kcal/mol.[11] The failure of I and II to undergo intramolecular exchange reactions is consistent with the Muetterties polarity rule[1a,b] which states that electropositive substituents preferentially occupy the equatorial sites of a trigonal bipyramid. Presumably the reluctance of the methyl groups to occupy axial sites raises the $\Delta G^{\ddagger}$ for pseudorotation above 16 kcal/mol, thus making the intermolecular process the energetically favored route.

While the present evidence does not completely eliminate the possibility of an impurity-catalyzed exchange process, we consider that such a mechanism is highly unlikely for the following reasons. (i) Consistent activation parameter data were obtained for three different samples for both I and II. In the case of I, one of the samples was prepared by an alternative synthetic procedure.[12] If the reaction were catalyzed by adventitious impurity, one would expect the rates and consequent activation parameters to vary incoherently. (ii) The results were unaffected by the presence of NaF. While NaF does not completely eliminate fluoride impurity from solution, one would, nevertheless, anticipate a sensitivity of the rate to the presence of the scavenger if the observations were due to fluoride ion catalysis. (iii) The reactions are second order in the phosphoranes I and II. Although it might be possible to devise a series of steps for a catalyzed reaction which resulted in a second-order dependence on phosphorane, we consider that such a sequence is improbable.

**Acknowledgment.** The authors are grateful to the Robert A. Welch Foundation and to the National Science Foundation (Grant No. GP 9518) for financial support.

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(11) *E.g.*, the $E_a$'s for $Cl_2PF_3$ and $(C_2H_5)_2NPF_4$ are 6.5 ± 2 and 12.8 ± 2 kcal/mol, respectively: E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 3, 1298 (1964); R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, 4, 496 (1965).

(12) The reaction of $(CF_3)_3P$ with $(CH_3)_3P$ produces useful yields of I. This reaction and other oxidative fluorinations with $(CF_3)_3P$ will be the subject of a forthcoming publication.

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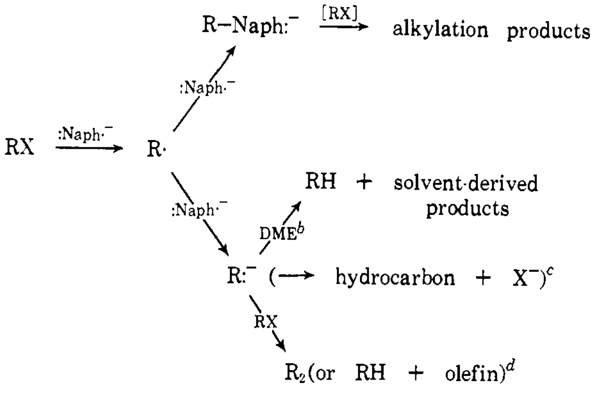
*Received June 8, 1970*

## Unusual Chemically Induced Nuclear Spin Polarization in Reactions of Sodium Naphthalene with Alkyl Halides

*Sir:*

There is strong chemical evidence that reactions of sodium naphthalene with alkyl halides proceed through intermediate alkyl radicals (Scheme I).[1] Acting on the presumption that this was sufficient grounds for seeking chemically induced nuclear spin polarization phenomena in these reactions, we sought and found them.[2] The conditions under which the polarizations appear to be maximal and the nature of the polarizations are of interest in connection with the theory of the phenomenon. In particular, they differ from those predicted using the model of Closs[3,4] and Kaptein and Oosterhoff[5] in its approximation intended for reactions carried out in large magnetic fields, thus experimentally confirming the prediction that this approximate theory would fail for reactions carried out in small magnetic fields.[4a]

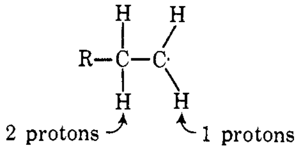
**Scheme I**[a]



[a] Metal counterions are omitted, but aggregates at least as high as ion pairs are considered to be involved for all anions considered. [b] DME = 1,2-dimethoxyethane. Other ethers, *e.g.*, tetrahydrofuran, may be used. [c] This pathway is available when R itself contains a halogen atom, so that RX is really a dihaloalkane. [d] This pathway is of major importance only for reactions of alkyl iodides.

The CKO model is one in which nuclear polarization is brought about through competitive processes of associated radical pairs. The rates of collapse of radical pairs to singlet products are considered to be nuclear spin state dependent, while the rates of diffusive separation of radical pairs are independent of their nuclear spin states. In the $t_0$–s approximation, mixing of electronic singlet states (s) of radical pairs with two of the electronic triplet states, those with $m_s = \pm 1$ ($t_+$ and $t_-$), are neglected, the only singlet–triplet mixing considered being that of singlet states with triplet states of $m_s = 0$ ($t_0$) This approximation is explicitly justifiable only for reactions run in large magnetic fields. Nonetheless, it might have proved sufficient for reactions run in any field.

Two predictions of the $t_0$–s CKO model are: (1) if $\Delta g$, the $g$-value difference for the radicals of the critical pairs, is very small, then maximal net ("energy")[3] polarization of products is predicted for reactions run in very large magnetic fields. (2) For reactions proceeding through critical pairs containing alkyl radicals, any energy polarization in the products should be of opposite sign for protons which were 1 and 2 protons in the radicals. This stems from the fact that the nuclear-electron hyperfine coupling constants of 1 protons are negative, while those of 2 protons are positive.



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(1) J. F. Garst, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 11, 8 (1970); J. F. Garst and J. T. Barbas, *Tetrahedron Lett.*, 3125 (1969); and references cited therein.

(2) This is apparently the first report of nuclear spin polarization induced in a reaction involving a paramagnetic initial reactant.

(3) G. L. Closs, *J. Amer. Chem. Soc.*, 91, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, 91, 4554 (1969).

(4) (a) G. L. Closs and A. D. Trifunac, *ibid.*, 92, 2183 (1970); (b) G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, 92, 2185 (1970); (c) G. L. Closs and A. D. Trifunac, *ibid.*, 92, 2186 (1970).

(5) R. Kaptein and J. L. Oosterhoff, *Chem. Phys. Lett.*, 4, 195, 214 (1969).

Figure 1. Nmr spectra of ethylene (left) and cyclobutane formed in the reaction of sodium naphthalene with 1,4-diiodobutane. The bottom spectra are the signals obtained after long times. The top spectra were taken a few seconds after the reaction was carried out.

Our results stand in sharp contrast to both these predictions.

Consider the reaction of sodium naphthalene with 1,4-diiodobutane to give cyclobutane. The appropriate portion of the reaction mechanism is given in eq 1. Radicals are generated singly in these reactions,

$$ICH_2CH_2CH_2CH_2\cdot \xrightarrow{:Naph\cdot^-} ICH_2CH_2CH_2CH_2:^- \longrightarrow \text{cyclobutane} \quad (1)$$

so the critical radical pairs in a CKO model would be [R·,:Naph·⁻] pairs formed by encounters of free radicals.

Our findings are that the cyclobutane is negatively polarized (nmr emitting) if the reactions are carried out *ca.* 2 ft from the magnet of the nmr spectrometer (see Figure 1), but barely polarized (if at all) if they are carried out 10 ft away, or in the strong field of the spectrometer magnet, or in the field of an auxiliary 5000-G magnet. Measurements of the magnetic fields at various positions indicate that maximum polarization is obtained in fields between 2 and a few hundred gauss. The polarization is strong for reactions carried out in a field of about 10 G, but it dies off rapidly as one goes to weaker fields.

Since the *g*-value difference between butyl radicals and sodium naphthalene is very small (*ca.* $1.5 \times 10^{-4}$), the optimum magnetic field for energy polarization is predicted by the $t_0$–s CKO model to be very large, about 35,000 G. Negligible polarization is expected in fields as low as a few gauss. This, of course, is prediction 1 above, and it stands in contrast to our experimental results.

Observations similar to those cited above have been made repeatedly for reactions of other alkyl halides with sodium naphthalene in DME. These include reactions of methyl iodide (giving polarized methane and ethane), neopentyl iodide (neopentane), and neopentyl iodide (neopentane and bineopentyl), in addition to isopropyl iodide, the results for which are discussed below. *All* the polarizations mentioned above were *negative*, the reactions being carried out in a field of a few gauss (*ca.* 20).

From the reaction of isopropyl iodide with sodium naphthalene in a field of about 20 G, 2,3-dimethylbutane was formed in which *all* the protons were negatively polarized, in contrast to prediction 2 of the $t_0$–s CKO model (see Figure 2).[6]

The $t_0$–s CKO model is clearly inadequate for these reactions.[7] However, inclusion of the heretofore neglected $t_+$ and $t_-$ interactions leads to CKO models whose predictions duplicate the major features of the anomalous observations reported here.[9] Using a Hamiltonian of the usual form,[3-5] one finds[3] that $t_-$–s "transitions" (or state mixings) in weakly coupled radical pairs are accompanied by $\alpha$ to $\beta$ nuclear spin flips for one (and only one) proton. This is true whether the hyperfine coupling constant of the proton and the odd electron of its radical is negative or positive. Thus, $t_-$–s "transitions" of triplet-born radical pairs always create product (derived from s collapse) with excess $\beta$ nuclear spins. This is manifest in nmr emission spectra for all protons, in accord with our observations.

Actually, $t_+$–s transitions are accompanied by the opposite sense of nuclear spin flips, $\beta$ to $\alpha$, so that if $t_-$–s and $t_+$–s interactions were equally important, no net polarization would result. This is the case in zero field, in accord with our finding that the net polarization vanishes in sufficiently low magnetic fields of reaction. Starting from zero field, and increasing the magnetic field in which reactions are carried out, $t_+$ states increase in energy while $t_-$ states decrease. Thus, the zero-field degeneracy of these levels is removed by quite small magnetic fields, and net polarization can then be obtained for reactions carried out

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(6) A referee's suggestion that the methyne protons in 2,3-dimethylbutane might *appear* to be negatively polarized through intensity borrowing from methyl protons could be applicable here, but it could not be applicable to, say, ethane formed from methyl iodide. In both cases the protons mentioned were 1 protons in the intermediate alkyl radicals, and in both cases the nmr spectra indicate negative polarization. Unless there is something grossly different about the mechanisms of formation of ethane and of 2,3-dimethylbutane, both 1 and 2 protons of the alkyl radical intermediates become negatively polarized in the products.

(7) The original Overhauser analog theory proposed by Bargon and Fischer and by Lawler also seems inadequate to account for these observations, since it requires that radicals be produced with nonequilibrium electron spin distributions,[8] a condition that is not met in the present reactions.

(8) (a) See H. Fischer and J. Bargon, *Accounts Chem. Res.*, 2, 110 (1969), and works cited therein; (b) J. Bargon and H. Fischer, *Z. Naturforsch. A*, 22, 1551 (1967); (c) R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5519 (1967).

(9) Our investigations of $t_+$ and $t_-$ inclusive CKO models as possible means of accounting for low-field observations were stimulated by the explicit neglect of $t_+$ and $t_-$ in the papers of Closs[3,4] and of Kaptein and Oosterhoff,[5] and by the presentations by H. Fischer and S. Glarum at the 159th National Meeting of the American Chemical Society (Houston, Tex., Feb 1970) of a "dynamic *J*" model for the treatment of radical pair spin transitions. The latter workers emphasized the possibility that $t_-$, especially, might lead to important interactions for reactions carried out in low fields.

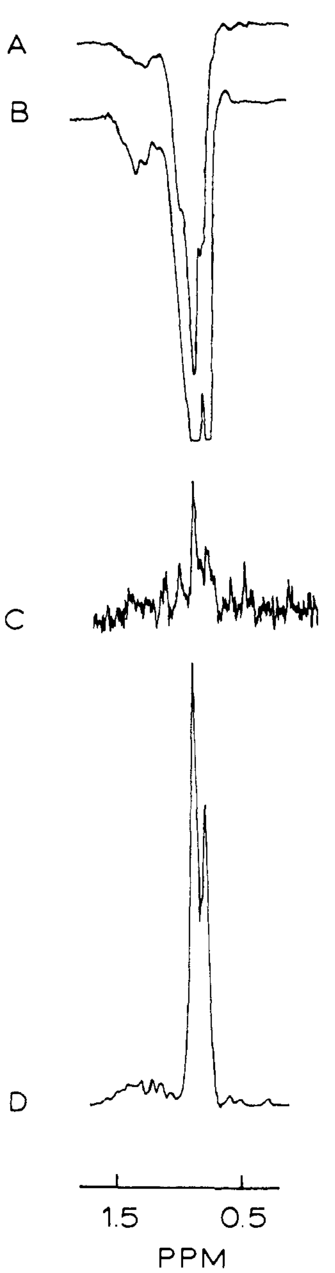

Figure 2. Nmr spectrum of 2,3-dimethylbutane formed in the reaction of isopropyl iodide with sodium naphthalene: (a) about 20 sec after reaction; (b) about 10 sec after reaction; this curve shows more clearly than a the polarization of the tertiary protons, to which the multiplet centered at about 1.3 ppm is due; it also shows more clearly the methyl doublet splitting; (c) after long times; (d) authentic sample of 2,3-dimethylbutane in DME scanned at approximately the same rate as for a and b above (about 0.1 ppm/sec).

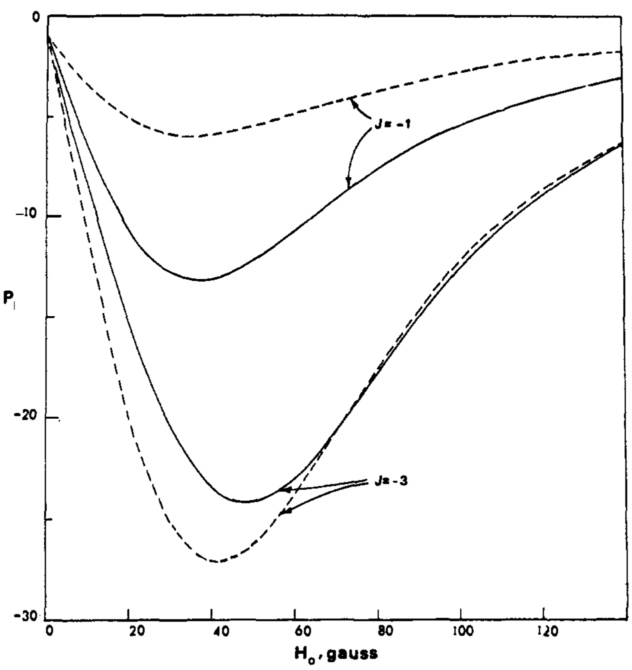

Figure 3. Polarization, $P_l$ (contribution due to $t_l$–s mixings calculated from $t_l$–s CKO model; for approximations see text), *vs.* reaction magnetic field, $H_0$: solid lines, $A$ (nuclear electron hyperfine coupling constant) = $-22$ G; dashed lines, $A$ = $+27$ G; $\tau$ = $10^{-9}$ sec; $w_0$ = $100k$, where $w_0$ is the rate constant for nuclear spin independent collapse of radical pairs and $k$ is the rate constant for collapse of pure singlet radical pairs. $J$, the "exchange coupling constant or integral," is in units of $10^8$ rads/sec. The calculations are for critical radical pairs containing one proton with initial radical pair states being taken as pure triplet, and initial condition which also applied, at least qualitatively, to randomly combining free radicals.[6c] Polarizations are referenced with respect to equilibrium nuclear spin distributions in a field of ~14,000 G.

in these fields. As the field gets larger, the competitions between $t_+$ and $t_-$ interactions continually change, resulting in field-dependent polarizations. Our calculations indicate that it is reasonable to expect maximum effects in fields of the order of 100 G.[10] Experiments with sodium naphthalene and 1,4-diiodobutane are in agreement with this kind of prediction. The polarization due to $t_-$ and $t_+$ interactions dies out for reactions run in large magnetic fields (thousands of gauss) for reasons mentioned earlier by Closs[3,4] and by Kaptein and Oosterhoff.[5] Figure 3 shows the predicted polarization for a model system calculated from an approximate CKO treatment in which $t_0$–s, $t_+$–$t_0$, and $t_-$–$t_0$ interactions are neglected, only $t_-$–s and $t_+$–s mixing being considered (the $t_l$–s CKO model).

We have also treated the CKO model without neglect of any interactions. Calculations for one- and two-proton radical pairs give families of polarization curves closely resembling those given in Figure 3 but with some differences. The most significant differences are that the polarizations are a little less negative in the general (as opposed to approximate) calculations, especially for very small values of $J$, and that for positive $A$ (+27 G) the polarizations of the corresponding protons rise from negative values at low fields to positive values at higher fields.[11] For negative $A$ (−22 G), the polarizations are always negative (at least in the range 0–140 G). Systems with two protons give superpositions of entropy and energy polarization, as expected.

The ability of the generalized CKO model to account for the kinds of observations reported here is additional

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(10) Subject to considerable variation for different experimental systems and choices of parameters for the calculations.

(11) In the approximate calculation, the curve for $A$ = $+27$, $J$ = 0, corresponds everywhere to positive polarization, with a maximum at $H_0$ = 35 G. This is virtually duplicated in the general calculation, but the polarization is about twice as great. For $J$ = $-1$ (see legend of Figure 3 for units), the general calculation predicts a polarization that is positive for $H_0 > 8$ G. For $J$ = $-2$, the polarization curve resembles that shown in Figure 3 for $J$ = $-1$, $A$ = $+27$, but it is a little deeper and it rises to positive values of $P$ for fields above 90 G. As $J$ becomes increasingly more negative, the results of the general calculation correspond more nearly to those of the approximate calculation.

support for the model. Some predictions based on considerations of the $t_1$–s contributions to polarization, and on the general treatment, are of interest. (1) The $t_1$–s contribution to polarization of products obtained by trapping of radicals which have undergone diffusive separation from the critical pairs is in the *same* direction as that of the products arising from radical pair collapse. (The $t_0$–s contribution is opposite.) (2) The $t_1$–s contribution to polarization does not depend on the existence of kinetic processes which compete with collapse of the critical pairs to products. This removes one of the barriers to the observation of polarization from reactions of short-chain diradicals, so even if the prediction of Closs and Trifunac[3] that these cannot lead to $t_0$–s polarization is correct, there still may be a chance to observe $t_1$–s polarization.

Another feature of $t_1$–s polarization is that a difference in *g* values of the radicals of the critical pairs is not necessary for energy polarization. Thus, one may observe polarizations from reactions at low fields which might not give any polarizations when carried out in high fields.

**Acknowledgments.** This work was supported by the National Science Foundation. The authors are indebted to many persons for helpful discussions of related material, especially G. L. Closs, S. H. Glarum, G. S. Handler, A. D. King, and D. W. Smith. Professor Closs also made available to us unpublished manuscripts.

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*Received March 26, 1970*

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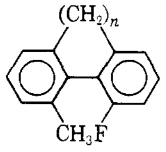
## Long-Range Proton–Fluorine Spin–Spin Coupling in Bridged Biphenyls. Compelling Evidence for a "Through-Space" ("Direct") Mechanism

*Sir:*

Although many "through-space" ("direct"[1]) proton–fluorine,[2] fluorine–fluorine,[3] and to a lesser extent, proton–proton[4] spin–spin couplings have been claimed or discussed in recent years, truly unequivocal examples of such interactions are rare indeed.

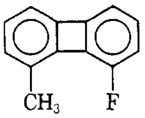
To provide compelling evidence for through-space contributions to spin–spin coupling mechanisms one needs to study systems where the internuclear distance between the interacting nuclei can be incrementally varied while keeping other variables (bond angles, dihedral angles, substituent effects, etc.) approximately constant.[2g] These systems should also be conformationally rigid so that the internuclear distances between the coupling nuclei can be determined confidently with suitable models.

We now wish to disclose our preliminary studies involving proton (methyl)–fluorine coupling over six bonds ($^6J_{CH_3,F}$) in the bridged-biphenyl system A. This system was selected for study because the compounds in the series would seem to precisely satisfy the aforementioned criteria for assessing the importance of through-space coupling and the requirements for its existence.[5]

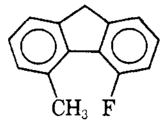


A

The first two members of the bridged-biphenyl series A (*n* = 0, 1), 1-fluoro-8-methylbiphenylene (**1**) and 4-fluoro-5-methylfluorene (**2**), have been synthesized and their nmr spectra recorded. **1** was prepared in a conventional manner.[6] An Ullmann copper-coupling reaction[7] between 2-iodo-3-nitrotoluene[8] and 2-fluoroiodobenzene gave 2-methyl-2′-fluoro-6-nitrobiphenyl (yellow-orange oil, 29%). This was catalytically reduced to 2-methyl-2′-fluoro-6-aminobiphenyl (colorless oil, 79%) which was diazotized and converted to 2-methyl-2′-fluoro-6-iodobiphenyl (amber oil, 66%). This in turn was oxidized[6] and converted to the corresponding iodonium iodide (mp 142–144° dec, 49%) which afforded 2-methyl-2′-fluoro-6,6′-diiodobiphenyl (mp 83–84°, 99%) on heating with commercial cuprous oxide. When this diiodobiphenyl was subsequently heated with freshly prepared cuprous oxide,[9] 1-fluoro-8-methylbiphenylene (**1**) was obtained (colorless oil, 27%) along with starting material. Heating the iodonium iodide with freshly prepared cuprous oxide afforded **1** in 74% yield. **1** was conveniently characterized as the 2,4,7-trinitrofluorenone 1:1 complex[10] (mp 173–174°) and could be regenerated in a pure state by passing the complex through alumina. Similarly, **2** was pre-



**1**



**2**

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[1] M. Barfield and M. Karplus, *J. Amer. Chem. Soc.*, **91**, 1 (1969).

[2] (a) D. R. Davis, R. P. Lutz, and J. D. Roberts, *ibid.*, **83**, 246 (1961); (b) M. Takahaski, D. R. Davis, and J. D. Roberts, *ibid.*, **84**, 2935 (1962); (c) M. S. Newman, R. G. Mentzer, and G. Slomp, *ibid.*, **85**, 4018 (1963); (d) A. H. Lewin, *ibid.*, **86**, 2303 (1964); (e) A. D. Cross and P. W. Landis, *ibid.*, 86, 4005, 4011 (1964); (f) J. Burdon, *Tetrahedron*, **21**, 1101 (1965); (g) P. C. Myhre, J. W. Edmonds, and J. D. Kruger, *J. Amer. Chem. Soc.*, **88**, 2459 (1966); (h) J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, 27 (1967); (i) R. J. Cushley, I. Wempen, and J. J. Fox, *J. Amer. Chem. Soc.*, **90**, 709 (1968); (j) C. W. Jefford, D. T. Hill, L. Ghosez, S. Toppet, and K. C. Ramey, *ibid.*, **91**, 1532 (1969); (k) R. Filler and E. W. Choe, *ibid.*, **91**, 1862 (1969).

[3] (a) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); **36**, 1087 (1961); (b) M. T. Rogers and J. D. Graham, *J. Amer. Chem. Soc.*, **84**, 3666 (1962); (c) S. Ng and C. H. Sederholm, *J. Chem. Phys.*, **40**, 2090 (1964); (d) J. Jonas, L. Borowski, and H. S. Gutowsky, *ibid.*, **47**, 2441 (1967); (e) K. L. Servis and K. Fang, *J. Amer. Chem. Soc.*, **90**, 6712 (1968); (f) R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Chem. Commun.*, 178 (1968); (g) R. A. Fletton, R. D. Lapper, and L. F. Thomas, *ibid.*, 1049 (1969); (h) R. D. Chambers, J. A. Jackson, W. D. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, **26**, 71 (1970).

[4] M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

[5] As methylene groups are inserted between the ortho positions of the biphenyl system (*i.e.*, A) the methyl and fluorine will be forced closer together for $n \leqslant 2$, as viewed with Dreiding models.

[6] J. W. Barton and K. E. Whitaker, *J. Chem. Soc. C*, 2097 (1967), and earlier papers.

[7] P. E. Fanta, *Chem. Rev.*, **64**, 613 (1964).

[8] M. B. Chenon, L. C. Leitch, R. N. Renaud, and L. Pichat, *Bull. Soc. Chim. Fr.*, 38 (1964).

[9] O. Grummitt, N. Vourlogianes, J. Mehaffey, and R. Tebbe, *Org. Prep. Proced.*, **2**, 5 (1970).

[10] M. Orchin and E. O. Woolfolk, *J. Amer. Chem. Soc.*, **68**, 1727 (1946).