Some benzene was added and evaporation was continued until separation of solids made further evaporation difficult. A mixture of 35 cc. of concentrated hydrochloric acid and 5 cc. of water was added. The solids dissolved and the two layers were separated. Addition of sodium carbonate to the aqueous layer caused the separation of an orange solid which was taken up in benzene. The residue from evaporation of the benzene was crystallized from absolute ethanol. Orange crystals, m.p. 92–94° not depressed on admixture with authentic II, weighing 0.35 g. were obtained; a second crop weighing 0.08 g. melted at 90–92.5°. The total yield of II was 57%.

The benzene layer from the first separation was evaporated nearly to dryness and chromatographed on alumina. The material eluted rapidly by petroleum ether was crystallized from 95% ethanol. 2,4-Dinitrodiphenyl sulfide (V) (0.13 g., 16%) was obtained as yellow crystals, m.p. 116.5–120° not depressed on admixture with an authentic sample. A second crop of light yellow crystals, weight 0.06 g., was recognized as diphenyl disulfide by its melting point, 55–60° not depressed on admixture with an authentic sample. No other well-defined substances were obtained from the chromatographic column.

From a reaction similar but for the absence of piperidine hydrochloride, a 38% yield of II and an approximately 6% yield of V were isolated. (The formation of V was first observed in preliminary experiments by Mr. R. F. Snipes.)

The yields of II and V under the conditions of the kinetics runs were estimated by a photometric procedure. Since V absorbs appreciably at 380 mμ, the optical density of the usual "experimental infinity" sample from 2,4-dinitrodiphenyl sulfoxide is not a valid measure of the yield of II. The modified procedure depends on the facts that II is colorless at 380 mμ in a "super quenching solution" (equal volumes of water, 95% ethanol and concentrated sulfuric acid) whereas V actually absorbs somewhat more strongly in "super quenching solution." Samples from typical runs allowed to go to completion were therefore quenched both in the usual way and in "super quenching solution." It was assumed that the optical density of the "super-quenched" solution was due wholly to V; from this value and from the known ratio of the optical densities of V in the usual and the "super" quenching solutions, it was possible to calculate what part of the optical density of the sample quenched in the usual way was due to V. The optical density due to II was then obtained by subtraction. Yields estimated in this manner were as follows: at 0°, 25% II and 26% V; at 0° in presence of piperidine hydrochloride, 73% II and 16% V; at 25.2°, 28% II and 18% V; at 25.2° in presence of piperidine hydrochloride, 74% II and 15% V; at 46.0°, 29% II and 14% V; at 46.0° in presence of piperidine hydrochloride, 74% II and 15% V. These estimates, being based on an assumption of uncertain validity, are only approximate, but reassurance is gained from the fact that rate coefficients for the formation of II in the absence and in the presence of piperidine hydrochloride calculated from the yields so estimated, are in fair agreement (Table II).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

Steric Inhibition of Hyperconjugation[1,2]

BY H. H. JAFFÉ AND JOE L. ROBERTS

RECEIVED AUGUST 23, 1956

The various manners are examined in which steric strain between an alkyl radical R linked to a bulky radical R′ can be relieved. It is concluded that torsional rotation can inhibit hyperconjugative resonance of cyclopropyl, but not of methyl or *t*-butyl groups, and can reduce, but not inhibit completely, hyperconjugative resonance of ethyl and isopropyl radicals. Of the other possible modes of reduction of steric strain, out of plane bending of the alkyl group appears the most effective means of inhibiting hyperconjugative resonance. Stretching of the bond between R and R′, and compression of the radical R are considered rather ineffective in inhibiting hyperconjugation. None of the modes considered are believed to be able to inhibit *completely* hyperconjugative resonance except for cyclopropyl groups, nor is any of them considered to be very effective in inhibition.

It has been suggested recently that hyperconjugative resonance may be inhibited sterically[3] in a manner resembling the well established steric inhibition of resonance[4] of radicals such as the nitro and substituted amino groups. A theoretical examination of the possibilities of steric inhibition of hyperconjugative resonance of alkyl groups seems indicated, particularly in the light of a recent theoretical investigation of hyperconjugation of the relatively complex ethyl and *t*-butyl groups.[5] Since the various alkyl radicals have different steric requirements, the various basic radicals, methyl, ethyl, isopropyl, *t*-butyl and cyclopropyl will be discussed separately. Before proceeding to discuss each group, we shall examine the various ways in which steric strain can be relieved. Assume an alkyl radical R attached to another radical R′ of sufficient complexity to produce a steric strain between R and R′. The possible ways in which R can be deformed from its "normal" configuration then include the following: (1) rotation (torsional) about the R–R′ bond; (2) stretching of the R–R′ bond; (3) bending of the R–R′ bond; (4) compression of the bond angles within the radical R; (5) further stretchings or distortions within the group R. The last of these is unlikely to be important, and will not be discussed further. Of all these modes, only torsional rotation involves no reduction in σ-bond energy, and hence is the deformation most likely to be involved in the reduction of steric strain. Information concerning the resistance to deformation of the remaining modes is available from a knowledge of force constants. Since torsional rotation of the rather bulky alkyl groups, however, cannot be very effective in relieving steric strain, some of the other modes must also be considered. It must then be realized that involvement of these deformations may cause changes in the σ-bonds and their energies and possibly in hybridization, and that the resulting effects on reactivity and spectra might be difficult to separate

(1) This work was sponsored by the Office of Ordnance Research, U. S. Army.

(2) Paper V in the series "Molecular Orbital Theory of Valence." For paper IV see *Z. Elektrochem.*, **59**, 823 (1955).

(3) *E.g.*, Illuminati, *Gazz. chim. ital.*, **83**, 905 (1953).

(4) *Cf.* G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 136 ff., 160 ff., 185 ff., 272 ff.

(5) Y. I'Haya, *Bull. Chem. Soc. Japan*, **28**, 369 (1955).

from the effects due to the inhibition of hyperconjugation.

Methyl Group.—The torsional rotation of the methyl group, in such a manner that a buttressing group fits between two hydrogen atoms, has been stressed as a means to reduce steric strain.[3] There is little doubt that the torsional rotation is the deformation most easily accomplished energetically; the energy barriers for torsional deformation in the absence of resonance effects are quite small, and steric inhibition of resonance is almost universally ascribed to this mode of deformation. However, in methyl groups, due to the high degree of symmetry of the group, this mode of deformation is not very effective in relieving steric strain.

The methyl group may occur in either of the two most symmetrical conformations A and B (*cf.* Fig. 1), or in any intermediate conformation. For conformation A, the hyperconjugating group orbital (GO) is

$$\psi_x = N_x^{-1}[\varphi(2) - \varphi(3)]$$

Construction of the GO ψ_x implies the simultaneous construction of the GO

$$\psi_y = N_y^{-1}[2\varphi(1) - \varphi(2) - \varphi(3)]$$

which is not hyperconjugating in conformation A since its nodal plane[6] is normal of the nodal plane of the π-electron system of the radical R′. In conformation B, ψ_y is the hyperconjugating GO. Since ψ_x and ψ_y are degenerate and orthogonal group orbitals, hyperconjugative resonance will be equal in conformations A and B, and will also be the same in any intermediate conformation since it is always possible to construct a GO $\psi_\alpha = \psi_x \sin\alpha + \psi_y \cos\alpha$ in such a manner that ψ_α will have its nodal plane[6] in common with the π-electron system of the radical R′. Hence, torsional rotation *cannot* inhibit hyperconjugative resonance of a methyl group.

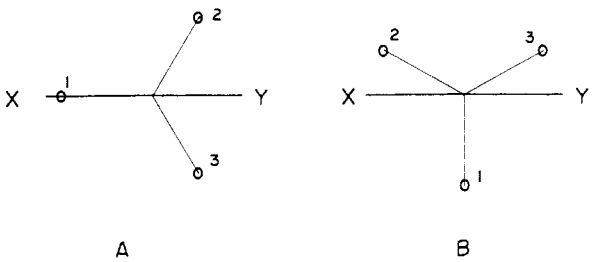

Fig. 1.—The various conformations of an alkyl radical (R) and their relation to hyperconjugation. The plane marked XY is the plane of the radical R′.

The other three ways (2, 3 and 4 above) in which the steric strain can be relieved will lead to a reduction of conjugation; however, in none of these modes can conjugation be inhibited as readily and completely as by the torsional rotation of a group (such as NO_2) which, to permit conjugation, must lie in the nodal plane of the π-orbitals of the radical R′. The force constant for R–R′ bond stretching is quite high, so that only a small amount of stretching can be anticipated. This would inhibit conjugation only through a relatively minor reduction of the overlap integral (and the associated resonance integral) between the π-orbitals of the C atoms bonding R and R′, and hence would lead to only a very small effect on conjugation energy. Compression of the bond angles in R would lead to a decrease in the overlap integral (and the associated resonance integral) between the C atom in the group R and the H_3 pseudo-atom, and to an increase of the coulomb integral for the pseudo-atom.[7] Both of these effects would decrease the conjugation energy. However, unless the distortion was extreme, the effect could be expected to be small. If the bending of the R–R′ bond left the C atom of R in the nodal plane of the orbitals of R′, as might be expected in a mono-*o*-substituted toluene, no reduction of hyperconjugation energy would result. However, if in toluene both *o*-positions were substituted, the methyl group might be bent out of the plane of the ring. This would lead to an appreciable reduction of the overlap integral (and the associated resonance integral) between the C atoms bonding R and R′. If the R–R′ bond is bent by an angle α, the overlap integral becomes $S(\alpha) = S(0) \cos\alpha$, where $S(0)$ is the normal overlap integral for the undistorted molecule. Since large distortion angles α are unlikely and since $\cos\alpha$ does not very rapidly for small α, it does not appear likely that large effects would result in this way.

t-**Butyl Group.**—Almost everything that has been said would apply almost exactly to the *t*-butyl group. Torsional rotation might, for this group, be slightly more effective in relieving strain but, since the same GO's apply and for the reasons explained above, hyperconjugative resonance must be independent of the torsional angle. Compression of the bond angles in the *t*-butyl group should be more difficult for steric reasons, and should have a smaller effect on the coulomb integral of the $(CH_3)_3$ pseudo-atom. With respect to the other modes, the *t*-butyl group will not differ from the methyl group.

Ethyl Group.—In the absence of steric strain, conformation A may be assumed to be the most effective conformation for hyperconjugation. This assumption may be made since A is the only conformation permitting "pure CH hyperconjugation," *i.e.*, hyperconjugation in which the GO involves only H orbitals of the pseudo-atom, which in this case is H_2CH_3, and since all the evidence indicates that CH hyperconjugation is more effective than CC hyperconjugation.[5] In the presence of appreciable steric strain, configuration B (1 = C, 2 = 3 = H) would be most effective in relieving strain; in this conformation the hyperconjugating GO would be ψ_y, so that mixed CH–CC hyperconjugation would result, which would be expected to be weaker than pure CH, but stronger than pure CC hyperconjugation. Thus, steric strain should be able to reduce the hyperconjugating ability of an ethyl group from a value approaching that of the methyl group to a value somewhat above the *t*-butyl radical. For the other modes of reduction

(6) Actually the nodal surface of one of the two pseudo-orbitals of the pseudo-atom H_3 is not quite planar, but it resembles the nodal plane of atomic π-orbitals sufficiently to be treated as if it were such a plane.

(7) See N. Muller, L. W. Pickett and R. S. Mulliken, THIS JOURNAL, **76**, 4770 (1954).

of steric strain everything said above would apply.

Isopropyl Group.—Most effective hyperconjugation might be expected from conformation A or B (2 = H, 1 = 3 = C) which allow mixed CH–CC hyperconjugation, whereas conformation A (1 = H, 2 = 3 = C), implying pure CC hyperconjugation, appears sterically most favorable. Hence, torsional rotation might again be expected to lead to a minor reduction in hyperconjugation energy from a value intermediate between the ones applicable to methyl and *t*-butyl to a value substantially the same as for *t*-butyl.

Cyclopropyl Group.—It is now well established that the cyclopropyl group can act as an electron donor through a hyperconjugative mechanism. The nodal plane of the GO involved in this resonance is the plane formed by the two extracyclic σ-bonds of the carbon atom at which the unsaturated radical is attached,[2] and no hyperconjugating GO's exist with nodal planes normal to this plane. Hence, a torsional rotation around the extracyclic σ-bond should be effective in inhibiting hyperconjugative resonance completely. Such steric inhibition of cyclopropyl resonance has been suggested previously and experimental evidence for its existence has been cited.[8] None of the other possible modes of relieving steric strain are likely to be important for the cyclopropyl radical.

It is thus seen that none of the distortions which are likely to be effective in relieving steric strain in molecules can *completely* inhibit hyperconjugative resonance except for the cyclopropyl group. The distortion which would most effectively reduce this resonance would be the out-of-plane bending of the alkyl group and, in unsymmetrical alkyl groups and particularly in cyclopropyl groups, the torsional rotation. Comparison of these predictions with the experimental evidence discussed by Illuminati[3] makes it unlikely that the phenomena cited by this author can be explained in terms of steric inhibition of resonance.

(8) J. D. Robert, W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3329 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

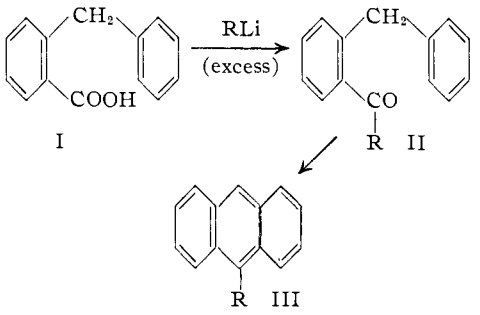
A New Base-catalyzed Cyclization Reaction

BY C. K. BRADSHER AND SIDNEY T. WEBSTER[1]

RECEIVED AUGUST 22, 1956

The reaction of *o*-benzylbenzoic acid (I) with an excess of methyllithium yields the readily cyclizable *o*-benzylacetophenone (II, R = CH_3). With phenyllithium, I affords a 70% yield of 9-phenylanthracene, by a new base-catalyzed cyclization. *p*- and *m*-tolyllithium afford smaller yields of the 9-arylanthracenes. With *o*-benzhydrylbenzoic acid and phenyllithium, no hydrocarbon is formed.

It has been shown earlier[2–5] that *o*-benzylphenones (II), in the presence of a boiling mixture of hydrobromic and acetic acids, cyclize, affording high yields of 9-substituted anthracene derivatives (III). The requisite ketones (II) were prepared in



a four-step synthesis starting with *o*-chlorobenzaldehyde. A classical approach to the synthesis of *meso* alkyl anthracene derivatives of known structure involves the cyclization of an *o*-benzylbenzoic acid derivative (I), affording an anthrone, which is allowed to react with a Grignard reagent, and the resulting product dehydrated to yield the anthracene derivative III.

While some substituted anthrones afford good yields of the expected hydrocarbons, others have proved unstable[6–8] or were found to be largely converted to resins by the action of the Grignard reagent.[9,10] Other anthrones, particularly 1,2-benzanthrones, show considerable tendency to exist in the tautomeric anthranol form.[11] These difficulties made it appear desirable to examine an alternate route from the acid I to the hydrocarbon III. It was found that when *o*-benzylbenzoic acid is treated with an excess of methyllithium,[12–15] *o*-benzylacetophenone (II, R = CH_3) is obtained in 80% yield. Since it was shown that this ketone may be cyclized in 79% yield, the over-all yield of 9-methylanthracene (III, R = CH_3) from the acid I is quite satisfactory.

(1) Taken in part from a thesis presented in partial fulfillment of the requirments for the M.A. degree, Duke University, 1956. This work was supported in part by a grant from the Duke University Research Council.

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(3) C. K. Bradsher, *ibid.*, **62**, 1077 (1940).

(4) C. K. Bradsher and F. A. Vingiello, *ibid.*, **71**, 1434 (1949).

(5) F. A. Vingiello, J. G. Van Oot and H. H. Hannabass, *ibid.*, **74**, 4546 (1952).

(6) L. F. Fieser and E. B. Hershberg, *ibid.*, **62**, 49 (1940).

(7) L. F. Fieser and A. K. Seligman, *ibid.*, **60**, 170 (1938).

(8) M. S. Newman, *ibid.*, **60**, 1141 (1938).

(9) E. de B. Barnett and F. C. Marrison, *Ber.*, **64**, 535 (1931).

(10) E. de B. Barnett and N. F. Goodway, *J. Chem. Soc.*, 1754 (1929).

(11) L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **59**, 1028 (1937).

(12) H. Gilman and P. Van Ess, *ibid.*, **55**, 1258 (1933).

(13) P. Karrer and J. Benz, *Helv. Chim. Acta*, **31**, 1607 (1948).

(14) M. S. Newman and J. Mangham, THIS JOURNAL, **71**, 3342 (1949); M. S. Newman and T. S. Bye, *ibid.*, **74**, 905 (1952).

(15) C. Tegner, *Acta Chem. Scand.*, **6**, 782 (1952).