H, 7.96), positive legal test.[4,9] Treatment of I with acetic anhydride–pyridine at room temperature yielded only starting material. The compound formed a mono-2,4-dinitrophenylhydrazone at C-3, m.p. 256° d., $\lambda_{\max}^{1\%\ \text{chloroform-abs. alc.}}$ 257 ($\epsilon$ 17,300) and 387–388 m$\mu$ ($\epsilon$ 29,000) (*Anal.* Calcd. for $C_{27}H_{32}N_4O_8$: C, 59.99; H, 5.97; N, 10.37. Found: C, 59.71; H, 6.15; N, 10.25).

A detailed report of this work will be forthcoming in this JOURNAL.

[9] W. D. Paist, E. R. Blout, F. C. Uhle and R. C. Elderfield, *J. Org. Chem.*, **6**, 273 (1941).

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## INDISCRIMINATE REACTION OF METHYLENE WITH THE CARBON-HYDROGEN BOND

*Sir:*

Methylene shows essentially no discriminatory power in its reaction with the carbon–hydrogen bonds[1] in the saturated hydrocarbons, *n*-pentane and 2,3-dimethylbutane and in the olefin, cyclohexene. When diazomethane is irradiated with these hydrocarbons either at −75° or at 15°, the distribution of products resulting from insertion of the carbene into a carbon–hydrogen bond is very close to statistical. For example, diazomethane may react with *n*-pentane at carbon atoms 1, 2 or 3 to give *n*-hexane, 2-methylpentane and 3-methylpentane in the statistical ratio 6:4:2 or 50:33.3:16.7, respectively; in fact, these three products are formed at −75° in the ratio 48:35:17; and at 15° in the ratio 49:34:17.

2,3-Dimethylbutane which contains primary and tertiary hydrogen in the ratio of 12:2 or 85.7:14.3 reacts with diazomethane to give 2,3-dimethylpentane and 2,2,3-trimethylbutane in the ratio 83:17. It is possible that the small difference between the statistical and actual values lies outside the experimental error but higher resolution in the form of considerably refined techniques would be required to decide.

In cyclohexene there are three types of carbon–hydrogen bonds of widely differing chemical characteristics: the "vinyl" hydrogen atoms at carbon atoms 1 and 2, the "allylic" hydrogens at $C_3$ and $C_6$ and the "aliphatic" hydrogens at $C_4$ and $C_5$. Reaction with methylene can occur in principle at each type of carbon–hydrogen bond to give 1-methylcyclohexene, 3-methylcyclohexene and 4-methylcyclohexene, respectively, in the statistical ratio of 2:4:4. Reaction can also occur by addition to the double bond to give norcarane. In fact, these four products are formed at −75° in the ration 10:25:25:40 and at 15° in the ratio 11:26:26:37. Here again one product, 1-methylcyclohexene, appears to be formed in amount differing slightly from the statistical, but the estimated error of 10% is too large to justify further comment at this time.

Finally diazomethane reacts with cyclopentane to give methylcyclopentane unaccompanied (less than 0.1%) by cyclohexane. Within much increased limits, one concludes that methylene does not react with the carbon–carbon bond.

Within a few per cent. it is clear that methylene fails to distinguish between different types of carbon–hydrogen bonds, reacting at random with 1°, 2° and 3° aliphatic C–H bonds as well as with "allylic" and "vinyl" types. Even more surprising is the fact that the reaction cross-section of the double bond is only about three times that of a hydrogen atom. One might reasonably have expected an overwhelming preference similar to that shown by dichlorocarbene.[2] Methylene must be classed as the most indiscriminate reagent known in organic chemistry.

The experiments were carried out in the usual way by irradiating very dilute solutions of diazomethane in the hydrocarbon with sun-lamps, removing most of the solvent by fractional distillation in a 50-plate column and analyzing the product by gas–liquid partition chromatography using a Perkin–Elmer Model 154 Vapor Fractometer and by infrared spectroscopy. In all cases but one, samples of pure product were isolated from the Fractometer and identified by comparing their infrared spectra with those of authentic samples (neat, 0.1-mm. cell). In the cyclohexene reaction where the Fractometer would not resolve 3- and 4-methylcyclohexene but easily separated this mixture from the other components, analysis was made infrared spectroscopically comparing with known mixtures of the authentic olefins.

[1] The photochemical decomposition of diazomethane was first investigated by H. Meerwein, H. Rathjen and H. Werner, *Ber.*, **75**, 1610 (1942), in ether where ethyl *n*-propyl and ethyl isopropyl ether were formed. Although the latter product appears to be formed by direct reaction of a carbon–hydrogen bond, the presence of the oxygen atom and the possibility it affords for initial "ylid" formation [see R. Huisgen, *Angew. Chem.*, **67**, 439 (1955)] makes the mechanism ambiguous. The direct reaction of carbethoxy carbene with saturated hydrocarbons has been reported by W. von E. Doering and L. H. Knox, 119th Meeting of the American Chemical Society, Boston, Mass., April 2, 1951 "Abstracts of Papers," p. 2M, and THIS JOURNAL, in press.

[2] W. von E. Doering and A. K. Hoffmann, THIS JOURNAL, **76**, 6162 (1954).

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## SYNTHESIS OF APOGOSSYPOL HEXAMETHYL ETHER

*Sir:*

Apogossypol hexamethyl ether, the primary degradation product of gossypol (I), has been formulated as 2,2′-bi-5-isopropyl-1,6,7-trimethoxy-3-methylnaphthyl (II) by Adams[1] as a result of his extensive and thorough studies. The Adams structures however, have been criticized recently by three separate groups of investigators.[2,3,4] The present

[1] R. Adams, R. C. Morris, T. A. Geissman, D. J. Butterbaugh and E. C. Kirkpatrick, THIS JOURNAL, **60**, 2193 (1938).

[2] D. A. Shirley and W. L. Dean, *ibid.*, **77**, 6077 (1955).

[3] R. T. O'Connor, P. Haar, E. F. DuPre, L. E. Brown and C. H. Pominski, *ibid.*, **76**, 2368 (1954).

[4] C. H. Boatner, "Pigments of Cottonseed and Cottonseed Products," Edited by A. E. Bailey, Interscience Publishers, Inc., New York, N. Y., 1948, Chap. VI, pp. 215–262.