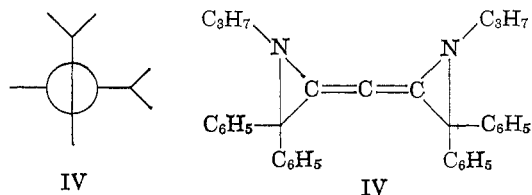


Stereochemical considerations indicate that four isomers of IIIa or IIIb should exist as a result of different orientations of the aziridine rings with respect to each other.

Reaction of C<sub>3</sub> with N-diphenylmethyleisopropylamine would be expected to produce one allenic product



(IV). Evidence for formation of this product is an allenic absorption in the infrared and an *m/e* peak at 241 in the mass spectrum of the crude reaction mixture.

No products attributable to reaction of monatomic carbon with the imines used were definitely found, though many components appeared in the chromatograms of the crude reaction mixtures. Such products might be expected since reaction of carbon vapor with alkenes leads to formation of spiropentanes.<sup>3</sup>

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### The Chlorination of Anilines. Proof of the Existence of an N-Chloro Intermediate

Sir:

An aniline, being an ambident<sup>1</sup> nucleophile, might be expected to react with a chlorinating agent chiefly on nitrogen because this atom constitutes the most highly nucleophilic site of the molecule. Ultimate carbon-chlorine covalency formation would then be attributable to the instability of this N-chloroaniline intermediate.<sup>2</sup>

We report here conclusive evidence that N-chloro-N-methylaniline is the intermediate in the chlorination of N-methylaniline by calcium hypochlorite in carbon tetrachloride.

When 10 equiv. of calcium hypochlorite<sup>3</sup> is stirred with 1 equiv. of N-methylaniline in carbon tetrachloride at 0°, removal of a filtered aliquot after 30 min. indicates the presence of almost 1 equiv. of active chlorine<sup>4</sup> in the solution. The infrared spectrum of this solution reveals a degree of disappearance of the N-H stretching band (at 3415 cm.<sup>-1</sup>) which closely parallels the titra-

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

(2) This suggestion has been made by numerous authors, e.g., F. D. Chattaway and K. J. P. Orton, *J. Chem. Soc.*, **79**, 462 (1901). The most recent use of this hypothesis has been made by R. S. Neale, R. G. Schepers, and M. R. Walsh [*J. Org. Chem.*, **29**, 3390 (1964)], who attribute the high *ortho:para* ratios which they observed to such N-chloro intermediates.

(3) J. T. Baker, Purified Powder, 30-35% available chlorine; our analysis just before use indicates 12.6% active chlorine.

(4) Measured by addition of solution to an excess of potassium iodide and titration with sodium thiosulfate. Stirring calcium hypochlorite in carbon tetrachloride in the absence of N-methylaniline, followed by filtration and titration of the carbon tetrachloride filtrate, produces a zero titer (certainly less than 1%) of active chlorine.

tion value (see Table I). Further substantiation that this is indeed a solution of N-chloro-N-methylaniline is the fact that analysis of the sample which has been treated with potassium iodide and sodium thiosulfate reveals it to consist mainly of N-methylaniline.<sup>5</sup>

Table I. Assay of N-Chloro-N-methylaniline Solution by Titration, by Infrared, and by the Nature of the Compounds Recovered on Treatment With Potassium Iodide

Time, min.	% yield of N-chloro compd. by		% recovered N-methylanilines Unsubstituted	<i>o</i> -Cl	<i>p</i> -Cl
	Titration	Infrared <sup>a</sup>			
10	57.5	54.3	93.5	5.2	2.3
30	88.5	85.4	81.0	10.3	5.8

<sup>a</sup> Yield = (1.00 - [absorbance at time *t*/absorbance at start])100.

On the other hand a filtered aliquot, removed after 30 min. but not treated with KI, was found after standing for 24 hr. to contain 66.7% *o*-chloroaniline, 3.1% *p*-chloroaniline, ~16.5% dichloroaniline, and no unreacted N-methylaniline. This proves that the N-chloro-N-methylaniline is indeed the *intermediate* in the reaction producing ring-chlorinated N-methylanilines.

Two additional observations appear to be of particular interest. (1) The *ortho:para* ratios differ significantly when the final products are formed in the presence of the inorganic chlorinating agent (*ortho:para* ~2) and when they are formed in a solution containing the N-chloro intermediate as the sole chlorinating agent (*ortho:para* >3.4).<sup>6</sup> (2) N-Chloro-N-methylaniline, though it rearranges in the course of hours to ring-chlorinated materials, is reasonably stable.<sup>7</sup> This raises hopes of the possibility of using such reactive intermediates as starting materials for other reactions. Work on these last two points is in progress.<sup>8</sup>

(5) I.e., C<sub>6</sub>H<sub>5</sub>N(Cl)CH<sub>3</sub> + 2KI + CH<sub>3</sub>CO<sub>2</sub>H = C<sub>6</sub>H<sub>5</sub>NHCH<sub>3</sub> + I<sub>2</sub> + KCl + CH<sub>3</sub>CO<sub>2</sub>K. The fact that some of this recovered material is already ring chlorinated suggests that some (less than 7.5% after 10 min.) of the N-chlorinated material, as assayed by both titration and infrared, may be *o*- and *p*-chloro-N-chloro-N-methylaniline.

(6) In fact this *ortho:para* ratio is the highest reported. Neale, *et al.*, ref. 2, obtained *ortho:para* 2.2 for N-methylaniline.

(7) In 0.02 M carbon tetrachloride solution the rate at which the N-H band in the infrared increased was quite slow; e.g., it did not increase noticeably in the first 10 min.

(8) Support of this work by a grant from the U. S. Public Health Service (AM 06834) is gratefully acknowledged.

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### Allylbenzene Isomerization Catalyzed by Deuteriocobalt Tetracarbonyl

Sir:

When an excess of a 1-olefin is treated with cobalt hydrocarbonyl (HCo(CO)<sub>4</sub>) at room conditions under a nitrogen atmosphere, olefin isomerization occurs very rapidly.<sup>1</sup> Two mechanisms<sup>2</sup> have been proposed to explain the isomerization: (a) allylic exchange involving hydrogen donation from the metal hydride to

(1) G. Karapinka and M. Orchin, *J. Org. Chem.*, **26**, 4187 (1961).

(2) R. W. Goetz and M. Orchin, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

the terminal carbon atom with concomitant double-bond migration and hydrogen abstraction from the allylic position<sup>1,2</sup>; and (b) reversible hydride addition and elimination.<sup>3,4</sup> In an effort to help distinguish between the mechanisms, we have studied the reaction of allylbenzene with  $\text{HCo}(\text{CO})_4$  and  $\text{DCo}(\text{CO})_4$  with results that are not compatible with either a or b.

$\text{HCo}(\text{CO})_4$  and  $\text{DCo}(\text{CO})_4$  were prepared as follows: to 4.344 g. (12.7 mmoles) of pure crystalline  $\text{Co}_2(\text{CO})_8$  in 85 ml. of hexane under CO was added 9 ml. of dimethylformamide (DMF). The two-phase system was cooled to 0° and 11 ml. of concentrated HCl (or DCl) was added dropwise, with stirring. The dark blue bottom phase was syringed away from the light yellow hexane phase. The hexane solution was washed twice with 5-ml. portions of  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ), and the hexane solution was cooled to -70°. The supernatant solution was syringed away from the ice crystals and placed in a second CO-filled flask. When the solution reached room temperature, a sample was removed and injected into excess 0.01 N NaOH solution previously degassed with CO. Titration (to a phenolphthalein end point) indicated that the concentration of  $\text{HCo}(\text{CO})_4$  [or  $\text{DCo}(\text{CO})_4$ ] was 0.180 mmole/ml. (about a 90% yield).

The catalytic isomerization of allylbenzene proceeds rapidly and gives *trans*-propenylbenzene as a major product.



The rate of the reactions was determined as follows: to 40 ml. of hexane solution containing  $\text{HCo}(\text{CO})_4$  or  $\text{DCo}(\text{CO})_4$  prepared as above was added 2.40 ml. (21.6 mmoles) of allylbenzene. Samples (0.25 ml.) were removed at 1-min. intervals and quenched with 0.01 N NaOH, and the hexane supernatant was analyzed by vapor phase chromatography on a 14 ft.  $\times$  0.25 in. column packed with Ucon-2000 on Chromosorb-P at 152°, with a helium flow rate of 35 ml./min. After the solvent peak, *n*-propylbenzene, allylbenzene, *cis*-propenylbenzene, and *trans*-propenylbenzene came off the column in that order. Titration of the 9-min. sample showed that 3.60 mmoles (50%) of the original  $\text{HCo}(\text{CO})_4$  had disappeared. About a third of the  $\text{HCo}(\text{CO})_4$  consumed could be accounted for by the *n*-propylbenzene; the rest was lost by decomposition to  $\text{Co}_2(\text{CO})_8$  and by formation of acylcobalt carbonyl complexes. Duplicate experiments were performed with both  $\text{HCo}(\text{CO})_4$  and  $\text{DCo}(\text{CO})_4$ ; results of the duplicates agreed to within about  $\pm 1\%$ . The averages of the results of these experiments were calculated and the values found for allylbenzene and *trans*-propenylbenzene are shown in Figure 1. After the isomerization was complete in the  $\text{DCo}(\text{CO})_4$  experiment (10 min.), the propenylbenzenes and the *n*-propylbenzene were separated by g.l.p.c. Although the infrared spectrum of the mixed propenylbenzenes was essentially superimposable on the spectrum of an authentic mixture of the same composition, the mass spectrographic analysis showed 5.3% monodeuterated propenylbenzene:

(3) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

(4) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada, and Y. Okuda, *Bull. Chem. Soc. Japan*, **37**, 1190 (1964).

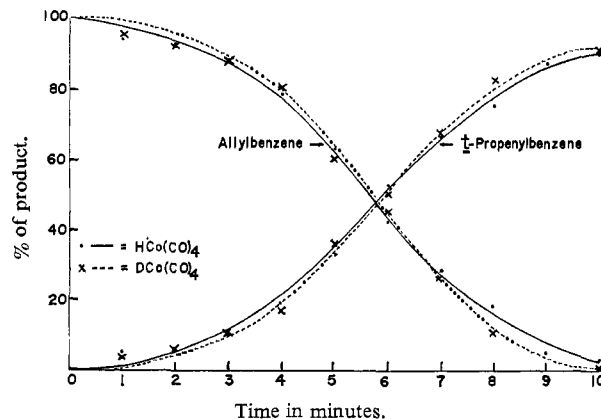
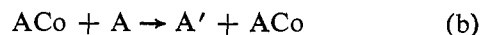
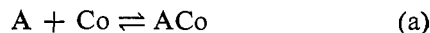


Figure 1. Rate of isomerization of allylbenzene with  $\text{HCo}(\text{CO})_4$  and with  $\text{DCo}(\text{CO})_4$ .

about 2.3% in the methyl group and 3.0% elsewhere. The infrared spectrum of the *n*-propylbenzene showed a strong C-D stretching band at 2170  $\text{cm}^{-1}$ .

In order to demonstrate that deuterium was still present as  $\text{DCo}(\text{CO})_4$  after isomerization occurred, an experiment was performed in which propylene was added to the mixture after most of the allylbenzene had been isomerized. The mixture of butyraldehydes produced by the hydroformylation was separated by g.l.p.c. The infrared spectrum of the sample showed the expected band at 2040  $\text{cm}^{-1}$  ( $-\text{CDO}$ ) and no band at 2825  $\text{cm}^{-1}$  ( $-\text{CHO}$ ).

The fact that the  $\text{DCo}(\text{CO})_4$ - and  $\text{HCo}(\text{CO})_4$ -catalyzed rates of isomerization are essentially equal indicates that breaking the D-Co bond is not involved in the rate-determining step. (In separate experiments it was shown that  $\text{NaCo}(\text{CO})_4$  is noncatalytic.) The presence of only a small amount of D in the propenylbenzene is further evidence that the Co-D bond remains intact. These facts seem to indicate that an internal 1,3-hydrogen shift accounts for most of the isomerization which is probably proceeding *via* complex formation, according to the scheme



where A = allylbenzene, Co =  $\text{HCo}(\text{CO})_4$ , ACo = complex, and A' = *trans*-propenylbenzene. The small amount of D incorporation might be accounted for by an exchange reaction involving the reversal of eq. a. Although our results might seem compatible with the controversial concerted 1,2-shift mechanism<sup>5</sup> recently suggested, the fact that 2-methyl-1-pentene is rapidly isomerized<sup>6</sup> by  $\text{HCo}(\text{CO})_4$  makes this proposal untenable in the present instance. Further work is in progress.

*Acknowledgment.* We wish to thank R. Vordenberg, R. Grasselli, and J. Collins for help with the mass spectral analyses; N. Phelan for help with some of the experimental work; and the Division of Air Pollution,

(5) N. R. Davies, *Australian J. Chem.*, **17**, 221 (1964); *Nature*, **201**, 290 (1964); J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **86**, 1776 (1964); *Nature*, **205**, 280 (1965); M. B. Sparke, L. Turner, and A. J. M. Wanham, *J. Catalysis*, **4**, 332 (1965).

(6) Unpublished work by N. Phelan in this laboratory.

(7) Public Health Service Predoctoral Fellow, 1962-1965.

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## Hydrocarbon Dianion Radicals

Sir:

When Koelsch's radical<sup>1</sup> ( $R\cdot$ ) is reduced with potassium in tetrahydrofuran (THF) the anion ( $R^-$ ) is readily formed. The e.s.r. signal of a dilute solution<sup>2</sup> ( $\sim 5 \times 10^{-5} M$ ) decreases in intensity with no change in spectrum as  $R\cdot$  is reduced to  $R^-$ , until a trace of radical remains. The complete conversion of the pale yellow solution of  $R\cdot$  to the blue  $R^-$  can also be followed spectrophotometrically where the 4860 Å. band for  $R\cdot$  disappears simultaneously with the appearance of the 6010 Å. for  $R^-$ . When the e.s.r. signal of  $R\cdot$  has decreased to a minimum, further reduction produces a radical with a  $g$ -value of 2.0039 and hyperfine splitting different from  $R\cdot$ . Whereas the spectrum of  $R\cdot$  is due to eight approximately equivalent hydrogens (1.8 gauss, ref. 3) the new spectrum can be well fitted to splitting from three pairs of hydrogens (3.0, 2.0, and 0.66 gauss). The new radical gives a new band at 3750 Å. with a broad shoulder 4500 Å. region. Further reduction produces first a green solution and finally a red-orange solution. The 6040 Å. band for  $R^-$  decreases simultaneously with a decrease in e.s.r. signal. Only a trace of radical is found in the red-orange solution.

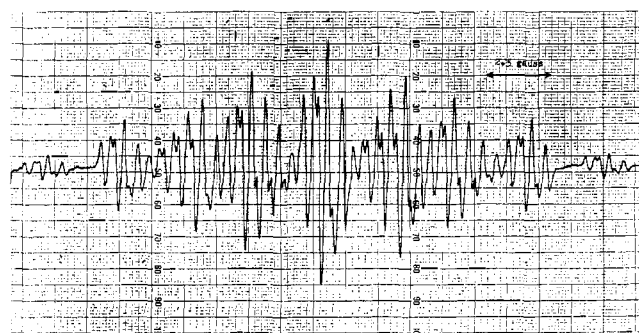


Figure 1. E.s.r. spectrum of phenanthrene-4,5-methide dianion radical in K-THF.

Solutions of the various reduction products appear to be stable for weeks. When air is admitted to the red-orange solution a rapid change of color to the blue solution of  $R^-$  is observed.<sup>4</sup> If a limited amount of air is used, the same e.s.r. spectrum is obtained as produced during the reduction sequence. Koelsch<sup>1</sup> found that  $R\cdot$

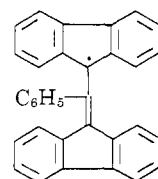
(1) C. F. Koelsch, *J. Am. Chem. Soc.*, **79**, 4439 (1957).

(2) (a) The complete e.s.r. spectrum of Koelsch's radical is difficult to resolve<sup>3</sup> although seven out of the nine groups of lines are readily obtained. (b)  $g$ -Value of Koelsch's radical = 2.0026 (J. E. Wertz, *Chem. Rev.*, **55**, 918 (1955)).

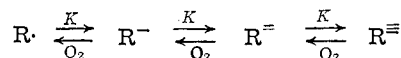
(3) R. Kuhn and F. A. Neugebauer, *Monatsh.*, **95**, 1 (1964); K. H. Hauser, *Z. Naturforsch.*, **14A**, 425 (1959); **17A**, 158 (1962).

(4) This carbanion is relatively stable to oxygen in THF but oxidizes slowly to Koelsch's radical: J. G. Pacifici, J. F. Garst, and E. G. Janzen, *J. Am. Chem. Soc.*, **87**, 3014 (1965).

could be reduced with sodium amalgam in ether to a brick-red solution containing the trisodium derivative ( $R^{3-}$ ), since upon addition of water 2-phenyl-1,3-bisbiphenylene propane could be isolated. These observations all point to the existence of a stable dianion radical<sup>5,6</sup> produced in a sequence of reductions starting from  $R\cdot$ .



Koelsch's radical



Because Koelsch's dianion radical has the same spectrum as fluorenone ketyl it can be concluded that the unpaired electron is localized in one biphenylene ring instead of equally in both of these rings as in the neutral radical.

Other hydrocarbon carbanions can be reduced to dianion radicals. 4,5-Methylenephenanthrene reacts with K-THF to produce the yellow carbanion.<sup>7</sup> When all the hydrocarbon is converted to the anion the red dianion radical I forms rapidly<sup>8</sup> (Figure 1). The orange carbanion derived from 9-phenylfluorene<sup>9</sup> is also reduced to a new radical attributed to the dianion radical.<sup>10</sup> Pentaphenylcyclopentadienyl chloride was reduced to the neutral radical<sup>11</sup> and to the orange anion. Upon further reduction a purple solution was obtained which gave a new e.s.r. spectrum of 76 lines with total line width of 21 gauss and  $g = 2.0030$ .<sup>12</sup> Quartet splitting of 0.51 gauss due to <sup>39</sup>K ( $I = 3/2$ ) was clearly resolved. At this time we are not certain if the spectrum is due to the pentaphenyl-

(5) There has been recent interest in the chemistry of polyanion radical ions: (a) N. L. Bauld, *ibid.*, **86**, 2305 (1964); (b) *ibid.*, **86**, 3894 (1964); (c) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962); (d) P. Brassem, R. E. Jesse, and G. J. Hoijsink, *Mol. Phys.*, **7**, 587 (1964).

(6) The e.s.r. spectrum of the dianion radical is essentially the same as fluorenone ketyl: (a) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963); (b) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964); (c) N. Hirota and S. I. Weissman, *ibid.*, **86**, 2537 (1964); (d) G. R. Luckhurst and L. E. Orgel, *Mol. Phys.*, **8**, 117 (1964). However, the  $g$ -value of Koelsch's dianion radical is higher than the  $g$ -value of fluorenone ketyl (2.0039 compared to 2.0028), and the visible absorption spectra are different (fluorenone ketyl has a strong absorption maximum at 5390 Å.). Because of the complete reversibility of the electron-transfer reactions (electron-transfer equilibria of the monoanion and dianion radical will be presented in a following paper) and isolation by Koelsch<sup>1</sup> of 2-phenyl-1,3-bisbiphenylene propane from the red solution of the trisodium adduct, we are convinced the spectrum is in fact due to the dianion radical and not fluorenone ketyl.

(7)  $pK_a = 22.6$ : A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Am. Chem. Soc.*, **87**, 384 (1965).

(8) The corresponding ketyl has fewer readily resolvable lines (27) and a narrower total line width (10.6 gauss in DMF, ref. 5a).

(9)  $pK_a = 18.5$ : C. H. Langford and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **82**, 1503 (1960).

(10) This spectrum is different from 9-phenylfluorenyl (E. G. Janzen, Abstracts of papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 12-17, 1965, p. 51S;  $g = 2.0029$  in nitrobenzene) or 9-fluorenone ketyl.<sup>6</sup> For 9-phenylfluorenyl dianion  $g = 2.0031$ ; coupling constants in gauss: 4.0 (four equivalent protons) and 2.7 and 0.55 (two equivalent protons).

(11) D. C. Reitz, *J. Chem. Phys.*, **34**, 701 (1961);  $g$ -value = 2.0025 (J. E. Wertz, C. F. Koelsch and J. L. Vivo, *ibid.*, **23**, 2194 (1955)).

(12) A pink solution of the corresponding ketyl gave a single unresolved line 4 gauss wide,  $g$ -value = 2.0033.