1,3-Diphenyl-2,2-dideuterio-1,3-propanedione. Dibenzomethane (4 g) was dissolved in 50 ml of dry THF and 25 g of D_2O was added. The mixture was refluxed 3 hr and then stirred at room temperature 72 hr. The solvent was removed, and the crystals were filtered. The procedure was then repeated, giving 2.4 g of the dideuterated compound, mp 78°. Dideuteration was confirmed by nmr. The dianion radical gave an esr spectrum identical with that obtained from the undeuterated substrate (alkali metal generation in THF and electrolytic generation in DMF).

1,1,1,3-Tetradeuterio-2,4-diphenyl-2-buten-4-one. Dypnone (5 g) was dissolved in 50 ml of DME. Potassium *t*-butoxide (0.5 g) and D_2O (20 ml) were then added, and the mixture was refluxed 56 hr. Work-up gave 4.1 g of tetradeuterated dypnone [bp 145° (0.25 mm)]. The nmr spectrum showed only aromatic protons. The esr spectrum of the corresponding dianion radical was unresolvable.

2,2,4,4,4-Pentadeuterio-1-phenyl-1,3-butanedione. Benzoylacetone (5 g) was dissolved in 50 ml of DME. Potassium *t*-butoxide (0.5 g) and D_2O (20 ml) were then added, and the solution was refluxed for 7 days. Work-up gave 3.9 g of pentadeuterated product, which again showed only aromatic protons in the nmr.

Acknowledgments. Financial support from the National Institutes of Health and the Robert A. Welch Foundation is gratefully acknowledged.

Dianion Radicals. II. Tropenide Systems

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Contribution from the Department of Chemistry, University of Texas,
Austin, Texas 78712. *Received March 15, 1967*

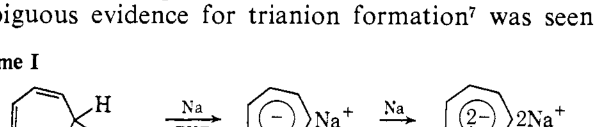
Abstract: The esr and visible spectra of the cycloheptatrienide (tropenide) dianion radical, the first and simplest reported dianion radical, are described and discussed. Disodium tropenide shows an extraordinarily large double metal splitting in its esr spectrum ($a_{2\mathrm{Na}^+} = 1.76$ gauss), at temperatures ranging from −100° to ambient and in several ethereal solvents. It is thus shown to exist as contact ion triplets (or higher agglomerates) under these conditions. Dipotassium tropenide evinces no metal splitting, apparently because of rapid metal ion exchange. The proton hyperfine splitting of tropenide ($a = 3.52$) is considerably less than that for tropyl under comparable conditions, a fact predicted by the Colpa–Bolton equation. The esr spectra of the benzo- and dibenzo[1,2:4,5]tropenide dianion radicals are also reported, simulated, and correlated with HMO and McLachlan calculations.

The cycloheptatrienide (tropenide) dianion radical, the first recognized hydrocarbon dianion radical, was the subject of a recent preliminary report.[1] It is the intent of this paper to elaborate on that report and to describe also the benzotropenide and dibenzo[1,2,4,5]-tropenide dianion radicals. Since the initial report, several other, more complex, hydrocarbon radicals have been described.[2-5]

Results and Discussion

Cycloheptatrienide Dianion Radical. Solutions of tropyl methyl ether in THF, DME, or 2-methyl-THF turn blue almost immediately upon contact with alkali metal mirrors. After only a few minutes the solutions are intensely blue ($\lambda_{\max}^{\mathrm{THF}}$ 620 mμ, Na^+ salt), but show no esr absorption. That these initially formed solutions contain the diamagnetic tropenide ion is affirmed by the work of Dauben and Rifi.[6] In about 15 min more, the solutions have turned blue green ($\lambda_{\max}^{\mathrm{THF}}$ 570 mμ, Na^+ salt) and have developed a large concentration of free radicals, as shown by esr measurements. The esr spectra are essentially solvent independent for the three solvents mentioned, but do vary significantly with the nature of the alkali metal used. With potassium, an octet, $a_H = -3.52$ gauss (7 H, sign assumed), is observed (Figure 1). When sodium is used, a more complex and well-resolved spectrum is obtained which, although a casual inspection does not necessarily reveal it, still contains the same basic octet ($a_H = -3.52$), further split into septets ($a_{2\mathrm{Na}^+} = 1.76$ gauss). Since ^{23}Na has nuclear spin $I = {}^3/_2$, two equivalent sodium gegenions should split each esr absorptionin to $2I + 1 = 7$ lines. The experimental and computer-simulated spectra, as well as a magnified version of the former, are reproduced in Figures 2, 3, and 4, respectively. The latter, magnified, spectrum reveals exactly the right number of lines for the aforementioned interpretation. (The outermost line of the basic octet is designated by an asterisk.) These visible and esr spectral observations, in conjunction with ancillary observations to be mentioned below, confirm beyond reasonable doubt the structure of the radical as the tropenide dianion radical, formed by the sequence shown in Scheme I. No unambiguous evidence for trianion formation[7] was seen either in the form of attenuation of the esr signal after prolonged reaction time in the presence of excess metal or of alteration of the visible absorption of the dianion radical or appearance of a new maximum. It seems clear that the trianion, if formed at all, is present in quite small amounts.

Scheme I



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[1] N. L. Bauld and M. S. Brown, *J. Am. Chem. Soc.*, 87, 4390 (1965).

[2] P. Dowd, *ibid.*, 87, 4968 (1965).

[3] E. G. Janzen and J. G. Pacifici, *ibid.*, 87, 5504 (1965).

[4] E. G. Janzen, J. G. Pacifici, and J. L. Gerlock, *J. Phys. Chem.*, 70, 302 (1966).

[5] N. L. Bauld and J. Zoeller, *Tetrahedron Letters*, 885 (1967).

[6] H. J. Dauben, Jr., and M. R. Rifi, *J. Am. Chem. Soc.*, 85, 3041 (1963).

[7] R. Breslow and H. W. Chang, *ibid.*, 87, 2200 (1965), have reported the heptaphenyltropenide ion to cleave to pentaphenylcyclopentadienide and stilbene upon reaction with potassium.

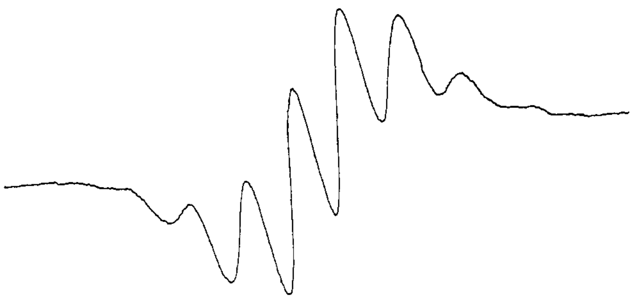


Figure 1. The esr spectrum of dipotassium tropenide.

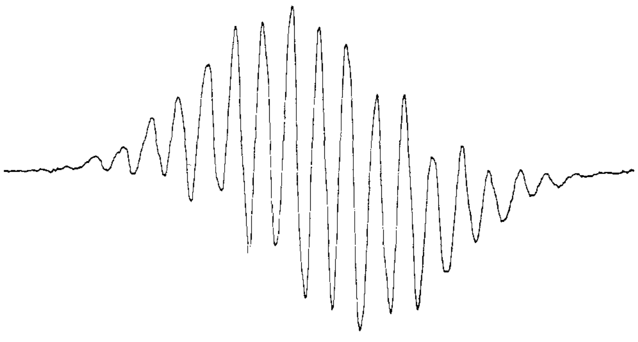


Figure 2. The esr spectrum of disodium tropenide.

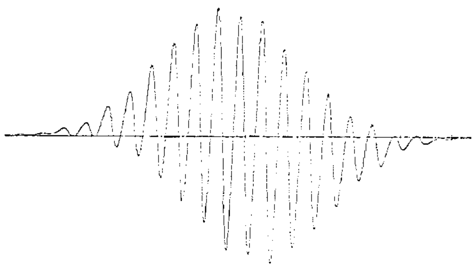


Figure 3. The simulated esr spectrum of disodium tropenide.

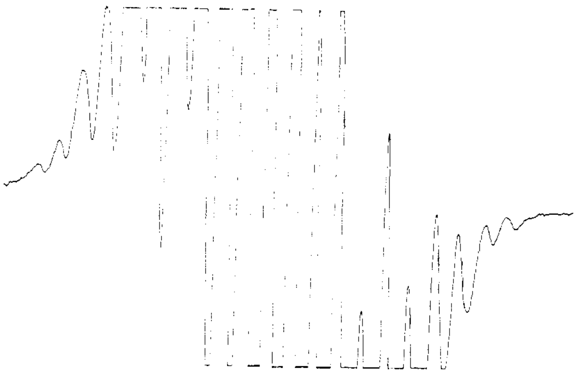
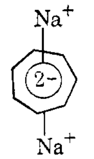


Figure 4. Amplified esr spectrum of disodium tropenide.

The fact that splittings are observed from two equivalent sodium ions is excellent evidence for the dianionic nature of the free radical. No instances of splittings from *two* alkali metals have been reported for hydrocarbon monoanion radicals in ethereal solvents. Sodium naphthalenide does exhibit such a double metal splitting in the relatively nonpolar solvent tetramethylethylenediamine, presumably reflecting ion quadruplet formation. Metal ketyls also tend to dimerize, even in ethereal solvents.[8] The magnitude of the metal splitting is also impressively large. In fact, we are aware of no other hydrocarbon anionic radical which has such a large metal splitting in any solvent. This provides excellent evidence that disodium tropenide exists as a contact ion triplet (**1**), or higher aggregates, in all of the three solvents studied.



1

The surprising disparity between the esr spectra of dipotassium and disodium tropenide has a close and reassuring precedent in the work of Atherton and Weissman on the naphthalene anion radical.[9] It was found that the esr spectrum of potassium naphthalenide is unsplit by the metal ion in any of the usual ethereal solvents. Sodium naphthalenide, on the other hand, manifests a large splitting ($a_{\mathrm{Na}^+} = 1.05$, one sodium ion) in THF solution. The smaller sodium ion thus appears to form tighter contact ion pairs or triplets than does potassium. It is further apparent that disodium tropenide is more tightly (electrostatically) bound than is sodium naphthalenide, since the latter is dissociated in DME solution (metal splitting vanishes) but the former maintains exactly the same metal splitting as in THF. This interpretation dovetails nicely with the fact that the metal splitting is greater in the tropenide system than in the naphthalenide system. With such a high charge density per unit area, it would be expected that the tropenide dianion radical would support exceptionally strong electrostatic bonding.

A monocyclic anion radical more nearly similar in size to the tropenide system is the COT anion radical.[10,11] Sodium cyclooctatetraenide has $a_{\mathrm{Na}^+} = 0.9$ gauss in THF, and a metal splitting appears to remain in DME.[10] The corresponding potassium salt yields an esr spectrum unsplit by metal nuclei in either THF or DME. This behavior is similar to that observed for the tropenide dianion radical except that the metal splitting is much larger in the latter.

The benzene anion radical apparently cannot be made using sodium. The potassium salt, as in the previous cases, shows no metal splitting.[12]

The esr spectra demonstrate that disodium tropenide is undissociated in the concentration range 10^{-2}–10^{-4} *M* and at temperatures ranging from ambient to −100° in any of the ethereal solvents studied. Visible spectral results confirm the lack of effect of solvent and concentration. The tropenide DAR has $\lambda_{\max}^{\mathrm{THF}}$ 570 mμ and $\lambda_{\max}^{\mathrm{DME}}$ 566 mμ, and neither is appreciably shifted in the concentration range mentioned. This is also true of sodium tropenide ($\lambda_{\max}^{\mathrm{THF}} = \lambda_{\max}^{\mathrm{DME}}$ 620 mμ). In both cases MeTHF causes a small shift ($\lambda_{\max}$ 586 and 610 mμ) which

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[8] A. H. Reddoch, *J. Chem. Phys.*, **43**, 3411 (1965).

[9] N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961).

[10] H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963).

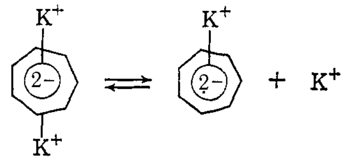
[11] R. D. Allendoerfer and P. H. Rieger, *ibid.*, **87**, 2336 (1965).

[12] T. R. Tuttle, Jr., and S. I. Weissman, *ibid.*, **80**, 5342 (1958). In our experience, either potassium or sodium–potassium alloy is required.

may reflect further ion agglomeration above that in THF or DME.

Although dipotassium tropenide gives no metal esr splitting, it nevertheless seems likely that it also exists primarily as ion triplets which are, however, rather easily dissociable (Scheme II). Such a rapid intermolecular exchange of metal ions would, of course, wipe out the metal splitting. The postulated exchange must be quite rapid even at −100°, since potassium splittings are not observed even at this low temperature.

Scheme II



As in the naphthalene and COT cases, no variation of the proton hfs of the tropenide DAR with temperature, solvent, or metal was observed.

The proton hfs of $Tr^{2-}\cdot$ is of great interest. Of course the fact that splittings are observed from seven equivalent protons does not necessarily imply a completely symmetrical dianion radical. Rapid oscillation between unsymmetrical structures would equally well explain this datum. The magnitude of the hfs splitting is of greater immediate utility. Various relationships have been developed for predicting hfs from calculated or known odd electron (or spin) densities. The first and simplest one was the McConnell equation (1).[13]

$$a_i = Q\rho_i = -27\rho_i \tag{1}$$

The σ–π interaction between an odd electron in a π orbital and a hydrogen σ bonded to carbon i was assumed to be proportional to the odd electron density (ρ_i) at that particular carbon. This relationship is semiquantitatively fairly satisfactory, but fails to explain the rather large difference in the hfs of anion and cation radicals of the same π system, which should, according to the pairing theorum, have the same odd electron density distribution. Evidence that they do have the same or nearly the same spin densities has been presented.[14] Accordingly, Colpa and Bolton[15] have revised the McConnell equation to include the effect of charge density (q_i). The σ–π interaction "constant" is allowed to vary with q_i, being greater for more positive q_i (eq 2). This equation correlates the available data fairly well, certainly much better than the simple McConnell version.[16] A third relationship has been suggested by Giacometti, Nordio, and Pavan (eq 3).[17] Here ρ^{nn} is the spin density

$$a_i = Q_{\mathrm{eff}}\rho_i = (-27 - 12.8q_i)\rho_i \tag{2}$$

$$a_i = -27\rho_i - 6.3\rho^{nn} \tag{3}$$

in the π bonds linking C_i to its nearest neighbors (*i.e.*,

$$\sum_j C_{ij}$$

where the atoms j are bonded to carbon i). In all three cases we have used the parameters recommended by Snyder.[16] The values of the proton hfs for the tropenide dianion radical and the tropyl radical predicted by each of these three equations and those actually observed are tabulated in Table I. Note that the Colpa–Bolton equation provides by far the best fit of the data. Both the McConnell and G–N–P equations predict $a_{Tr\cdot} = a_{Tr^{2-}\cdot}$. We believe this is excellent evidence for the essential correctness of the C–B approach, in which q_i is the most important factor causing variations in Q_{eff}.

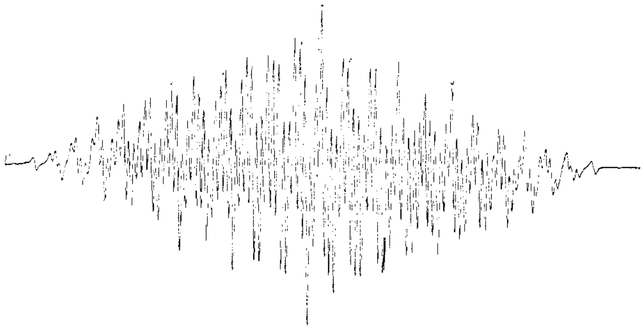


Figure 5. The esr spectrum of disodium benzotropenide.

Table I

Equation	$a_H^{\mathrm{calcd}}(Tr\cdot)^a$	$a_H^{\mathrm{calcd}}(Tr^{2-}\cdot)^b$
McConnell	−3.86	−3.86
Colpa–Bolton	−3.86	−3.34
Giacometti–Nordio–Pavan	−3.46[c]	−3.46[c]

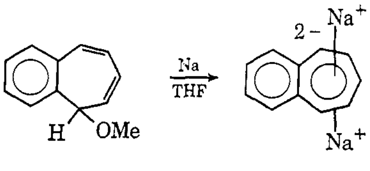
[a] $a_H^{\mathrm{exptl}}(Tr\cdot) = -3.92$ at −50°. [b] $a_H^{\mathrm{exptl}}(Tr^{2-}\cdot) = -3.52$. [c] An average was taken over the two HMO degenerate ABMO's.

The a_H for $Tr^{2-}\cdot$ is temperature invariant over the range −100° to ambient. That a variation of 0.1 gauss would have been detected was verified by computer simulations. The hfs of the tropyl radical changes by 0.04 gauss over the same range.[18] Such a small variation might not have been detected in our spectra.

Three separate determinations of the g value of the tropenide dianion radical gave 2.00270 ± 0.00001, a value unexceptional among organic anion radicals.

Benzotropenide Dianion Radical. The benzotropenide anion has a vacant HMO at $E = \alpha - 0.55\beta$ which, although of higher energy than the corresponding HMO of tropenide, is still quite low lying for an anion. As expected, the dianion radical was readily generated in a manner similar to that used in the tropenide case (Scheme III). The first detectable radical was the dianion radical. Apparently the neutral radical is reduced too rapidly for detection under our conditions. The experimental and computer-simulated esr spectra are reproduced in Figures 5 and 6. The experimental

Scheme III



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(13) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(14) J. R. Bolton and G. K. Fraenkel, *ibid.*, **40**, 3307 (1964). The ^{13}C splittings from the 9,10 positions of the anthracene anion and cation radicals are nearly equal, in contrast to the 9,10 proton splittings in the two species.

(15) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

(16) L. Snyder and T. Amos, *J. Chem. Phys.*, **42**, 3670 (1965).

(17) G. Giacometti, C. L. Nordio, and M. V. Pavan, *Theoret. Chem. Acta*, **1**, 404 (1963).

(18) G. Vincow, *et al.*, *J. Am. Chem. Soc.*, **87**, 3527 (1965).

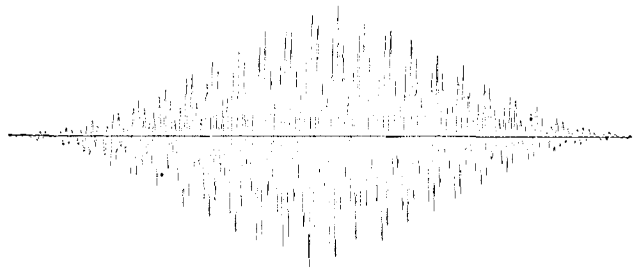


Figure 6. The simulated esr spectrum of disodium benzotropenide.

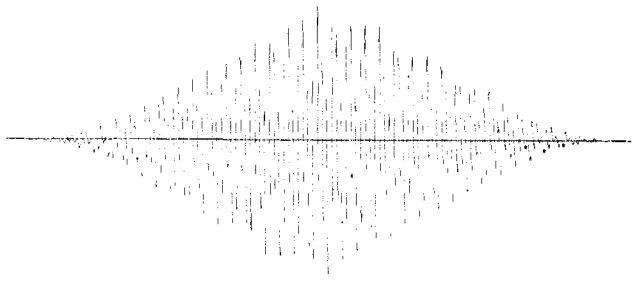


Figure 8. The simulated esr spectrum of disodium dibenzotropenide.

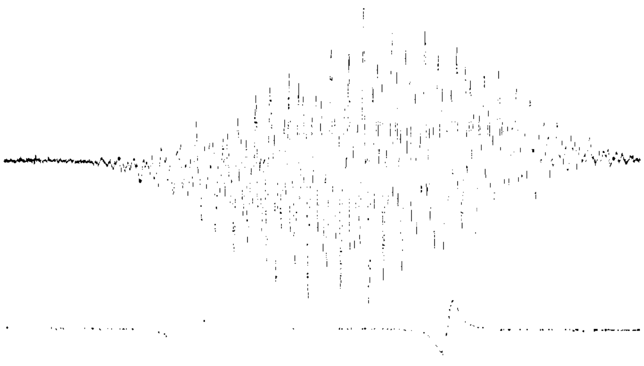
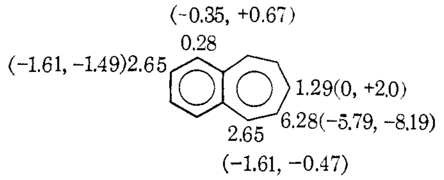


Figure 7. The esr spectrum of disodium dibenzotropenide.

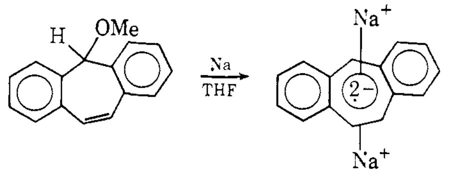
and calculated splittings are given in structure **2**. The first number given inside the parentheses represents the HMO, the second a McLachlan spin density calculation. The experimental hfs are given outside the parentheses. The C–B equation was used in both cases. The agreement is only fair, but the qualitative predictions of both calculations are born out. A large triplet and doublet are observed. In addition, a metal ion septet is observed ($a_{2\mathrm{Na}^+}$ = 1.04 gauss), as in the tropenide case. Since the benzotropenide dianion radical has a smaller charge density per carbon, it is unsurprising that the metal hfs is smaller than that for $\mathrm{Tr}^{2-}\cdot$. In addition to the double metal splitting, the benzotropenide dianion radical is distinguished from the corresponding neutral radical by the fact that the latter should have a large doublet splitting arising from the proton at the 1 position ($a_1^{\mathrm{HMO}} \approx$ 13 gauss).

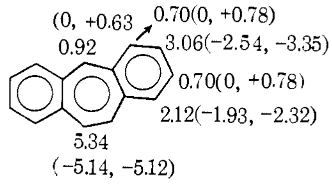


2

The *g* value (2.00245 ± 0.00001) is slightly but not dramatically smaller than that for the tropenide dianion radical.

Dibenzotropenide Dianion Radical. The energy of the relevant HMO is $E = \alpha - 0.50\beta$. The previously described procedure was again used to generate the dianion radical. The splittings are represented in structure **3** (Figures 7 and 8). Excellent agreement with the McLachlan calculations is observed. The Hückel predictions are also fairly accurate except for the failure to predict negative spin density and therefore splitting at the 1, 3, and 5 positions. A double metal splitting ($a_{2\mathrm{Na}^+}$ = 0.70) is observed once more and is further reduced in magnitude in comparison to the benzotropenide DAR. Once more, the DAR was readily distinguished from the neutral radical by the absence of a large (*ca.* 15 gauss) predicted splitting from the 1 position of the latter. The 1-deuteriodibenzotropenide dianion radical gave a very similar esr spectrum which could be simulated by omitting the doublet splitting (a_1^{H} = 0.70 gauss) and replacing it with a deuterium splitting of 0.10 gauss.





3

The *g* value (2.00268 ± 0.00002) was again unexceptional and is nearly identical with that of the parent tropenide dianion radical.

Experimental Section

The equipment and general procedures used were described in the previous paper. In the generation of the dianion radicals of this paper the sodium hydride treatment was unnecessary and was omitted.

1-Methoxy[2,3]benzocycloheptatriene. [2,3]Benzotropone[19] (0.85 g) in dry methanol (10 ml) was added dropwise to 0.38 g of sodium borohydride at 0°. After stirring the solution 15 min, concentrated sulfuric acid was added dropwise to the cooled solution, giving an intense yellow, thick, solution. A further 25 ml of dry methanol containing 4 ml of concentrated sulfuric acid was added, the mixture was stirred 30 min, then poured into 50 ml of ether and extracted once with 50 ml of water. The ether layer was worked up to give 0.35 g of the ether, bp 65° (50 μ), characterized by its nmr and infrared spectra. The former excluded any appreciable admixture of the isomeric benzo[4,5]tropyl methyl ether. The proton α to the methoxyl function appeared as a clear doublet (τ 6.1) instead of the triplet expected for the isomeric ether.

1-Methoxy[2,3:6,7]dibenzocycloheptatriene. Aluminum hydride (0.13 g) was suspended in 25 ml of anhydrous ether (0°). To this was added 2.0 g of [2,3:6,7]dibenzotropone[20] in 30 ml of ether, during a period of 20 min. The mixture was refluxed 1 hr and cooled to 0°, whereupon ice water (50 ml) and then cold concentrated hydro-

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(19) G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1959).

(20) Aldrich Chemical Company, Inc.

chloric acid (10 ml) were added. The ether layer was separated, washed several times, and treated with 5 ml of concentrated hydrochloric acid. The deep pink color was dispelled by 25 ml of methanol; the mixture was stirred 30 min and worked up as usual. The ether (1.1 g) boiled at 131° (40 μ) (colorless, viscous oil). The 1-deuterio derivative was prepared similarly using aluminum hydride. Both were characterized by their infrared and nmr spectra.

Acknowledgments. Financial support from the National Institutes of Health and the Robert A. Welch Foundation is gratefully acknowledged.

A Stereospecific Friedel–Crafts Reaction. The Alkylation of Benzene with γ-Valerolactone

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Received February 17, 1967

Abstract: Alkylation of benzene with (*S*)-(−)-γ-valerolactone in benzene solvent with 1.2 equiv of aluminum chloride gives (*R*)-(−)-γ-phenylvaleric acid with 40% net inversion of configuration. The reaction appears to involve racemization of an intermediate species with the alkylation competing with return to starting material.

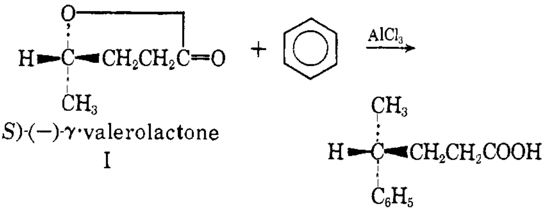
Friedel–Crafts reactions have been studied extensively and used widely in organic chemistry. The entire field has been reviewed recently in great detail[1] and needs little introduction. In the general case, the Friedel–Crafts alkylation can be written as

$$RY + ArH \xrightarrow{\text{Lewis acid}} RAr + HY \qquad (1)$$

where Y can be almost any leaving group.[1] Among the more common RY's are alkyl halides, alcohols, ethers, and esters.

Because of the general utility of this reaction, it is natural to examine the stereochemistry in order to expedite synthetic schemes as well as to help in understanding the reaction. All previous studies have demonstrated at best only minute stereospecificity; the general result in these reactions is extensive racemization and rearrangement. Thus, for example, Price and Lund[2] observed 1% net inversion in alkylation of benzene with 2-butanol and boron trifluoride. Similarly, Burwell and his co-workers found small but measurable inversion in alkylation with alcohols[3] and ethers.[4] In an experiment designed to distinguish racemization occurring independently from rearrangement, Streitwieser and Stang[5] showed that 2-propanol-1,1,1-d_3 gives racemic products in the presence of BF_3, while neither starting material nor products are racemized under the reaction conditions. These experiments suggest that, in general, Friedel–Crafts reactions of secondary and tertiary moieties proceed through intermediates which can racemize (or are racemic) and then give the products without return to starting material. Sharman[6] has discussed a generalized mechanism which includes this requirement and also accounts for the reactions of primary systems. Such reactions apparently proceed by a displacement process since the kinetics are first order in aromatic species and the products are not completely rearranged.[7]

A convenient synthesis of γ-phenyl-substituted carboxylic acids can be achieved by the alkylation of benzene with γ-lactones and aluminum chloride. This reaction has been known for many years and has been studied by Eijkman,[8] Christian,[9] and Truce and Olson.[10] Studies of its scope have shown that it proceeds in good yield and, surprisingly, without rearrangement. In an effort to synthesize γ-phenylvaleric acid-γ-*d*, we attempted the alkylation of benzene with γ-valerolactone-γ-*d*. After observing that this reaction proceeded with more than 96% incorporation of deuterium in the γ position of the product, we then examined the reaction to see whether there was any stereospecificity. We observed that reaction 2 proceeds with as much as 40% over-all net inversion, making it the first-known Friedel–Crafts reaction with extensive stereochemical integrity.



(*S*)-(−)-γ-valerolactone
I

(2)

(*R*)-(−)-γ-phenylvaleric acid
II

Results

In order to determine the stereochemical course of this reaction, it is necessary to know the absolute configurations of starting material and product. Fortunately these have both been related through unequivocal chemical means to lactic acid. Most of the relationships are known from the work of Levene and Haller. The configurations are related as follows:

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[1] G. A. Olah, Ed., "Friedel–Crafts and Related Reactions," Interscience Publishers, Inc., New York, N. Y., 1963.

[2] C. C. Price and M. Lund, *J. Am. Chem. Soc.*, **62**, 3105 (1940).

[3] R. L. Burwell, Jr., and S. Archer, *ibid.*, **64**, 1032 (1942).

[4] R. L. Burwell, Jr., L. M. Elkin, and A. D. Shields, *ibid.*, **74**, 4570 (1952).

[5] A. Streitwieser, Jr., and P. J. Stang, *ibid.*, **87**, 4953 (1965).

[6] S. H. Sharman, *ibid.*, **84**, 2945 (1962).

[7] H. Jungk, C. R. Smoot, and H. C. Brown, *ibid.*, **78**, 2185 (1956), and earlier papers cited therein.

[8] J. F. Eijkman, *Chem. Zentr.*, [I] 1416 (1904).

[9] R. V. Christian, *J. Am. Chem. Soc.*, **74**, 1591 (1952).

[10] W. E. Truce and C. E. Olson, *ibid.*, **74**, 4721 (1952).