C, 49.26; H, 3.85; N, 13.89. The methyl ester had mp 190°; mass spectrum *m/e* calcd for $C_{13}H_{13}N_3O_6$, 307.0804 (found, 307.0779); ir (KBr) 1720 (C=O), 1667 (C=O ester), 1639 (COCHCO), 1510 and 1345 cm^{-1} (NO_2).

Registry No.—2-Nitro-5-(1-acetylacetonyl)azobenzoic acid, 30669-54-6, 30669-55-7 (Me ester); 3-carboxy-4-nitrobenzenediazonium chloride, 30685-31-5.

Acknowledgments.—This research was supported in part by Grant 2102 a/67 from Consejo Nacional de Investigaciones Cientificas y Técnicas, Argentina. We wish to thank Dr. R. C. Dougherty for the mass spectra and Dr. J. F. Bunnett for helpful discussions.

Reaction of Trichloromethyllithium with 4-Halonitrobenzenes

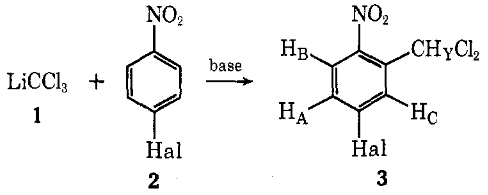
E. T. McBee,* E. P. Wesseler,[1] and T. Hodgins

Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907

Received February 17, 1971

Solutions of trichloromethyllithium (**1**) in tetrahydrofuran are reported to be stable[2,3] at temperatures below −65°. Above this temperature, decomposition occurs *via* formation of the intermediary dichlorocarbene.[4] When the reaction of **1** and 4-halonitrobenzene (**2**) was carried out in the presence of base, the product was α,α-dichloro-5-halo-2-nitrotoluene (**3**). The lack of facile methods for the direct dichloromethylation of aromatic systems, the unusual stereoselectivity, and the mechanistic possibilities prompted the following examination of this reaction.

The substrate **2** was added to a solution containing trichloromethyllithium and a catalytic amount of lithium *n*-butoxide at *ca.* −100°; a rapid color change indicated formation of a charge-transfer complex. Aliquots were withdrawn as the temperature was allowed to increase gradually to −70° but their analysis showed that the starting materials had not reacted. A reaction commenced in the region of −70 to −65° and the product isolated was subsequently identified as **3** by spectral methods and, for Hal = Cl, F, alternative syntheses.



1 **2** **3**

Thus, the nmr of **3** (Table I) contained three protons in the aromatic region; two of these protons were coupled to the third (H_A) by 8.6–9.2 and 1.7–2.8 Hz, values which indicated that the two protons were in ortho and meta positions, relative to H_A. The increased deshielding of H_A and H_C with increasing size of the halogen is consistent with previously observed[5] behavior of halobenzenes. Also the chemical shifts of H_Y were very close to the value of 451 Hz observed for α,α-dichloro-2-nitrotoluene.[6]

TABLE I

Halogen	Nmr[a] of **3**			
	H_Y	H_A	H_B	H_C
F[b,c]	453	435	483	470
			9.2	2.8
Cl[c,d]	450	450	476	486
			8.8	2.2
Br[e]	450	461	472	496
			8.7	1.9
I[f]	449	473	460	505
			8.6	1.7

[a] Chemical shifts (first entry) given in hertz downfield from TMS; coupling constants, *J* (second entry), to H_A in hertz. [b] *J*: H_Y–F 1.2; H_A–F 7.0; H_B–F 5.0; H_C–F 9.2 Hz. See also ref 6. [c] 100% conversion. [d] A trace amount of 4-chlorobenzotrichloride or an isomer was isolated and identified by mass spectroscopy. [e] 84% conversion. [f] 82% conversion.

The mass spectra for the four products (Table II) all showed the molecular ion with the correct isotopic distribution. Their fragmentation patterns were similar and the base ion in each case corresponded to loss of HCl_2 (71 mass units).

TABLE II

m/e	F	Cl	Br	I
P[a]	1.14	3.56	5.56	20.2
P − 17	2.19	1.78	1.78	2.30
P − 35	24.7	24.0	18.6	25.9
P − 45	2.97	4.0	3.33	0.57
P − 46	4.16	4.7	3.24	2.71
P − 63	24.5	26.0	21.8	22.3
P − 70	18.7	20.0	17.2	15.7
P − 71	100	100	100	100

[a] P is the molecular ion.

Alternate syntheses of **3** (Hal = Cl, F) provided conclusive evidence for the accuracy of the assigned structures. The former compound was prepared by treatment of 5-chloro-2-nitrobenzaldehyde with phosphorus pentachloride. The 5-fluoro derivative was obtained by side-chain chlorination of 5-fluoro-2-nitrotoluene; incidentally, a coproduct of this reaction was the corresponding benzotrichloride, a compound whose nmr shifts differed little or were upfield of the corresponding protons in **3** (Hal = F). The distortions caused by the interaction of the bulky trichloromethyl substituent with the nitro group are presumably responsible for this feature.

Crude yields were estimated to be nearly quantitative, since aromatic material was not present in the tarry residue that accompanied product formation in all the reactions. Handling losses and product insta-

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(1) Supported in part by the Walter Reed Army Institute of Research (DA 49-193-MD-3003); acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *J. Amer. Chem. Soc.*, **87**, 4147 (1965).

(3) G. Koebrich, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967).

(4) P. S. Skell and M. S. Cholod, *J. Amer. Chem. Soc.*, **91**, 6035, 7131 (1969), and references cited therein. The question of the precise structure of the intermediate, *i.e.*, free carbene or carbenoid, is unimportant with respect to the conclusions of this study.

(5) F. C. Stehling, *Anal. Chem.*, **35**, 773 (1963).

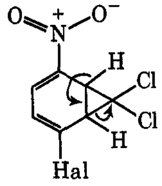
(6) The long-range H_Y coupling indicates that the conformation of this compound has the dichloromethyl proton planar and adjacent to the nitro group; such a situation satisfies the requirements of G. P. Newsoroff and S. Sternhell [*Aust. J. Chem.*, **21**, 747 (1968)]. Attempts to detect a similar long-range proton–proton coupling in α,α-dichloro-2-nitrotoluene, prepared according to the procedure of A. Kliegl [*Ber.*, **40**, 4937 (1907)], were unsuccessful; the half-height width of the $CHCl_2$ proton resonance was 1.2 Hz.

bility contributed to lower values of the actual yields. Substrate reactivity appears to follow the resonance donor properties[7] of the halogen: F > Cl > Br > I. An essential point discovered in preliminary studies was that without additional base no reaction occurred.[8] The base was conveniently prepared *in situ* from *n*-butyl alcohol and *n*-butyllithium, one of the precursors of trichloromethyllithium.[9]

Other aromatic substrates,[10] notably 4-fluorobenzonitrile and nitrobenzene,[11] failed to yield analogous products under similar reaction conditions; the former compound was totally unreactive. Unfortunately, deductions drawn later from this data may be unreliable depending on the importance of extraneous factors, such as differences in substrate solubility or the difficulties encountered with the variable quality of the *n*-butyllithium, which was always a problem.

The principal evidence against the likelihood that the trichloromethyl anion[12] was trapped by **2** is derived from the following information: (i) the proximity of the reaction temperature to the known[2] decomposition point of $LiCCl_3$; (ii) lack of reaction with 4-fluorobenzonitrile, whose susceptibility to nucleophilic attack should parallel[13] that of **2**; (iii) failure to isolate any 4-trichloromethylnitrobenzene.

Least motion chloride elimination from the trichloromethyl anion generates the electrophilic dichlorocarbene[4] as a ground-state singlet.[14] The normal mode for electrophilic attack on **2** is at the 3 position,[15] requiring in this instance cyclopropanation as in **4** in order to obtain the actual product. Alternatively, the dichlorocarbene is trapped by the nitro oxygen to give **5**, which undergoes intramolecular cyclization to **6**. Both **4** and **6** with catalytic base yield the product by the same route. However, **4** is an unlikely intermediate because aromatic compounds more reactive than **2** to electrophiles are known to be stable to dichlorocarbene.[16] Other considerations reinforce this contention. The formation of **4** (or a derivative from irreversible rearrangement[16]) should be independent of additional base. Also, the cyclopropyl protons in **4** do not appear so dissimilar in acidity, especially where Hal = F, as to yield **3** exclusively.



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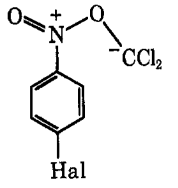

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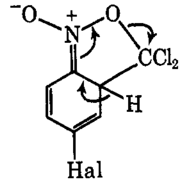

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In conclusion, if the arguments presented heretofore are valid, then the nitro oxygen is trapping dichlorocarbene. Reversibility of this process, namely **5** to **2**, accounts both for the lack of reaction in the absence of base and the lack of reaction of nitrobenzene. In addition, this explanation is in accord with the observed order of reactivity of **2**, the observed stereoselectivity, and the unreactive nature of 4-fluorobenzonitrile. There is also evidence for dihalocarbene attack on oxygen in other systems.[16,17]

Experimental Section[18]

Trichloromethyllithium was prepared from carbon tetrachloride (0.2 mol) and *n*-butyllithium (0.15 mol) according to the literature procedure.[2] *n-Butyl alcohol* (0.005 mol) was added to generate base. An external pentane–liquid nitrogen bath was used for temperature control.

α,α-Dichloro-5-halo-2-nitrotoluene (3). General Procedure.—Compound **2** (0.05 mol) was added to a stirred solution of trichloromethyllithium (*ca.* 0.1 mol) and base at −100°. The reaction vessel was covered with Dry Ice such that, when allowed to warm, the temperature was maintained at −70 to −65° for about 4 hr, whereupon it increased slowly to room temperature. The reaction mixture was rotary evaporated and the residue, preferably coated on 100 g of Chromosorb, was extracted with pentane.

α,α-Dichloro-5-fluoro-2-nitrotoluene.—The residue was chromatographed on silica gel with pentane–ether (9:1 v/v) and 8.8 g of crude product was isolated. Distillation gave the pure compound (60%): bp 85–90° (0.5 mm); $n^{25}{}_{\mathrm{D}}$ 1.5523.

Anal. Calcd for $C_7H_4Cl_2FNO_2$: C, 37.53; H, 1.80; Cl, 31.65. Found: C, 37.80; H, 1.75; Cl, 31.81.

Chlorine was bubbled for 30 hr through an irradiated solution of 5-fluoro-2-nitrotoluene in carbon tetrachloride. The solvent was removed, and samples of the residue were separated by gas chromatography. Material corresponding to the first peak *was identical* with the dichloro compound isolated in the previous experiment. For the other peak, a product was identified by nmr as α,α,α-trichloro-5-fluoro-2-nitrotoluene: H_A, 423, H_B, 447; H_C, 473 Hz (J_{AB} = 8.9; J_{AC} = 2.9; J_{AF} = 7.0; J_{BF} = 5.2; J_{CF} = 13.0 Hz).

α,α,5-Trichloro-2-nitrotoluene.—Crude product from Soxhlet extraction of the residue was distilled and gave the pure compound (56%): bp 105–109° (0.4 mm); $n^{25}{}_{\mathrm{D}}$ 1.5928.

Anal. Calcd for $C_7H_4Cl_3NO_2$: C, 34.96; H, 1.67; Cl, 44.23. Found: C, 35.14; H, 1.83; Cl, 44.43.

5-Chloro-2-nitrobenzaldehyde was treated with phosphorus pentachloride according to the procedure of Kliegl.[6] A sample of product identical with that prepared previously was isolated by gas chromatography.

α,α-Dichloro-5-bromo-2-nitrotoluene.—The pentane extract gave material which was examined by nmr; analysis of the aromatic region indicated the presence of only product and starting material. Repetitions of this reaction never decreased the proportion of the latter below 16%. Attempted distillation of the mixture was unsuccessful; however, pure samples of the desired compound were isolated by gas chromatography and identified by spectral methods.

α,α-Dichloro-5-iodo-2-nitrotoluene was prepared as described in the previous experiment. Identification was made on the crude product, since some decomposition occurred in the gc separation.

Analytical Data.—The intensities relative to the base ion (P − 71) in the mass spectra of **3** for the ions of higher molecular

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[7] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 3146 (1963).

[8] Equimolar amounts of powdered LiOH gave low conversions.

[9] Dichloromethyllithium also reacts with **2**, though the conversions to the corresponding 2-chloromethyl-4-halonitrobenzenes were low (<20%).

[10] Other compounds studied included 4,4,-dichlorobiphenyl, 2,4-dinitrofluorobenzene, 1,4-dinitrobenzene, 3,4-dichloronitrobenzene, and 3-chloronitrobenzene.

[11] In one experiment with nitrobenzene, a trace amount of material tentatively identified as bis(4-nitrophenyl)tetrachloroethane was isolated.

[12] Aryllithiums add to aromatic nitro groups [P. Buck, *Angew. Chem., Int. Ed. Engl.*, **8**, 120 (1969)] and there are examples of direct carbanionic attack on nitro aromatics [R. B. Davis, L. C. Pizzini, and J. D. Benigni, *J. Amer. Chem. Soc.*, **82**, 2913 (1960)]. In both cases, the nitro group was deoxygenated in the process of yielding products.

[13] H. Suhr and H. Grube, *Ber. Bunsenges. Phys. Chem.*, **70**, 544 (1966).

[14] R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).

[15] (a) Z. J. Allan, *Chem. Listy*, **52**, 2014 (1958); (b) P. M. Heertjes, *Recl. Trav. Chim. Pays-Bas*, **77**, 693 (1958).

[16] (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, pp 178 ff; (b) W. von E. Doering and W. A. Henderson, *J. Amer. Chem. Soc.*, **80**, 5274 (1958).

[17] T. G. Miller and J. W. Thanassi, *J. Org. Chem.*, **25**, 2009 (1960).

[18] All boiling points are uncorrected. Elemental analyses were determined by Dr. C. S. Yeh, Purdue University. Ir and nmr spectra were recorded by a Beckman IR-8 spectrophotometer or Varian A-60A spectrometer, respectively. Mass spectra were measured with a Hitachi Perkin-Elmer HU-6D high-resolution instrument. A Varian Aerograph Model 200 gas chromatograph equipped with a 6 ft × 0.25 in. stainless steel column packed with QF-1 on Chromosorb W was used in the separations. *n*-Butyllithium was obtained from Alfa Inorganics, Inc.

weight are given in Table II. The results were simplified by ignoring isotopic variations.

The infrared spectra of the products were very similar, in particular for absorptions in the regions 3.18–3.50 (w, aryl H), 7.36–7.48 and 6.50–6.60 (s, NO_2), 6.20–6.40 (m, aryl ring), and 11.0–14.0 μ (s, Hal).

Registry No.—**1**, 2146-66-9; **3** (Hal = F), 30669-49-9; **3** (Hal = Cl), 30669-50-2; **3** (Hal = Br), 30669-51-3; **3** (Hal = I), 30669-52-4; α,α,α-trichloro-5-fluoro-2-nitrotoluene, 712-17-4.

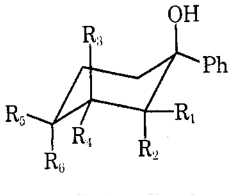
Stereochemical Considerations of the Reactions of Phenylmagnesium Bromide and Phenyllithium with Isomeric Methylcyclohexanones

John R. Luderer, John E. Woodall,
and James L. Pyle*

*Hughes Chemical Laboratories, Miami University,
Oxford, Ohio 45056*

Received January 12, 1970

We wish to describe the preparation of isomeric methyl-1-phenylcyclohexanols (**1**–**6**) prepared by the addition of phenylmagnesium bromide or phenyllithium to the corresponding methylcyclohexanones. In each instance the possibility of formation of two geometric isomeric products exists. The relative propensity of the phenyl to add cis or trans to the methyl as a function of the position and conformation of the methyl, and as PhMgBr or PhLi, is of interest. Also we wish to describe the respective separations of the 2-methyl, 3-methyl, and 4-methyl mixtures and the distinctions which permit structure assignments.



1, $R_1 = CH_3$; all others H
2, $R_2 = CH_3$; all others H
3, $R_3 = CH_3$; all others H
4, $R_4 = CH_3$; all others H
5, $R_5 = CH_3$; all others H
6, $R_6 = CH_3$; all others H

The results of the syntheses of the respective isomers are given in Table I. In each instance the percentages refer to material recovered by elution from a silica gel column. Some olefin formation arising from dehydration of the carbinols during work-up was usually observed, but this was not significant. The analysis of the 2-methyl mixture was also accomplished by gas chromatographic separation on Carbowax 20M and gave the same result as elution from silica gel. The other carbinol mixtures did not separate under the same conditions by gas chromatography.

The establishment of stereochemistry was based on the frequency of the OH stretching absorption in the infrared spectra, on the relative mobility on the silica column, and most importantly on the nmr spectrum. In the case of the 4-methyl system the compounds had previously been reported and their structures rationalized by a similar approach.[1]

It is known that the coupling of a methyl group with an adjacent methine proton in a cyclohexane ring will be dependent upon the conformational status of the coupling moieties.[2] If the methyl is equatorial, signal broadening due to virtual coupling reduces the apparent coupling constant. If one can assign a preferred conformation to the molecule on the basis of the steric requirements of CH_3, OH, and C_6H_5, then the nmr spectra may distinguish the stereoisomers.

Upon consideration of conformational preferences and relative stabilities of the two chair conformations, it is clear that the phenyl-equatorial, hydroxyl-axial arrangement is energetically preferred in all isomers except that of **3**, where there is a serious 1,3-cis diaxial interaction in that conformation between the methyl and hydroxyl groups.[3] The pyridine solvent shift for **3** also questions this latter conformation. A methyl–hydroxyl cis diaxial arrangement would be expected to lead to a deshielding of the methyl signal in pyridine of about 0.20–0.40 ppm compared with the chemical shift in $CDCl_3$.[4] No such deshielding is observed.

The nmr spectra of the 4-methyl compounds **5** and **6** are in agreement with these configurational and conformational assignments, with the predicted J values observed (Table I). Moreover, the expected assignment conforms with the observed elution order from silica–**5** is eluted first—and a slight difference in the infrared spectrum showing more extensive H bonding in **6** where the OH is less hindered. The 3-methyl compounds **3** and **4** show similar correlation of coupling constants with elution order. The more hindered **3** is eluted first. No definitive difference is observed in the infrared spectra.

The coupling constant for **2** is consistent with prediction, but that for **1** is larger than expected for the equatorial methyl–axial proton coupling. Moreover, methyl signals in both compounds are significantly shielded compared to the other isomers. The effect of the phenyl group is expected to cause the shielding observed for the 2-methyl, and its effect on the axial 2-methine proton can explain the large J observed for **1**. The shielding of this proton by the phenyl results in a larger value for $\Delta\nu/J$ than observed in the other instances. Hence, virtual coupling of the methyl signal disappears. The significant diminution in H bonding in 1 and the elution order both support these structure assignments. It is also noteworthy that the less polar **1** is the only isomer of the six compounds reported here which is a liquid at ambient conditions.

Reported results of additions of Grignard reagents or organolithium reagents to cycloalkanones vary markedly depending upon reagents and conditions. One tendency noted, however, is that 2-substituted alkylcycloalkanones result in preference for the product in which the adding group is trans to the alkyl group in the

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(1) E. W. Garbisch, Jr., and D. B. Patterson, *J. Amer. Chem. Soc.*, **85**, 3228 (1963).

(2) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, p 298, and references cited therein.

(3) E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 236; J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

(4) P. V. DeMarco, E. Farkas, D. Doddrell, B. L. Mylari, and E. Wenkert, *J. Amer. Chem. Soc.*, **90**, 5480 (1968); B. V. Paranjape and J. L. Pyle, *J. Org. Chem.*, **36**, 1009 (1971).