than a few tenths of a degree,[7] so ordinary sigma-electron contributions to the observed coupling would be expected to be very small.[8]

Karplus[4] has shown that anomalously large spin-spin interactions between protons on carbon atoms which are separated by one or more pi bonds may be explained by including contributions from low-lying $^3\Pi$ states and σ-π interactions[9] in the C–H bonds. He related the proton–proton coupling constant to the isotropic electron–proton splitting constants for the pi-radical fragments corresponding to the $^3\Pi$ states and the excitation energies for the ($^1\Pi \to {}^3\Pi$) transitions.

We wish to point out that such $^3\Pi$ states would be expected to contribute significantly to proton–proton coupling through sigma systems which are geminal to an unsaturated bond, as in acetone or in ethylene.

The coupling constant A_{HH} may be expressed as

$$A_{H_aH_b} = K \sum_n \frac{\langle \Psi_0 | \mathcal{K}_a | \Psi_n{}^T \rangle \langle \Psi_n{}^T | \mathcal{K}_b | \Psi_0 \rangle}{E_0 - E_n} \quad (1)$$

in the notation used by Karplus.[4] We assume that the only excited state of importance in the calculation of the pi electron contribution to the coupling is the triplet $(CH_3)_2C'$-$O\cdot$ and we estimate an excitation energy $\Delta\pi$ of about 6.3 eV.[10,11] We use a simple valence bond approach and write the ground state Ψ_0 and the triplet state $\Psi_0{}^T$ functions as

$$\Psi_0 = \eta\psi_{covalent} + \sqrt{1 - \eta^2}\psi_{ionic}$$
$$= \left\{ \eta \left[\frac{C(1)O(2) + O(1)C(2)}{\sqrt{2}} \right] + \sqrt{1 - \eta^2}[O(1)O(2)] \right\}$$
$$\left[\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} \right] \quad (2)$$

and

$$\Psi_0{}^T = \left[\frac{C(1)O(2) - O(1)C(2)}{\sqrt{2}} \right] \left[\frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}} \right] \quad (3)$$

where C and O are $2p_z$ atomic orbitals of carbon and oxygen, respectively, α and β represent electronic spin states with $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$, respectively, and $1 - \eta^2$ is the ionic character of the bond. Overlap integrals of the form $\langle C | O \rangle$ are neglected. We can separate the acetone triplet into the fragments $(CH_3)_2C\cdot$ and $O\cdot$, and neglect the contribution from the latter. Both groups of protons then couple with the same pi electron. The coupling constant a_H for a H_3C-$C\cdot$ fragment is known from e.s.r. measurements.[5,10] With these wave functions and an approach similar to that of Karplus,[4] we obtain

$$A_{HB}(\pi) \cong -k\eta^2(a_H)^2/\Delta\pi \quad (4)$$

where k has the same numerical value as in Karplus' expression. This result implies that the pi contribution to the coupling is negative in sign and is related to the long-range methyl–methyl coupling observed in the 2-butene system by the expression

(7) P. W. Allen, H. J. M. Bowen and O. Bastiansen, Trans. Faraday Soc., 48, 951 (1952).

(8) H. S. Gutowsky, M. Karplus and D. M. Grant, J. Chem. Phys., 31, 1278 (1959).

(9) H. M. McConnell, ibid., 24, 764 (1956).

(10) R. S. Holdsworth and A. B. F. Duncan, Chem. Revs., 41, 311 (1947).

(11) J. M. Parks and R. G. Parr, J. Chem. Phys., 32, 1657 (1960).

$$A_{HH}(\text{acetone}) = -\eta^2 \frac{\Delta\pi_{C=C}}{\Delta\pi_{C=O}} A_{HH}(\text{2-butene}) \quad (5)$$

The observed value of A_{HH}(2-butene) is about 1.2 cps.[12] and $\Delta\pi_{C=C}$ has been estimated[5] to be about 6.0 eV. Values of A_{HH} (acetone) and $\Delta\pi_{C=O}$ have been indicated above. These figures when inserted into Eq. 5 yield an ionic character $1 - \eta^2$ of 0.53, in reasonable agreement with the range 0.42 to 0.52 given by Pauling[13] for the ionic character of the C=O bond. The explanation for the coupling in acetoxime is similar.

In acetone the negative value of A_{HH} arises because the two groups of protons are both coupled directly to the same unpaired electron which orients the proton spins parallel to each other.

It is of interest to point out that this treatment predicts a pi contribution of about -1.5 cps. to the gem proton–proton coupling in the vinyl group and in ethylene (assuming $\Delta\pi = 6.0$ eV.) in addition to the sigma contribution of $+ 3.1$ cps. estimated by Gutowsky, Karplus and Grant[8] for a $120°$ H–C–H bond angle. It seems probable that this effect can account for the fact that observed values of $A_{HH}(gem)$ (1 to 2 cps.) in these systems are smaller than previously calculated values by small but significantly consistent amounts.

The long-range proton–proton interactions observed by Roberts[1] in methacrolein dimer and by Fraenkel[14] in methyl formate also may be due in part to enhanced coupling from the C=O groups in these molecules.

It is a pleasure to acknowledge financial support in the form of a grant from the Research Corporation under which this work was carried out.

(12) R. R. Fraser, Can. J. Chem., 38, 549 (1960).

(13) Linus Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, New York, 1960, p. 190.

(14) G. Fraenkel, J. Chem. Phys., 34, 1466 (1961).

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A NEW SYNTHESIS OF α-ω-DINITROALKANES

Sir:

We wish to report a new ring opening reaction of mono-potassium α,α'-dinitrocyclanones (I) which provides a highly convenient route for the preparation of α,ω-dinitroalkanes.

Hitherto, the only methods which have been available for preparing α,ω-dinitroalkanes were the Victor Meyer reaction[1] and a modification of this reaction.[2,3]

The new synthesis involves the alkaline nitration[4] of the readily available C_5-C_7 cyclic ketones, the in situ conversion with glacial acetic acid of the resulting dipotassium α,α'-dinitrocyclanones to I and the hydrolytic cleavage of the latter to α,ω-dinitroalkanes.
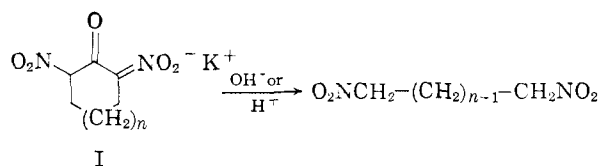
Nitration of cyclopentanone[4] and acidification of the reaction mixture at $10°$ with glacial acetic acid gave 88% of Ia ($n = 2$). Acidification of Ia

(1) H. Feuer and G. Leston, Org. Syntheses, 34, 37 (1954).

(2) N. Kornblum, et al., J. Am. Chem. Soc., 78, 1497 (1956).

(3) J. K. Stille and E. D. Vessel, J. Org. Chem., 25, 478 (1960).

(4) H. Feuer, J. W. Shepherd and C. Savides, J. Am. Chem. Soc., 78, 4364 (1956).

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with dilute sulfuric acid, followed by ether extraction, washing with cold 5% sodium bicarbonate solution, concentrating *in vacuo* and recrystallizing with 95% ethanol gave 72% of 1,4-dinitrobutane, m.p. 33–34°, lit. value[1] m.p. 33–34° (based on starting cyclopentanone). Treating Ia with base resulted in very little cleavage and converted it to dipotassium α,α'-dinitrocyclopentanone. On the other hand, potassium 2,6-dinitrocyclohexanone (Ib, $n = 3$) and potassium 2,7-dinitrocycloheptanone (Ic, $n = 4$) underwent cleavage in basic as well as in acidic media. Dissolving Ib in hot water, basifying with 85% potassium hydroxide at room temperature, acidifying with glacial acetic acid, extracting with ether and distilling gave 78% 1,5-dinitropentane. Its infrared spectrum was superimposable with that of authentic 1,5-dinitropentane.[1] Similar treatment of Ic gave 75% 1,6-dinitrohexane, m.p. 37–39°, lit. value,[1] m.p. 38–39°.

The basic cleavage of negatively substituted ketones has been known for some time. Hauser, *et al.*,[5] have noted the effect of ring size on the site of basic cleavage of negatively substituted ketones. The cleavage of the five-membered compound Ia in acidic medium only is the first example of the effect of ring size on the pH at which cleavage occurs.

Extension of this ring opening reaction to the synthesis of substituted α,ω-dinitroalkanes, which are at present unknown or which are accessible only with difficulty, is in progress.

Support of this work by the Office of Naval Research is gratefully acknowledged.

(5) P. J. Hamrick Jr., C. F. Hauser and C. R. Hauser, *J. Org. Chem.*, **24**, 583 (1959).

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THE DIRECT DETERMINATION OF THE ABSOLUTE CO-POLYMERIZATION RATE CONSTANT IN ANIONIC POLYMERIZATION[1]

Sir:

The conventional method for determining the absolute co-polymerization rate constants $k_{1,2}$ and $k_{2,1}$ is tedious and laborious.[2] It involves two steps, (1) analysis of the co-polymer composition from which one calculates the reactivities ratios, *e.g.*, $k_{1,1}/k_{1,2}$ ($k_{1,1}$ refers to the reaction $\sim\sim M_1 + M_1 \rightarrow \sim\sim M_1.M_1$. whereas $k_{1,2}$ to the reaction $\sim\sim M_1 + M_2 \rightarrow \sim\sim M_1.M_2$): and (2) determination of the absolute value of the rate constant $k_{1,1}$ of the respective homopolymerization. The latter entity is not easily available and its de-

(2) T. Alfrey, J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952.

termination requires studies of the kinetics of polymerization in a non-stationary stage. In addition, there is a doubt whether the approach based on the composition of the copolymer is reliable in studies of ionic co-polymerization.[3]

We now have developed a technique which permits the direct determination of the co-polymerization rate constant $k_{1,2}$ in an anionic polymerization. The method is illustrated by an example of styrene addition to α-methylstyrene polymer.

A solution of "living" α-methylstyrene tetramer of a known concentration of "living" ends is mixed rapidly in a three-way T-shaped stopcock (2 mm. bore) with a dilute solution of styrene monomer in tetrahydrofuran. The mixture flows through a capillary into a beaker containing wet tetrahydrofuran which terminates the reaction instantly. If CH_3I is used instead of water, titration of NaI determines the concentration of "living" ends at the end of the capillary. Thus it has been shown that no "killing" takes place in the reaction. The time of mixing is less than 5% of time of flow. The time of reaction, *i.e.*, the total time of flow, is varied from less than 0.1 of a sec. to less than a second by changing the pressure of pure nitrogen above the ingredients solutions. The final concentration of the unreacted monomer is determined by measuring the optical density at 290 mμ. To correct for a very small absorption due to the polymer, a solution of the polymer of the same concentration has been inserted in the second beam of the spectrophotometer.

In all these experiments the concentration of monomeric styrene in the capillary was smaller than that of the "living" ends; thus, on the average less than one molecule of styrene was added to the "living" α-methylstyrene. The log of the ratio initial styrene concentration over its final concentration, plotted against time gives a straight line, at least for the initial stages of the reaction. The slopes of these lines divided by the concentration of "living" ends give the respective copolymerization rate constant $k_{1,2}$ (1-α-MS, 2-Styrene). The data obtained by this method are

["living" ends] × 10^3 M	1.3	1.3	1.3	3.0	3.0	3.5
[styrene] × 10^3 M	1.1	1.0	1.1	2.2	2.6	3.0
$k_{1,2}$ l. moles⁻¹ sec.⁻¹	1100	1070	990	780	780	780

["living" ends] × 10^3 M	4.0	4.0	5.4	7.0	7.3	9.5	13.0
[styrene] × 10^3 M	2.0	3.0	3.0	3.0	2.6	5.5	3.0
$k_{1,2}$ l. moles⁻¹ sec.⁻¹	665	660	610	645	565	655	640

The increase in the rate constant for very low concentration of "living" ends was observed also in the homo-polymerization of "living" poly-styrene.[4] The reason for this phenomenon is not yet clear.

It is interesting to compare these $k_{1,2}$ values to those obtained for styrene homo-polymerization[4] (*i.e.*, $k_{2,2}$). At the same temperature and concentration of "living" ends $k_{1,2}$ is slightly larger than $k_{2,2}$ (*e.g.*, 770 l. moles⁻¹ sec.⁻¹ as compared

(3) R. K. Graham, D. L. Dunkelberger and W. E. Good, *J. Am. Chem. Soc.*, **82**, 400 (1960).
(4) C. Geacintov, J. Smid and M. Szwarc, *ibid.*, **83**, 1253 (1961).