

been shown to be very sensitive to stereochemical differences of similar carbohydrates.¹³ The earlier assignment¹ of stereochemistry to neosamine C is thus confirmed.

Acknowledgments.—This investigation was supported in part by a research grant, No. E-1278 from the National Institute of Allergy and Infectious Diseases, Public Health Service.

(13) Cf. J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 395-399.

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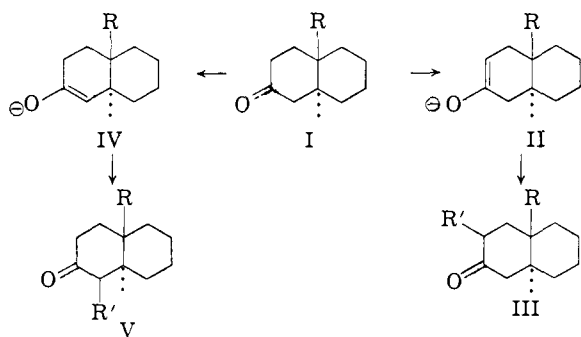
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THE α -ALKYLATION OF ENOLATES FROM
THE LITHIUM-AMMONIA REDUCTION
OF α,β -UNSATURATED KETONES

Sir:

The alkylation of carbonyl compounds is an important synthetic reaction which is attended by a number of problems some of which we have attempted to deal with previously with the introduction of the enamine alkylation reaction.¹



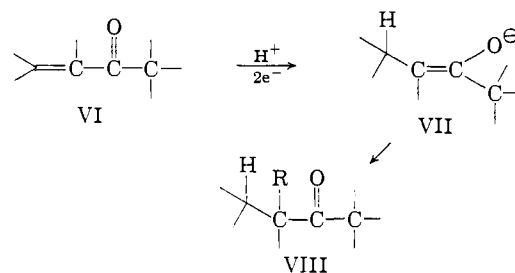
An important problem with which this communication is concerned is that of introducing a group on either side of the carbonyl of an unsymmetrical ketone. The *trans*-2-decalone system (I) will serve to illustrate this problem: Direct alkylation of I with electrophilic reagents in the presence of base leads to structures of type III,² via the anion II which happens to be the more stable one in this particular system.

We have now shown that it is possible to generate the less stable anion (IV) and to make use of it to introduce groups on the other side of the carbonyl (leading to V).

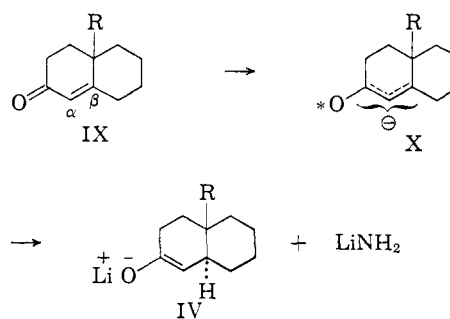
The principle of this new synthetic process is illustrated by the general equation VI \rightarrow VII \rightarrow VIII.

(1) G. Stork, R. Terrell and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954); G. Stork, *Abst. of the 16th National Organic Symposium*, June 1959, pp. 44-52.

(2) Cf. Y. Mazur and F. Sondheimer, *J. Am. Chem. Soc.*, **80**, 5220 (1958).



We will first consider the generation of the anion (e.g., IV) from an α,β -unsaturated ketone (e.g., IX). Addition of an electron from lithium and liquid ammonia to IX produces an intermediate X with carbanion character at the β -carbon atom.³ This intermediate was postulated to remove a proton from ammonia with the formation, for reasons which we have discussed previously,⁴ of a



trans decalone derivative as its enolate IV which is precisely that which we are trying to generate. That a proton is transferred to X by ammonia was established as follows: decomposition with D_2O (after replacing the ammonia by benzene) of the product from the addition of lithium to a liquid ammonia solution of IX, R = H, gave a saturated ketone (I, R = H) which contained deuterium as shown by its infrared spectrum, but all of the deuterium could be removed by warming with dilute aqueous base: the product after such treatment showed no excess deuterium over the natural abundance. No deuterium therefore was introduced on the β -carbon, where it would have remained, and the proton on that carbon must have come from the ammonia rather than from subsequent acidification.

Two experiments serve to show that the resulting enolate is indeed IV: addition of methyl iodide to the reduction mixture from IX, R = H, instead of decomposition by acid, with the usual work-up, gave in 55% yield *trans* 1-methyl-2-decalone (V, R = H, R' = CH_3) characterized by the formation in good yield of its 2,4-dinitrophenylhydrazone, m.p. 180-182° (reported⁵ m.p. 179-180°), mixed melting point determination with an authentic sample confirmed the identity of the substance.

Replacement of the ammonia, following the lithium reduction of IX, R = CH_3 , by ether, and addition to a mixture of Dry Ice and ether, produced a β -keto acid salt which gave, after acidifica-

(3) G. Stork and J. Tsuji, *ibid.*, **83**, 2783 (1961).

(4) G. Stork and S. D. Darling, *ibid.*, **82**, 1512 (1960).

(5) D. K. Banerjee, S. Chatterjee and S. P. Bhattacharya, *ibid.*, **77**, 408 (1955).

tion and esterification with diazomethane, a 45% yield of the β -keto ester V ($R = \text{CH}_3$, $R' = \text{CO}_2\text{-CH}_3$) 2,4-dinitrophenylhydrazone m.p. 184–185.5° (Found: C, 56.15; H, 5.96). (The β -keto ester, V, $R = \text{CH}_3$, $R' = \text{CO}_2\text{Et}$, also could be obtained by the use of ethyl chlorocarbonate in benzene, but the yield was lower.) The substance showed the expected⁶ absence of enolic properties (infrared, ferric chloride), but alkylation of the salt (NaH) with methyl iodide, then hydrolysis and decarboxylation, gave the known 1,4a-dimethyl-2-decalone (V, $R, R' = \text{CH}_3$) identified by mixed melting point of its 2,4-dinitrophenylhydrazone m.p. 185–186° (reported⁷ m.p. 186°) with that of an authentic sample.

The success of the trapping of the enolate ion IV depends on the alkylation reaction being faster than equilibration of the initially produced enolate IV to the more stable II *via* proton transfer with some initially formed neutral alkylated ketone. In the same manner transfer of proton between the monoalkylated ketone and unchanged anion will lead to di-(and poly)alkylation. The success of the alkylation in liquid ammonia solution suggests that *in that solvent* the alkylation is faster than the enolate equilibration. However, exchange of the ammonia for *dimethyl sulfoxide* before alkylation of IV, $R = \text{H}$, with butyl iodide led to a monobutyldecalone which was shown to be the 3-butyl compound III ($R = \text{H}$, $R' = \text{Bu}$) by comparison with an authentic sample made by an unambiguous route (2,4-dinitrophenylhydrazone, m.p. 173–174.5° (Found: C, 61.97; H, 7.32)).

When, on the other hand, treatment of the enolate ion IV, $R = \text{CH}_3$, with butyl iodide was carried out *in liquid ammonia* the monobutyl compound, formed in 50% yield, turned out to be again the product of trapping without rearrangement, the 1-butyl derivative V ($R = \text{H}$, $R' = \text{Bu}$), identical with an independently synthesized authentic sample (2,4-dinitrophenylhydrazone, m.p. 125–126.5°) (Found: C, 62.16; H, 7.34).

It is evident from these results that proton transfer reactions which lead to equilibration of the anions are, perhaps not unexpectedly, much more affected by the extent of dissociation of the enolate ion-lithium cation ion pair than is the C-alkylation reaction⁸ and that the sequence described here may—if it can be extended—be a solution to the problem of directing alkylation to a specific α -carbon of an unsymmetrical ketone.

(6) Cf. F. Sondheimer, R. Mechoulam and M. Sprecher, *Tetrahedron Letters*, No. 22, 38 (1960).

(7) M. Yanagita and R. Futaki, *J. Org. Chem.*, **21**, 949 (1956).

(8) Cf. D. Cram, B. Rickborn and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).

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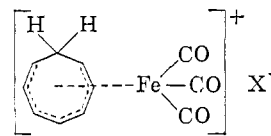
SALTS OF THE CYCLOOCTATRIENIUM IRON TRICARBONYL CATION

Sir:

Since the discovery of cyclooctatetraene iron carbonyl complexes by at least three independent

research groups in 1958 to 1959,^{1,2,3} these compounds have received much attention. The mononuclear $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ is particularly interesting as the results of nuclear magnetic resonance measurements indicate that all four double bonds of the C_8H_8 ring are involved in the bonding to iron. It has been proposed by several authors^{1,4,5} that in this complex the C_8H_8 should be planar. However, the results of a recent refined spectroscopic investigation make it increasingly apparent that at least deviations from perfect planarity must be present⁶; the question is not yet fully settled. The complex is remarkably stable. It dissolves in, and is recovered from, anhydrous acetic acid without decomposition. Also, it fails to decolorize bromine, and resists hydrogenation and normal Diels-Alder reactions.

It now has been observed by the writer that $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ is converted into a salt of composition $\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3^+\text{BF}_4^-$ if it is dissolved in an ethereal solution of fluoroboric acid. This compound forms yellow crystals (m.p. gradual darkening above 150°). *Anal.* Calcd.: Fe, 16.8; C, 39.8; H, 2.7. Found: Fe, 16.7; C, 39.4; H, 2.9; infrared (Nujol), carbonyl region, 4.70 μ (neat), 4.84 μ (broader). It readily dissolves in water, acetone and methanol, is almost insoluble in ether and in non-polar solvents. Aqueous solutions are stable at room temperature but undergo hydrolysis when heated; $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ can be recovered from such solutions by extraction with benzene. If to



Structure I

the solutions of $\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3^+\text{BF}_4^-$ sodium tetraphenylborate or Reinecke salt is added, salts of the complex cation with the corresponding anions are formed. Similarly, $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ dissolves in 70–80% HClO_4 . Upon addition of water, yellow crystals of the perchlorate, $\text{C}_8\text{H}_9\text{Fe}(\text{CO})_3^+\text{ClO}_4^-$, precipitate. This was found to be violently explosive in the dry state; C–H analysis was not possible. *Anal.* Calcd.: Fe, 16.2. Found: Fe, 16.2; infrared (Nujol), carbonyl region, 4.69 (neat), 4.81 μ (broader). Finally, $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ was found to dissolve even in concentrated hydrochloric acid. The yellow needles of the hydrochloride (m.p. 61° dec.) separate upon cooling the solution of $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$ in ethereal hydrogen chloride. *Anal.* Calcd.: Fe, 19.9; C, 47.1; H, 3.2; Cl, 12.6. Found: Fe, 19.5; C, 47.8; H, 3.44; Cl, 11.1; infrared (Nujol), carbonyl region, 4.72, 4.84 and 4.89 μ respectively. The hydrochloride slowly decomposes at room temperature. The binuclear complex $\text{C}_8\text{H}_8\text{Fe}_2$

(1) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 366 (1960).

(2) M. D. Rausch and G. N. Schrauzer, *Chemistry and Industry*, 957 (1959).

(3) A. Nakamura and N. Hagihara, *Bull. chem. Soc. (Japan)*, **32**, 880 (1959).

(4) F. A. Cotton, *J. Chem. Soc.*, 400 (1960).

(5) D. A. Brown, *J. Inorg. Nucl. Chem.*, **10**, 39 (1959).

(6) Personal communication from Dr. H. P. Fritz, Munich.