cumyl and hexafluorocumyl radicals, not much can be said to compare quantitatively their rates of abstraction of hydrogen atoms from toluene.

Reaction Kinetics. We prefer to discuss the kinetics of the present reaction in the context of the data for the group of substituted azotoluenes collected in Table IV.

The trend of entropies of activation must be considered in the evaluation of the effect of structure on reactivity in the above group. For entries 1–3, it is generally argued that the increasing importance of hyperconjugation is responsible for the steady decrease in the energy of activation. The fact that the entropies of activation also

Table IV. Energies and Entropies of Activation for the Thermal Disproportionation of RN_2R^2

Entry	R	ΔE , kcal mole ⁻¹	ΔS , eu
1	$\text{C}_6\text{H}_5\text{CH}_2$	36	5
2	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)$	32.2	7.2
3	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2$	29.0	11.0
4	$\text{C}_6\text{H}_5\text{C}(\text{CF}_3)_2$	32.8	20.0

increase steadily leads us to suggest that steric crowding in the azo compound is increasing as we go from entry 1 to entry 4 and that this crowding is relieved in the transition state, resulting in the observed trend in the activation entropies. (Stuart models show that the radicals are substantially less crowded than the parent azo compounds.) We feel this crowding also results in weakened carbon-to-nitrogen bonds in the azo compounds and hence that it is reasonable to attribute the drop in activation energy when hydrogens are replaced by trifluoromethyl groups to this effect. It seems clear that hyperconjugation does play a role in determining the activation energies of entries 2 and 3 since otherwise the activation energy of 4 should be less than that of entry 3 but both factors must be considered. Implicit here is the proposal that hyperconjugative stabilization of radical centers *via* participation by β carbon-fluorine bonds is much less effective than that involving β carbon-hydrogen bonds (*cf.* however ref 17).

Experimental Section

Chemicals. Most of the thermal decomposition reactions were carried out in reagent grade benzene and toluene which had been distilled and stored over calcium sulfate. Trial kinetic experiments carried out with spectroscopic grade solvents showed no differences.

Hexafluorocumylamine was prepared according to the method of Gale and Krespan¹⁸ from benzene and hexafluoroacetoneimine. The infrared, ultraviolet, and proton nmr spectra were all in good agreement with those reported.¹⁸

Azohexafluorocumene was prepared from the above amine by the method of Stevens¹⁹ as modified by Timberlake and Martin.²⁰ The reaction gave an average yield of 14% based on the amine and the white solid obtained was recrystallized from an ether-ethanol mixture. Analysis yielded the percentages, C 45.07, H 2.29, N 6.07, F 47.35; corresponding values calculated for $\text{C}_{18}\text{H}_{10}\text{F}_{12}\text{N}_2$ are 44.83, 2.09, 5.81, 47.27. The melting point was 89–90°. The proton nmr spectrum in carbon tetrachloride (internal TMS standard, Varian A60) showed a singlet at τ 2.6. The ¹⁹F nmr spectrum (Varian HA-100) in benzene showed only a singlet at 6258 Hz upfield from CFCl_3 . The ultraviolet spectrum (Cary 14) showed a maximum at 382 $m\mu$ (ϵ 3.81).

Product Analysis. Examination of the reaction products on an SE-30 column (3% SE-30 on 100–200 mesh Anachrom) and on a QF-1 column (5% QF-1 on 60–80 mesh Chromosorb W) at column temperatures of 150° and helium flow rates of 65 ml min⁻¹ showed the same number of product peaks. Separation was better on the SE-30 column and it was used for all the product analyses except for the case where heptafluoroisopropylbenzene was sought (see below).

Mass spectra were taken of samples carried to complete reaction in rate measurement experiments. A Perkin Model 270 mass spectrometer equipped with a 3 ft \times 1/8 in. SE-30 column was used.

It proved most convenient to look for the disproportionation product, heptafluoroisopropylbenzene, using the QF-1 column at 45° and a helium flow rate of 50 ml min⁻¹. It was established by trial experiments that a concentration of 2×10^{-4} M was

(14) H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 2, 249 (1968).

(15) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, p 203.

(16) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, 15, 89 (1967).

(17) G. R. Underwood, V. L. Vogel, and I. Krefting, *J. Amer. Chem. Soc.*, 90, 5019 (1970).

(18) D. M. Gale and C. G. Krespan, *J. Org. Chem.*, 33, 1002 (1968).

(19) T. E. Stevens, *ibid.*, 26, 2531 (1961).

(20) J. W. Timberlake and J. C. Martin, *ibid.*, 33, 4054 (1968).

readily detectable. Samples of the azo compound in benzene, 0.1 M, were heated at 55° for periods exceeding ten half-lives and the resultant solution was examined on the gas chromatograph. No detectable heptafluoroisopropylbenzene peak was found and it was therefore concluded that the fraction of radicals reacting by disproportionation was less than 0.4%.

Proton and fluorine nmr spectra of the dimer product were taken on a sample that had undergone thermal decomposition in benzene since only the dimer product was formed there. For this purpose 0.08 g (0.2 mmole) of azohexafluorocumene was dissolved in 1 ml of spectroscopic grade benzene. Half of this was placed in an nmr tube. The remainder was placed in a small glass tube, degassed under vacuum three times, sealed, and heated at 55° for 42 hr (ten half-lives). The tube was then cooled and opened and the contents were transferred to another nmr tube. The contents of the unheated tube were used to determine the nmr spectra of the azo compound while those of the heated tube were used to determine the nmr spectrum of the dimer.

Reaction Rate and Cage Effect Measurements. Reaction rate measurements were made both manometrically and spectroscopically. The manometric measurements were made using a 30-ml Pyrex bulb equipped with a 1-mm bore, side-arm capillary tube which served as a mercury manometer. The bulb was immersed in a thermostated oil bath and the capillary tube between the mercury column and the bath level was electrically heated to the bath temperature to prevent solvent condensation. Experiments were carried out with 10 ml of a solution containing in each case about 0.003 g, ~ 7 μ moles, of the azo compound. The azo compound was weighed out in each case to ± 0.01 mg. The solutions were degassed thrice in each case by a freezing, pumping, thawing cycle. The bulb was then sealed under vacuum with a hand torch. The bulb volume was found for each experiment by measuring the volume of water needed to fill it. The apparatus was tested by measuring the rate of thermal decomposition of α, α' -azobisisobutyronitrile. The rate constant found at 70.0° was 3.85×10^{-5}

sec^{-1} which is in satisfactory agreement with the value of $3.98 \times 10^{-5} \text{ sec}^{-1}$ calculated from the data of Van Hook and Tobolsky.²¹

Spectroscopic rate measurements were made by following the decrease in the absorption of iodine at 495 $m\mu$. The apparatus for these measurements consisted of an electrically heated aluminum block furnace which could be thermostated and inserted in a Beckman DU spectrophotometer and which was machined to hold a Pyrex absorption cell in the light path. The cell was 22 mm in diameter and 50 mm long and was equipped with a side-arm bulb which permitted degassing of a solution in the usual way and subsequent transfer of the solution to the cell. The apparatus has been described in detail elsewhere.²²

In a typical experiment 16 ml of toluene containing 0.002 mmole of azo compound and 0.004 mmole of iodine was placed in the bulb and degassed three times as above. The bulb was then sealed under vacuum, the liquid was transferred to the cell, filling it, and the cell was placed in a preheated aluminum block furnace which was located in the light path of a Beckman Model DU spectrophotometer. From the change in absorbance with time, a reaction rate curve could be plotted. From the total decrease in absorbance, the extinction coefficient of iodine, and the weight of azo compound used, the cage effect values could be calculated.

The procedure for determining the effect of iodine on the reaction products is illustrated by the following example. A solution of 4.5 mg (9.3×10^{-6} mole) of the azo compound and 2.0 mg of bibenzyl in 1 ml of toluene was divided into two equal parts. One part was placed in a tube containing 3.0 mg (1.2×10^{-5} mole) of iodine and the other part into an empty tube. Both tubes were degassed three times, sealed, and heated for 10 half-lives. The tubes were then cooled and opened, and the contents were analyzed.

(21) J. P. Van Hook and A. V. Tobolsky, *J. Amer. Chem. Soc.*, **80**, 779 (1958).

(22) J. B. Levy, *J. Phys. Chem.*, **66**, 1092 (1962).

The Transition Metal-Catalyzed Displacement Reaction between Organometallic Compounds and Olefins. II.¹ On the Role of Some Nickel Complexes in the Homogeneous Displacement Reaction between Organoaluminum Compounds and α -Olefins

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Abstract: The nickel-catalyzed displacement reaction between optically active organometallic compounds of Be, Zn, B, Al, and α -olefins is investigated, under homogeneous conditions, by using nickel(II) complexes containing *N*-alkylsalicylaldimino or acetylacetonate groups as ligands. The displacement reaction, carried out in the presence of nickel complexes containing optically active ligands, shows a small stereospecificity. Uv and CD investigations have shown the existence of mutual interactions among the reactants according to chemical findings. On the basis of these results and the different catalytic activities of Ni(acac)₂ and Ni(mesal)₂, it is concluded that at least one of the ligands originally present in the nickel complex is still contained in the catalytic species. The different reactivities of the organometallic compounds used and the lack of catalytic activity of Ni(mesal)₂ in the racemization of optically active 2-methylbutylberyllium and aluminum derivatives indicate that the alkylation and the subsequent hydride formation of the nickel do not play an important role in the catalytic process. A possible mechanism, in agreement with the experimental results, is proposed for the displacement reaction.

The catalytic effect of nickel compounds on the "displacement reaction"¹ between alkylaluminum compounds and olefins was first studied by Ziegler² in

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1954 but the mechanism is by no means well understood. Ziegler was of the opinion that the actual catalyst was "colloidal" nickel,³ while Lucas,⁴ in the nickel-cata-

(1) Part I: P. Pino, L. Lardicci, P. Palagi, and G. P. Giacomelli, *Chim. Ind. (Milan)*, **50**, 355 (1968).

(2) K. Ziegler, *Brennstoff Chem.*, **35**, 321 (1954).